

Different cyclic motifs in phosphoric triamides containing a C(O)NHP(O)-(NH)₂ skeleton and an R₂²(10) graph set in three new compounds: a data-base analysis of hydrogen-bond strengths based on motifs

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In the crystal networks of *N,N'*-bis(2-chlorobenzyl)-*N''*-(2,6-difluorobenzoyl)phosphoric triamide, C₂₁H₁₈Cl₂F₂N₃O₂P, (I), *N*-(2,6-difluorobenzoyl)-*N',N''*-bis(4-methoxybenzyl)phosphoric triamide, C₂₃H₂₄F₂N₃O₄P, (II), and *N*-(2-chloro-2,2-difluoroacetyl)-*N',N''*-bis(4-methylphenyl)phosphoric triamide, C₁₆H₁₇ClF₂N₃O₂P, (III), C=O···H—N_{C(O)NHP(O)} and P=O···H—N_{amide} hydrogen bonds are responsible for the aggregation of the molecules. This is the opposite result from that commonly observed for carbacylamidophosphates, which show a tendency for the phosphoryl group, rather than the carbonyl counterpart, to form hydrogen bonds with the NH group of the C(O)NHP(O) skeleton. This hydrogen-bond pattern leads to cyclic R₂²(10) motifs in (I)–(III), different from those found for all previously reported compounds of the general formula RC(O)NHP(O)[NR¹R²]₂ with the *syn* orientation of P=O *versus* NH [R₂²(8)], and also from those commonly observed for RC(O)NHP(O)[NHR¹]₂ [a sequence of alternate R₂²(8) and R₂²(12) motifs]. In these cases, the R₂²(8) and R₂²(12) graph sets are formed through similar kinds of hydrogen bond, *i.e.* a pair of P=O···H—N_{C(O)NHP(O)} hydrogen bonds for the former and two C=O···H—N_{amide} hydrogen bonds for the latter. This article also reviews 102 similar structures deposited in the Cambridge Structural Database and with the International Union of Crystallography, with the aim of comparing hydrogen-bond strengths in the above-mentioned cyclic motifs. This analysis shows that the strongest N—H···O hydrogen bonds exist in the R₂²(8) rings of some molecules. The phosphoryl and carbonyl groups in each of compounds (I)–(III) are *anti* with respect to each other and the P atoms are in a tetrahedral coordination environment. In the crystal structures, adjacent molecules are

linked *via* the above-mentioned hydrogen bonds in a linear arrangement, parallel to [010] for (I) and (III) and parallel to [100] for (II). Formation of the N_{C(O)NHP(O)}—H···O=C instead of the N_{C(O)NHP(O)}—H···O=P hydrogen bond is reflected in the higher N_{C(O)NHP(O)}—H vibrational frequencies for these molecules compared with previously reported analogous compounds.

