Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The double H-atom acceptability of the P═O group in new *X*P(O)(NH-CH$_2$C$_6$H$_4$-2-Cl)$_2$ phosphoramidates [*X* = C$_6$H$_5$O– and CF$_3$C(O)NH–]: a database analysis of compounds having a P(O)(NH*R*) group

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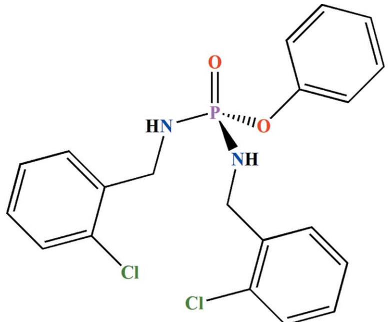
Received 16 September 2011
Accepted 2 December 2011
Online 6 January 2012

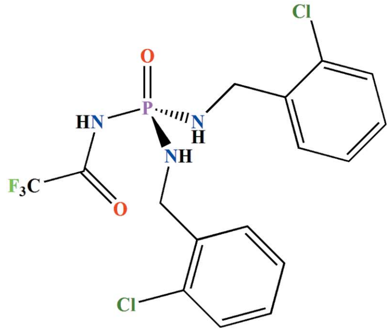
In the hydrogen-bond patterns of phenyl bis(2-chlorobenzylamido)phosphinate, $C_{20}H_{19}Cl_2N_2O_2P$, (I), and *N*,*N*′-bis(2-chlorobenzyl)-*N*″-(2,2,2-trifluoroacetyl)phosphoric triamide, $C_{16}H_{15}Cl_2F_3N_3O_2P$, (II), the O atoms of the related phosphoryl groups act as double H-atom acceptors, so that the $P{=}O\cdots(H{-}N)_2$ hydrogen bond in (I) and the $P{=}O\cdots(H{-}N_{amide})_2$ and $C{=}O\cdots H{-}N_{C(O)NHP(O)}$ hydrogen bonds in (II) are responsible for the aggregation of the molecules in the crystal packing. The presence of a double H-atom acceptor centre is a result of the involvement of a greater number of H-atom donor sites with a smaller number of H-atom acceptor sites in the hydrogen-bonding interactions. This article also reviews structures having a P(O)NH group, with the aim of finding similar three-centre hydrogen bonds in the packing of phosphoramidate compounds. This analysis shows that the factors affecting the preference of the above-mentioned O atom to act as a double H-atom acceptor are: (i) a higher number of H-atom donor sites relative to H-atom acceptor centres in molecules with P(═O)(NH)$_3$, (N)P(═O)(NH)$_2$, C(═O)NHP(═O)(NH)$_2$ and (NH)$_2$P(═O)OP(═O)(NH)$_2$ groups, and (ii) the remarkable H-atom acceptability of this atom relative to the other acceptor centre(s) in molecules containing an OP(═O)(NH)$_2$ group, with the explanation that the N atom bound to the P atom in almost all of the structures found does not take part in hydrogen bonding as an acceptor. Moreover, the differences in the H-atom acceptability of the phosphoryl O atom relative to the O atom of the alkoxy or phenoxy groups in amidophosphoric acid esters may be illustrated by considering the molecular packing of compounds having (O)$_2$P(═O)(NH) and (O)P(═O)(NH)(N) groups, in which the unique N—H unit in the above-mentioned molecules almost always selects the phosphoryl O atom as a partner in forming hydrogen-bond interactions. The P atoms in (I) and (II) are in tetrahedral coordination environments, and the phosphoryl and carbonyl groups in (II) are *anti* with respect to each other (the P and C groups are separated by one N atom). In the crystal structures of (I) and (II), adjacent molecules are linked *via* the above-mentioned hydrogen bonds into a linear arrangement parallel to [100] in both cases, in (I) by forming $R_2^2(8)$ rings and in (II) through a combination of $R_2^2(10)$ and $R_2^1(6)$ rings.