Comment

In a recently published paper by Toghraee *et al.* (2011), the patterns of hydrogen bonds were studied in the crystal packing of phosphoric triamides (PTAs) containing a C(O)NHP(O) skeleton. The authors classified this category of phosphoramidate compounds into different subclasses with C(O)NH-P(O)(N)₂ and C(O)NHP(O)(NH)₂ moieties, denoted subclasses *A* and *B*, respectively. It was found that the phosphoryl group is a better donor than the carbonyl counterpart, so that in all deposited CIF files in the Cambridge Structural Database (CSD, Version 5.32, November 2010 update; Allen, 2002) belonging to subclass *A*, only the PO···H—N hydrogen bond was observed in the crystal packing. When the P=O group and N—H unit are *syn* with respect to one another, this type of hydrogen bond forms a hydrogen-bonded dimer [R₂²(8) ring; for graph-set notation, see Bernstein *et al.* (1995)] (Fig. 1). Moreover, for most cases of compounds in subclass *B*, the NH group of the C(O)NHP(O) moiety is hydrogen bonded to P(O), whereas the H atom of the NHR' unit is involved in a hydrogen-bond interaction with C(O). These interactions usually produce two different kinds of centrosymmetric cyclic motifs, *viz.* R₂²(8) and R₂²(12), which are alternate in a linear arrangement. The R₂²(8) motif is formed through a pair of N_{C(O)NHP(O)}—H···O=P hydrogen bonds, while the R₂²(12) ring is built *via* two C=O···H—N_{amide} hydrogen bonds (Fig. 2). Among the published structures, the C=O···H—N_{C(O)NHP(O)} interaction was found for only two examples, *i.e.* C₆H₅C(O)NHP(O)[NHCH₂C₆H₅]₂ (Gholivand *et al.*, 2006) and C₆H₅C(O)NHP(O)[NHC₆H₁₁]₂ (Pourayoubi, Rostami Chaijan *et al.*, 2011*a*). However, the existence of the PO···HNR' interaction has been observed for four compounds as a PO[···HN_{C(O)NHP(O)}][···HNR'] (Gubina *et al.*, 2009; Gholivand, Shariatinia, Mashhadi *et al.*, 2009) and a PO[···HNR']₂ hydrogen bond (Gholivand *et al.*, 2006; Pour-

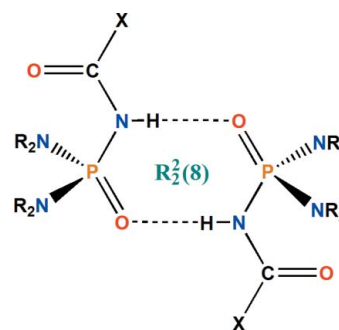
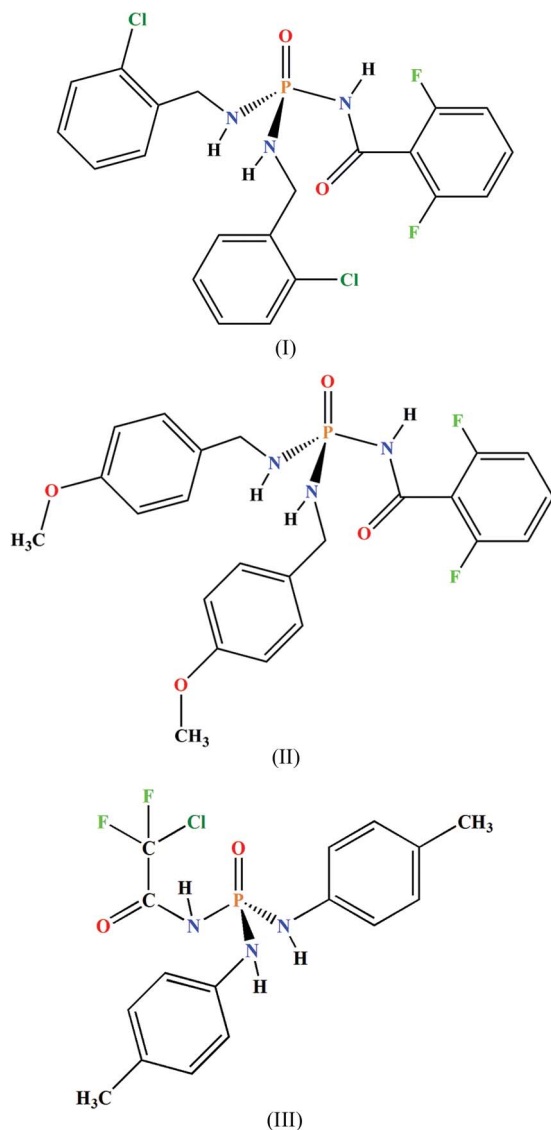


Figure 1

The R₂²(8) graph set in compounds containing a C(O)NHP(O)(N)₂ skeleton and a *syn* orientation of P=O *versus* NH.

ayoubi, Rostami Chaijan *et al.*, 2011a), where the O atoms act as double hydrogen-bond acceptors (Steiner, 2002).

We present here the three new compounds, *N,N'*-bis(2-chlorobenzyl)-*N''*-(2,6-difluorobenzoyl)phosphoric triamide, (I), *N*-(2,6-difluorobenzoyl)-*N',N''*-bis(4-methoxybenzyl)phosphoric triamide, (II), and *N*-(2-chloro-2,2-difluoroacetyl)-*N',N''*-bis(4-methylphenyl)phosphoric triamide, (III), which show relatively rare $C=O \cdots H-N_{C(O)NHP(O)}$ and $P=O \cdots H-N_{amide}$ hydrogen bonds. In addition, we attempted to analyse the strength of the hydrogen bonds based on their motifs, and also to find a relationship between the N–H stretching frequency and the hydrogen-bond pattern.



For compounds (I)–(III), single crystals were obtained at room temperature from a 1:2 mixture of $CH_3OH/CHCl_3$ for (I) and (II), and from a 1:4 mixture of CH_3CN/CH_3OH for (III). Their molecular structures are shown in Figs. 3, 4 and 5, respectively. The P atoms exhibit a distorted tetrahedral environment, as has been noted for other phosphoric triamides and their chalcogeno-derivatives (Rudd *et al.*, 1996). For example, in (I), the bond angles at the P atom vary in the range

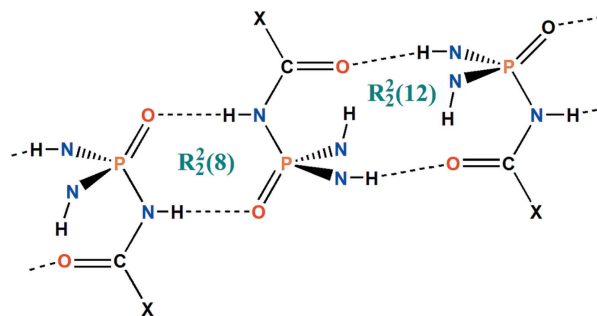


Figure 2
A view of the $R_2^2(8)$ and $R_2^2(12)$ motifs in compounds containing a $C(O)NHP(O)(NH)_2$ skeleton.

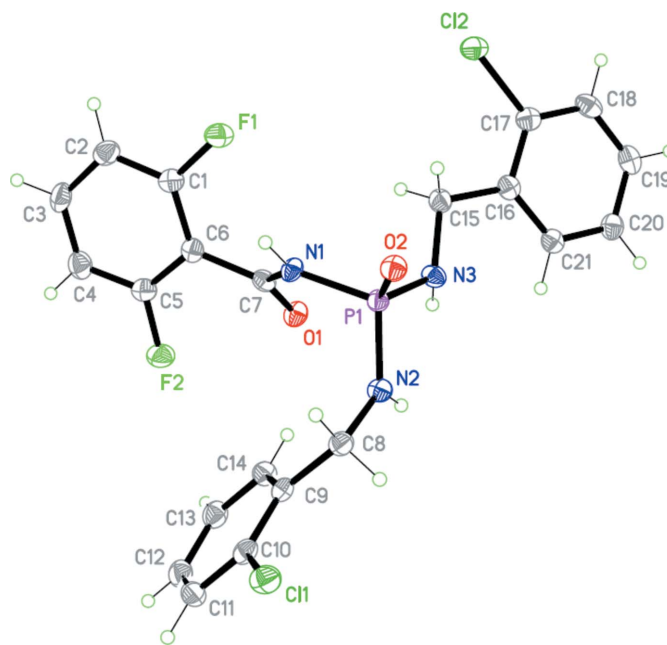


Figure 3
The molecular structure and atom-labelling scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