Comment

A three-centred $(D{-}H)_2\cdots A$ hydrogen bond is formed when two H-atom donor sites interact with a single acceptor which is called a double H-atom acceptor (Steiner, 2002). The term 'bifurcated' is commonly used to describe another type of three-centred hydrogen bond, *viz.* $D{-}H\cdots(A)_2$ (Steiner, 2002). To predict the hydrogen-bond pattern of a molecule with more H-atom donor sites than H-atom acceptor sites, one would anticipate that some H-atom acceptors would be suitable to act as double H-atom acceptors. Of course, the positions of the H-atom acceptors and donors and their relative directionalities are important too. Moreover, if the H-atom acceptabilities of the two H-atom acceptor centres in a molecule are very different, the better H-atom acceptor may act as a double H-atom acceptor. In such cases, the competing hydrogen bonds involved in the three-centred hydrogen bond may each reduce the strength of the other.



(I)



(II)

In this paper, the syntheses and crystal structures of phenyl bis(2-chlorobenzylamido)phosphinate, $C_6H_5OP(O)(NHCH_2C_6H_4\text{-}2\text{-}Cl)_2$, (I), and *N*,*N*′-bis(2-chlorobenzyl)-*N*″-(2,2,2-trifluoroacetyl)phosphoric triamide, $CF_3C(O)NHP(O)(NHCH_2C_6H_4\text{-}2\text{-}Cl)_2$, (II), are reported. Their molecular structures are

doi:10.1107/S0108270111052097

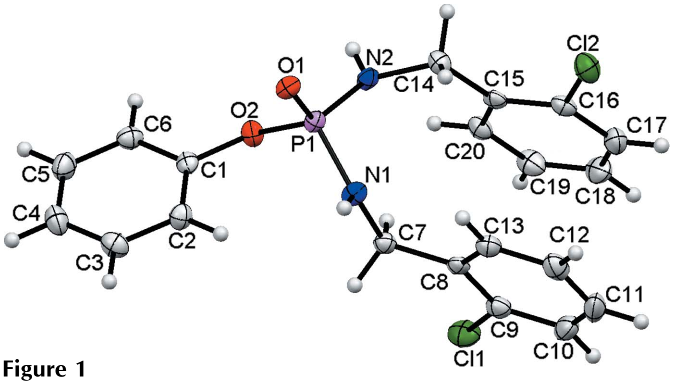


Figure 1
The molecular structure and atom-labelling scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

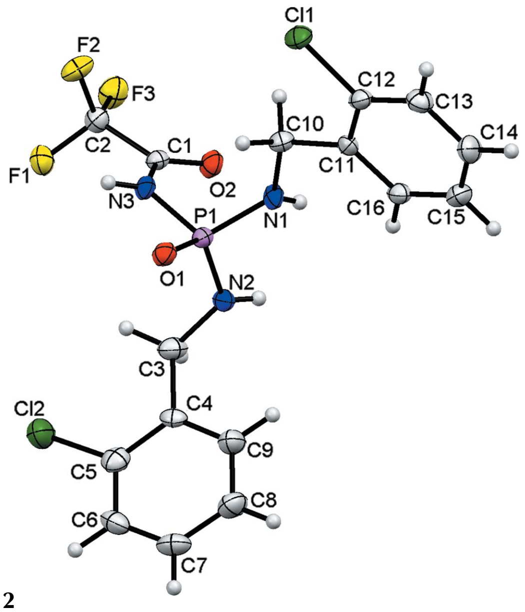


Figure 2
The molecular structure and atom-labelling scheme for (II). Displacement ellipsoids are drawn at the 50% probability level.

shown in Figs. 1 and 2, respectively. Additionally, we have attempted to analyse the three-centred hydrogen bonds in (I) and (II) and in analogous phosphorus compounds of the formula XP(O)(NHR)$_2$ having CIFs deposited in the Cambridge Structural Database (CSD, Version 5.32, May 2011 update; Allen, 2002) and papers published recently in IUCr journals. Either X is OR' ($R' \neq$ H) or NR^1R^2, *i.e.* compounds having a P(O)(NH)$_3$, (N)P(O)(NH)$_2$ or OP(O)(NH)$_2$ skeleton, or X is a group containing both H-atom donor and acceptor sites, such as R'C(O)NH or (NHR)$_2$P(O)O in compounds with a C(O)NHP(O)(NH)$_2$ or (NH)$_2$P(O)OP(O)(NH)$_2$ fragment.