$102.33(13)$ – $116.04(12)^\circ$, while the P–N bond lengths range from 1.616 (2) to 1.707 (2) Å (Table 1). The phosphoryl and carbonyl groups adopt an *anti* relationship in these structures, which is in agreement with all previously reported acyclic phosphoramidate compounds (Gholivand & Pourayoubi, 2004; Gholivand, Shariatinia, Mashhadi *et al.*, 2009) containing a $C(O)NHP(O)(NH)_2$ skeleton. This conformation is the opposite of the orientation of P(O) and C(O) groups in the diazaphosphorinanes $CCl_3C(O)NHP(O)X$ ($X = NHC_{10}H_6NH$; Gholivand, Shariatinia, Ansar *et al.*, 2009), $4-F-C_6H_4C(O)NHP(O)X$ [$X = NHCH_2C(CH_3)_2CH_2NH$; Tarahhomi *et al.*, 2011] and $CCl_2HC(O)NHP(O)X$ [$X = NHCH_2C(CH_3)_2CH_2NH$; Toghraee *et al.*, 2011], and a few examples of compounds with the formula $RC(O)NHP(O)[NR^1R^2]_2$, which show a *gauche* orientation of $P=O$ versus $C=O$ (Toghraee *et al.*, 2011).

The P=O bond lengths are standard in (I) [1.475 (2) Å], (II) [1.4804 (12) Å] and (III) [1.475 (4) Å]. As expected, the

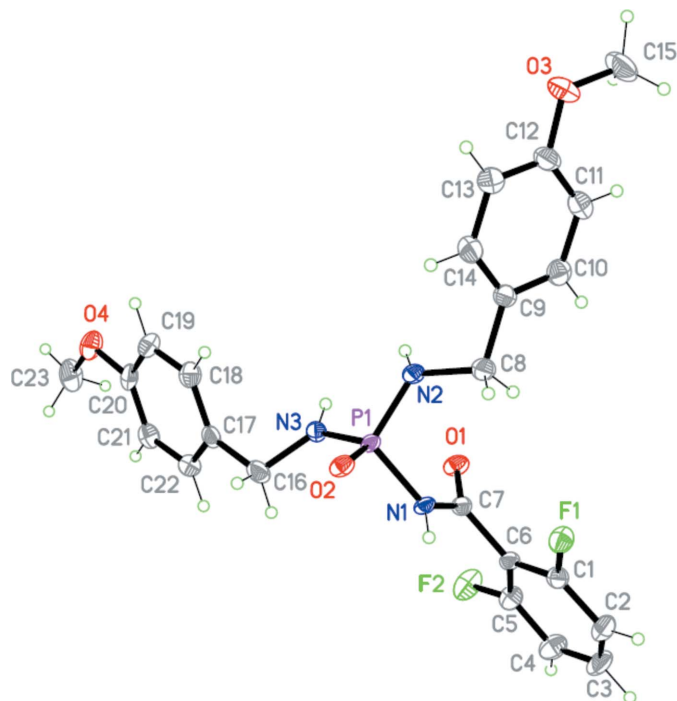


Figure 4

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

P–N_{amide} bond lengths in all three compounds were found to be significantly shorter than the related P–N_{C(O)NHP(O)} bond lengths (Tables 1, 3 and 5).

In (I) and (II), the chemical natures of the N atoms in both compounds are different, so that the N atom of one benzyl-amido moiety exhibits a slight deviation from planarity, while