Usually in phosphoramidates, no N atom bonded to phosphorus takes part in any hydrogen bond as an acceptor, showing its low Lewis base character. A search of the CSD revealed one phosphoramidate molecular packing (belonging to the diazaphosphorinane family) containing a very weak N—H$\cdots$N—P hydrogen bond (CSD refcode HESCEO; Gholivand *et al.*, 2006). In most cases, the N atom has a nearly planar environment (Toghraee *et al.*, 2011). Of course, the N-atom environment of some substituents, such as aziridine, for example, in NH$_2$P(O)[NCH$_2$C(CH$_3$)$_2$]$_2$ (GOMDOB; Hempel *et al.*, 1999), shows some deviation from planarity, but such an N atom does not take part in hydrogen-bonding interactions as an acceptor. Moreover, the O atom of the phenoxy and alkoxy groups in the 47 structures with an (O)P(=O)(NH)(N) skeleton [for example, 4-CH$_3$-C$_6$H$_4$O-P(O)[N(CH$_3$)$_2$][NHC(CH$_3$)$_3$]; GUDGIW; Ghadimi *et al.*, 2009] does not take part in hydrogen-bonding interactions, as it cannot compete with the phosphoryl O atom for the unique H-atom donor site in the molecule.

Focusing on the (O)(O)P(=O)(NH) skeleton in the 106 related deposited CIFs (and recently published structures), only the structure of (CH$_3$O)$_2$P(O)[NHCH{CH(CH$_3$)[O-C(O)CH$_3$]}{C(O)[C(NN)(COOC$_2$H$_5$)]}] (IJUMAB; Sa *et al.*, 2003) shows N—H$\cdots$O(CH$_3$) and not N—H$\cdots$O(P) hydrogen bonding. Thus, this skeleton almost always has one H-atom acceptor (the O atom of the phosphoryl group) and one H-atom donor site in the P(O)NH group. In this study, some structures were not included because their CIFs were unavailable; hydrated (or solvated with a protic solvent) molecules were also excluded. Additionally, some molecules show the other types of hydrogen bonds, such as N—H$\cdots$O=C or N—H$\cdots$N, due to the substituent linked to the mentioned skeleton.

The O atom of the OR group in some examples of compounds with a higher number of H-atom donor sites, such as compounds containing an (O)P(=O)(NH)(NH) skeleton, has a lower H-atom acceptability than the phosphoryl O atom, enforcing involvement in the hydrogen-bonding interaction (MUBPIJ; Pourayoubi *et al.*, 2009) (Fig. 3).

In some cases, the better H-atom acceptability of the O atom of P=O relative to the RO group, *e.g.* C$_6$H$_5$OP(O)(NHC$_6$H$_{11}$)[NHC$_6$H$_4$(4-CH$_3$)] (ERUFIH; Sabbaghi, Pourayoubi, Karimi Ahmadabad & Parvez, 2011), leads it to act as a double H-atom acceptor (Fig. 4), similar to what is observed in the crystal packing of (I) (Fig. 5). For example, in the molecular packing of (C$_6$H$_5$O)P(O)(NHC$_6$H$_{11}$)$_2$·CH$_3$OH (HIVLOO; Gholivand *et al.*, 2008), a linear arrangement is formed through a P(O)($\cdots$H—O)($\cdots$H—N) group, where the P(O) group acts as a double H-atom acceptor and the OH unit belongs to the methanol solvent molecule. In the two-dimensional hydrogen-bonded arrangement of diazaphosphorinanes 4-CH$_3$C$_6$H$_4$OP(O)X (X is NHCH$_2$CH$_2$CH$_2$NH; KIVXIX; Gholivand, Shariatinia *et al.*, 2007) and C$_6$H$_5$O-P(O)Y [Y is NHCH$_2$C(CH$_3$)$_2$CH$_2$NH; KIVXOD; Gholivand, Shariatinia *et al.*, 2007], the P(O) functions as a double H-atom acceptor.