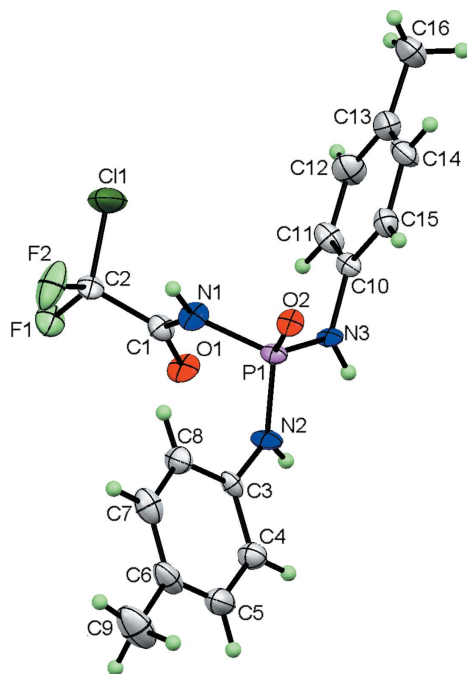


Figure 5

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

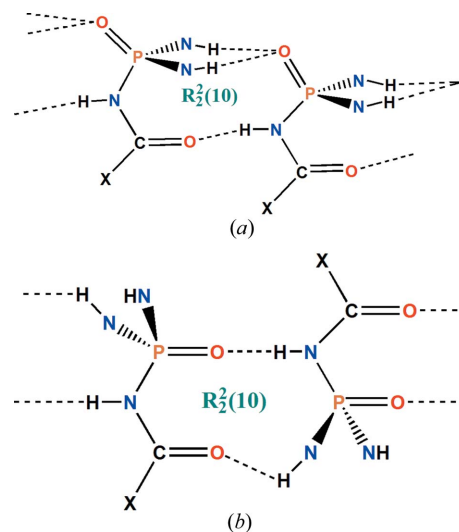


Figure 6

Two types of $R_2^2(10)$ graph sets in compounds containing a C(O)NH-P(O)(NH)₂ skeleton.

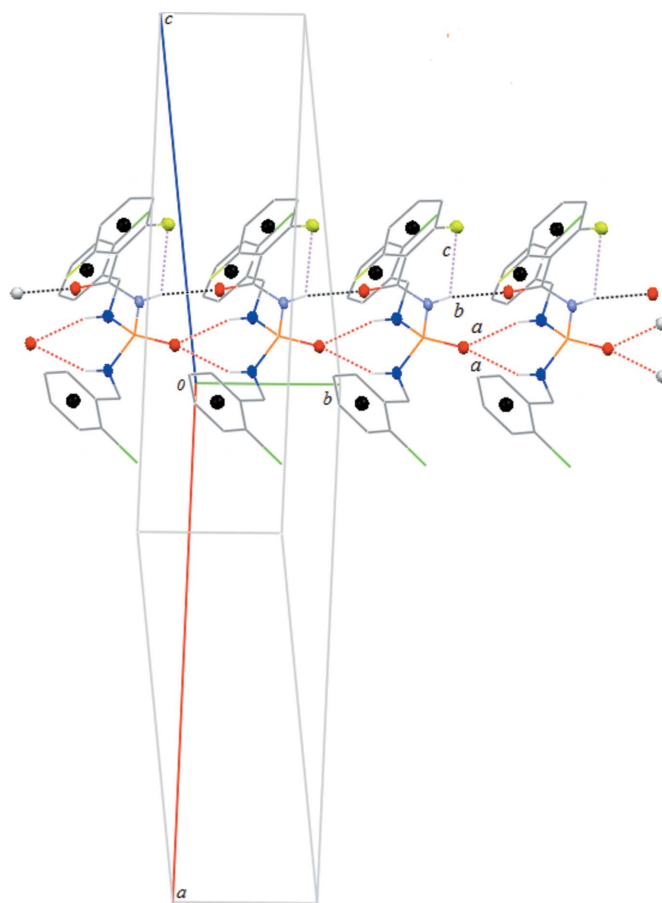
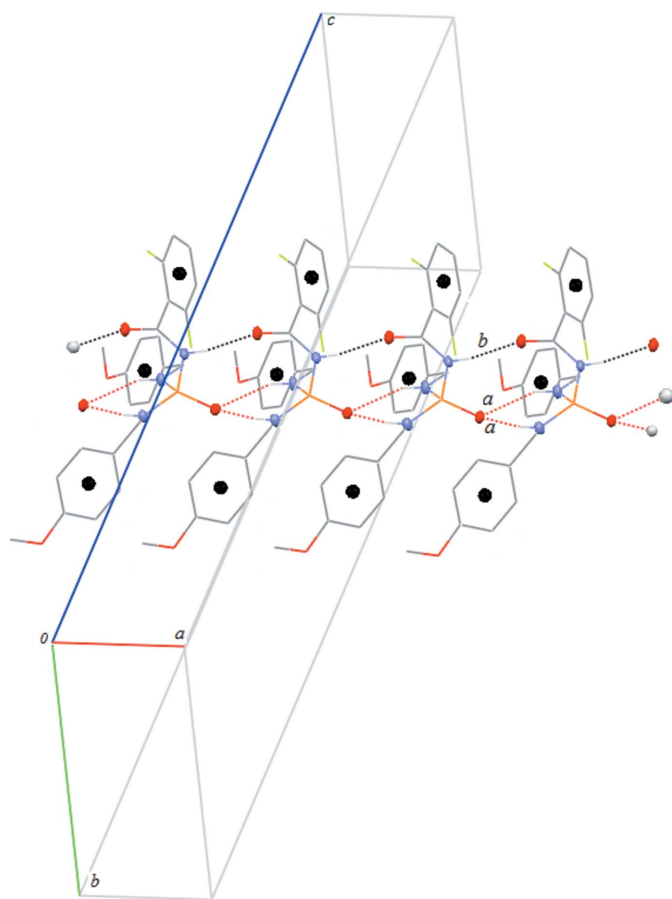
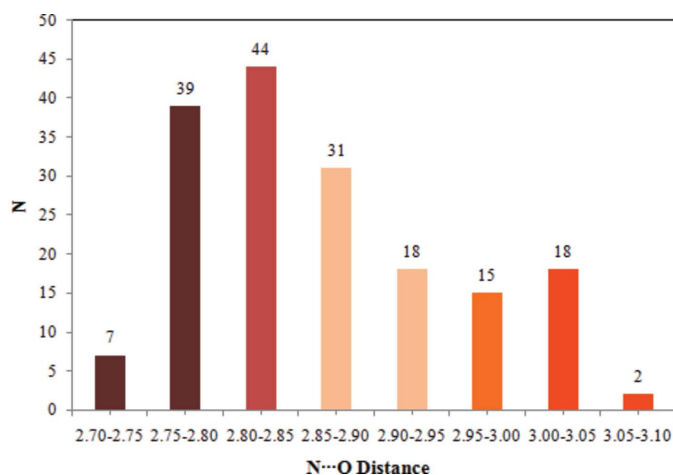