In other cases, both O atoms are involved in hydrogen-bond interactions with the two N—H units [or the other H-atom

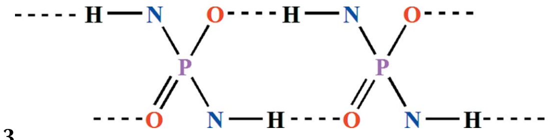


Figure 3
Participation of the O atoms of both P=O and RO groups in the hydrogen-bond pattern.

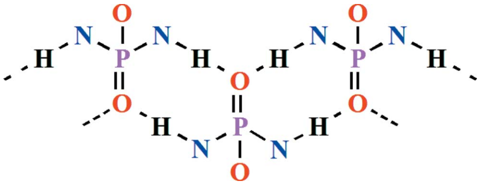


Figure 4
The role of the P═O O atom as a double H-atom acceptor.

donor site(s) in the molecule or in the crystal structure], forming hydrogen bonds with different strengths in which the P(O) group takes part in a stronger hydrogen bond. For example, in the crystal packing of (4-CH_3-C_6H_4O)P(O)-(NHC_6H_4-4-CH_3)$_2$ (MUBPIJ), N···O(P) = 2.805 (2) Å and N···O(C_6H_4-4-CH_3) = 3.068 (2) Å, while in $C_6H_5OP(O)$(NH-C_6H_4-4-CH_3)($NHCH_2C_6H_5$) (Pourayoubi, Karimi Ahmadabad & Nečas, 2011), these distances are 2.761 (3) and 3.127 (3) Å, respectively.

In the crystal packing of compounds with the general formula (R^1O)P(O)(NHR^2)$_2$, both linear and two-dimensional hydrogen-bonded arrangements are observed; for example, $C_6H_5OP(O)(NHC_6H_{11})_2$·$CH_3OH$ (HIVLOO), 4-CH_3-C_6H_4O-P(O)(NHC_6H_4-4-CH_3)$_2$ (MUBPIJ), 4-CH_3-$C_6H_4OP(O)$(NH-C_6H_4-2-CH_3)$_2$ (YUPVEL; Sabbaghi *et al.*, 2010) and 4-CH_3-$C_6H_4OP(O)X$ [X is $NHCH_2C(CH_3)_2CH_2NH$; NIBNOC; Gholivand, Pourayoubi & Shariatinia, 2007] exist as linear hydrogen-bonded arrangements, whereas a two-dimensional array is found, for instance, in 4-CH_3-$C_6H_4OP(O)X$ (X is $NHCH_2CH_2CH_2NH$; KIVXIX), $C_6H_5OP(O)X$ [X is $NHCH_2C(CH_3)_2CH_2NH$; KIVXOD], $C_6H_5OP(O)(NH_2)_2$ (PPOSAM; Bullen & Dann, 1973) and $C_6H_5OP(O)X$ [X is NHNHP(O)(OC_6H_5)NHNH; FIMVUS; Engelhardt & Franzmann, 1987].

For (I), single crystals were obtained at room temperature from a mixture of CH_3OH and CH_3CN. The P atom exhibits a distorted tetrahedral environment (Fig. 1), as has been noted for other amidophosphoric acid esters (Sabbaghi *et al.*, 2010). This distortion is illustrated by the bond angles at the P atom [in the range 97.42 (7)–119.79 (7)°] and the bond lengths in the P(═O)(O)(N)$_2$ skeleton (Table 1). The C—O bond length and the P—N—C and P—O—C angles are within the expected ranges (Sabbaghi, Pourayoubi, Karimi Ahmadabad & Parvez, 2011).

The molecules of (I) are linked by two intermolecular N—H···OP hydrogen bonds (Table 2) into a one-dimensional arrangement in the direction of the *a* axis, in which the O atom of the P═O group acts as a double H-atom acceptor (Steiner, 2002) (Fig. 5). From this arrangement, $R_2^2(8)$ rings are formed (Bernstein *et al.*, 1995).

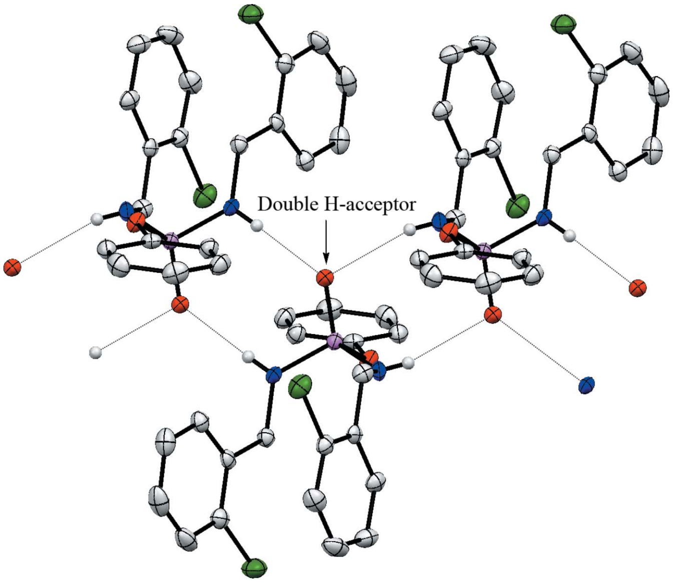


Figure 5
The phosphoryl O atom as a double H-atom acceptor in the hydrogen-bond pattern of (I). C-bound H atoms have been omitted for clarity.

Similar cases are observed in compounds containing an (N)P(═O)(NH)(NH) moiety [MIFYIJ (Gholivand *et al.*, 2002) and IKASAP (Sabbaghi, Pourayoubi, Karimi Ahmadabad, Azarkamanzad *et al.*, 2011)], where ‘one H-atom acceptor and two H-atom donor’ sites exist in the molecules (the N atoms are not involved in hydrogen bonding as H-atom acceptors). In [N(CH_3)(C_6H_{11})]P(O)(NHC_5H_4-2-N)$_2$ (HIVLII; Gholivand *et al.*, 2008), one of the N—H units is involved in an intramolecular hydrogen bond with one of the pyridine N atoms, the other N—H unit takes part in the P(O)···H—N hydrogen bond.

Compound (II) (Fig. 2) is an example of a compound containing two H-atom acceptor and three H-atom donor sites; all of these sites exist in the C(O)NHP(O)(NH)$_2$ skeleton of the molecule. Single crystals were obtained at room temperature from a mixture of C_2H_5OH and CH_3CN. As has been noted in a recently published paper by Toghraee *et al.* (2011), and similar to the amidophosphoric acid esters, the N atoms are not involved as H-atom acceptors in hydrogen-bonding interactions. Similar to all reported acyclic phosphoric triamides containing a C(O)NHP(O)(NH)$_2$ skeleton, the C(O) group adopts an *anti* orientation with respect to P(O) (the P and C groups are separated by an N atom). Of course, in the diazaphosphorinanes containing a similar skeleton, a *gauche* position was observed (Toghraee *et al.*, 2011).

The tetrahedral P(═O)(N)(N)$_2$ environment is distorted, and the P═O, C═O and P—N bond lengths and C—N—P angles are within the expected ranges (Pourayoubi, Tarahhomi *et al.*, 2011; Tarahhomi *et al.*, 2011). The O—P—N—C torsion angle in the C(O)NHP(O) group is within the expected range for analogous compounds having an *anti* orientation of P(O) with respect to C(O). As expected, the P—N bonds in the P(O)($NHCH_2C_6H_4$-2-Cl)$_2$ group are shorter than the P—N bond in the C(═O)NHP(═O) fragment (Table 3).

In the crystal packing of (II), adjacent molecules are linked *via* $N_{C(O)NHP(O)}$—H···O(C) hydrogen bonds and also through two different N_{amide}—H···O(P) hydrogen bonds involving the same pair of molecules (Table 4), building $R_2^2(10)$ rings combined with $R_2^1(6)$ rings (Fig. 6) in a linear arrangement parallel to [100]. This means that, in this structure, the phosphoryl group acts as a double hydrogen-bond acceptor to form a P═O(···H—N_{amide})$_2$ group.

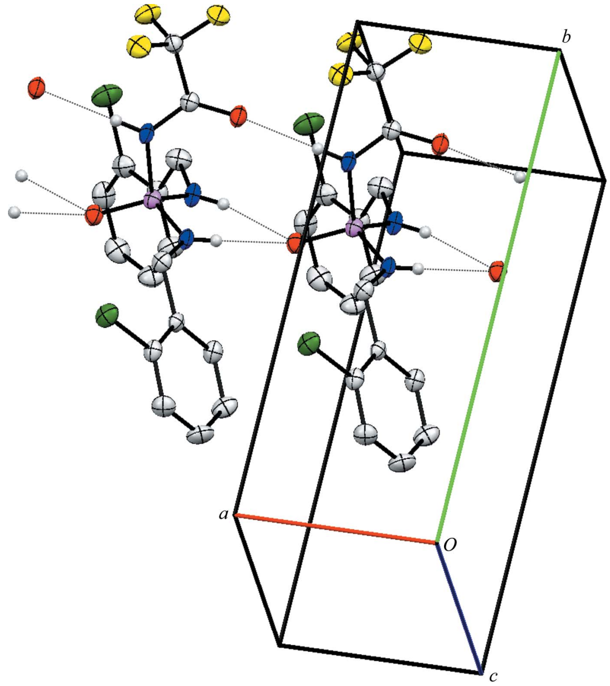


Figure 6
Part of the crystal packing of (II), with the hydrogen bonds shown as dotted lines. C-bound H atoms have been omitted for clarity.

For compounds of the formula *R*C(O)NHP(O)(NH*R*′)$_2$, the two H-atom donors [H—N$_{C(O)NHP(O)}$ and one of the H—N*R*′ groups] participate with the two O atoms in the intermolecular hydrogen bonding; the other H—N*R*′ group may make one of three choices: (*a*) taking part in an additional hydrogen bond with P(O) as in the above-mentioned three-centred hydrogen bond; (*b*) involvement in an intramolecular hydrogen bond with C(O); (*c*) no participation in any hydrogen bond.

The structure of one neutral molecule with an (NH)$_2$P(O)-OP(O)(NH)$_2$ skeleton has been reported [OXPOTU (Cameron *et al.*, 1978) and OXPOTU01 (Pourayoubi, Padělková *et al.*, 2011)]. In this case, one of the phosphoryl O atoms acts as a double H-atom acceptor to form one inter- and one intramolecular N—H···O hydrogen bonds.

In summary, the CIF files of all published compounds with the (N)P(=O)(NH)$_2$, (O)P(=O)(NH)$_2$, (O)$_2$P(=O)(NH), (O)P(=O)(NH)(N), C(=O)NHP(=O)(NH)$_2$, P(=O)(NH)$_3$ and (NH)$_2$P(=O)OP(=O)(NH)$_2$ skeletons (belonging to phosphoramidate compounds) were investigated and the following 'empirical rules' were obtained. (i) In virtually none of the reported structures does the N atom take part in a hydrogen-bonding interaction as an acceptor. There is only one example of a hydrogen bond of the type N—H···N—P (N···N distance more than 3.2 Å). (ii) In almost all compounds having (O)$_2$P(=O)(NH) and (O)P(=O)(NH)(N) skeletons, the O atom of the *R*O group does not take part in a hydrogen-bonding interaction, as it cannot compete with the phosphoryl O atom for the single H-atom donor site in the molecule. There is only one example of a hydrogen bond of the type N—H···O(*R*)—P in this family of compounds; a compound containing some H-atom acceptor centres in addition to one phosphoryl group. (iii) The O atom of the O*R* group in some examples of compounds with higher numbers of H-atom donor sites than H-atom acceptor centres, such as compounds containing an (O)P(=O)(NH)$_2$ skeleton, even though it has a lower H-atom acceptability than the phosphoryl O atom, is forced to be involved in a hydrogen-bond interaction. (iv) In compounds having an (O)P(=O)(NH)$_2$ skeleton, the better H-atom acceptability of the phosphoryl O atom compared with the *R*O group leads it to act in some cases as a double H-atom acceptor. (v) In compounds having a C(=O)NHP(=O)(NH)$_2$ skeleton containing two H-atom acceptor and three H-atom donor centres, two H-atom donors [H—N$_{C(O)NHP(O)}$ and one of the H—N*R*′ groups] participate with the two O atoms in intermolecular hydrogen bonds, while the other H—N*R*′ group may act in one of the three following ways: (*a*) involved in an additional hydrogen bond with P(O), (*b*) participation in an intramolecular hydrogen bond with C(O), and (*c*) not taking part in any hydrogen bond. (vi) In the crystal packing of (II), the C(=O)···H—N$_{C(O)NHP(O)}$ hydrogen bond and a P(=O)···(H—N$_{amide}$)$_2$ group are responsible for the aggregation of the molecules. This type of aggregation, a combination of $R_2^2(10)$ and $R_2^1(6)$ rings, has been observed for a few structures having a C(O)NHP(O)(NH)$_2$ skeleton. The other hydrogen-bond pattern is alternating $R_2^2(8)$ and $R_2^2(12)$ motifs [formed through pairs of P(=O)···[H—N$_{C(O)NHP(O)}$] and pairs of C(=O)···H—N$_{amide}$ hydrogen bonds, respectively]. The $R_2^2(12)$ loop may also be accompanied by $R_2^1(6)$ or $S(6)$ rings. A few different hydrogen-bond patterns are also observed.

Experimental

CF$_3$C(O)NHP(O)Cl$_2$ was prepared according to the procedure reported by Narula *et al.* (1999). Compound (I) was synthesized from the reaction of phenyl dichlorophosphate (2.507 mmol) and 2-chlorobenzylamine (10.028 mmol) in chloroform (30 ml). After stirring for 4 h at 273 K, the solvent was evaporated in a vacuum and the solid obtained was washed with distilled water. Single crystals of (I) suitable for X-ray crystallography were obtained from their solution in a mixture of CH$_3$OH and CH$_3$CN (3:1 *v*/*v*) by slow evaporation at room temperature. IR (KBr, ν, cm^{-1}): 3262, 3176, 2915, 1581, 1486, 1201, 1115, 1030, 916, 745, 683. Compound (II) was synthesized by a similar method to that used for the preparation of (I), but using CF$_3$C(O)NHP(O)Cl$_2$ instead of C$_6$H$_5$OP(O)Cl$_2$. Single crystals of (II) suitable for X-ray crystallography were obtained from their solution in a mixture of C$_2$H$_5$OH and CH$_3$CN (3:1 *v*/*v*) by slow evaporation at room temperature. IR (KBr, ν, cm^{-1}): 3323 (sh), 3257, 2904, 1725, 1482, 1410, 1315, 1205, 1162, 1076, 1043, 900, 790, 761, 690.

Compound (I)

Crystal data

$C_{20}H_{19}Cl_2N_2O_2P$
M_r = 421.24
Triclinic, $P\overline{1}$
a = 7.4673 (4) Å
b = 10.4338 (5) Å
c = 12.9911 (6) Å
α = 86.215 (4)°
β = 79.611 (4)°
γ = 78.588 (4)°
V = 975.41 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.43 mm^{-1}
T = 120 K
0.50 × 0.40 × 0.40 mm

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

Cl1—C9	1.7470 (19)	P1—N2	1.6302 (15)
P1—O1	1.4837 (11)	O2—C1	1.4003 (19)
P1—O2	1.6095 (12)	N1—C7	1.461 (2)
P1—N1	1.6157 (15)	N2—C14	1.468 (2)
O1—P1—O2	110.93 (7)	N1—P1—N2	106.23 (8)
O1—P1—N1	109.90 (7)	C1—O2—P1	123.36 (10)
O2—P1—N1	112.03 (7)	C7—N1—P1	125.65 (12)
O1—P1—N2	119.79 (7)	C14—N2—P1	120.13 (12)
O2—P1—N2	97.42 (7)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O1^{i}	0.85 (1)	2.01 (1)	2.8551 (17)	173 (2)
N2—H2N$\cdots$O1^{ii}	0.84 (1)	2.13 (1)	2.9365 (17)	160 (2)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y, -z+1$.

Data collection

Oxford Xcalibur Sapphire2 diffractometer (large Be window)
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
$T_{\min} = 0.952$, $T_{\max} = 1.000$
6980 measured reflections
3429 independent reflections
2750 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.074$
$S = 1.07$
3429 reflections
250 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Compound (II)

Crystal data

$C_{16}H_{15}Cl_2F_3N_3O_2P$
$M_r = 440.18$
Triclinic, $P\overline{1}$
$a = 4.8860$ (8) Å
$b = 12.192$ (2) Å
$c = 15.838$ (3) Å
$\alpha = 103.714$ (17)°
$\beta = 94.636$ (15)°
$\gamma = 96.099$ (15)°
$V = 905.9$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.49$ mm^{-1}
$T = 120$ K
0.30 × 0.20 × 0.20 mm

Data collection

Oxford Xcalibur Sapphire2 diffractometer (large Be window)
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
$T_{\min} = 0.652$, $T_{\max} = 1.000$
5706 measured reflections
3179 independent reflections
1971 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.080$
$S = 0.81$
3179 reflections
253 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

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

Cl1—C12	1.750 (3)	F1—C2	1.336 (3)
P1—O1	1.469 (2)	O2—C1	1.216 (3)
P1—N1	1.609 (2)	N1—C10	1.465 (3)
P1—N2	1.613 (2)	N2—C3	1.464 (4)
P1—N3	1.714 (2)	N3—C1	1.337 (3)
O1—P1—N1	115.42 (12)	C10—N1—P1	122.87 (19)
O1—P1—N2	117.70 (12)	C3—N2—P1	121.2 (2)
N1—P1—N2	103.43 (13)	C1—N3—P1	124.3 (2)
O1—P1—N3	102.57 (11)	O2—C1—N3	125.3 (3)
N1—P1—N3	110.46 (12)	F3—C2—F1	108.2 (2)
N2—P1—N3	107.06 (12)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O1^{i}	0.86 (1)	2.05 (1)	2.875 (3)	159 (2)
N2—H2N$\cdots$O1^{i}	0.87 (1)	2.14 (2)	2.947 (3)	155 (3)
N3—H3N$\cdots$O2^{ii}	0.87 (1)	2.00 (1)	2.866 (3)	176 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$.

For (I) and (II), carbon-bound H atoms were placed at calculated positions and refined as riding, with C—H = 0.95 (aromatic) or 0.99 Å (methylene) and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Nitrogen-bound H atoms were located in difference Fourier maps and refined isotropically, with N—H restrained to 0.88 (1) Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

The authors thank Ferdowsi University of Mashhad for a Research University Grant (No. 15144/2).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3159). Services for accessing these data are described at the back of the journal.

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