Figure 7

A crystal packing diagram for (I). H atoms bound to C atoms have been omitted for clarity. The P=O...H–N_{amide} (marked *a*), C=O...H–N_{C(O)NHP(O)} (marked *b*) and F...H–N_{C(O)NHP(O)} (marked *c*) hydrogen bonds are shown. [Colour key for the electronic version of the paper: red, black and violet dashed lines, respectively. Additionally, O atoms are red, amide N atoms are dark blue, N_{C(O)NHP(O)} atoms are light blue, F atoms are green–yellow and H atoms are light grey.]


Figure 8

A crystal packing diagram for (II). H atoms bound to C atoms have been omitted for clarity. The $\text{P}=\text{O}\cdots\text{H}-\text{N}_{\text{amide}}$ (marked *a*) and $\text{C}=\text{O}\cdots\text{H}-\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}$ (marked *b*) hydrogen bonds are shown. (Colour key for the electronic version of the paper: red and black dashed lines, respectively; the atomic colour scheme is the same as for Fig. 7.)


Figure 9

A histogram of $\text{N}\cdots\text{O}$ distances in $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds for phosphoric triamides with a $\text{C}(\text{O})\text{NHP}(\text{O})$ skeleton (for an $\text{N}-\text{H}\cdots\text{O}$ angle more than 110°). The data shown in the first two and last two columns (brown and red, respectively, in the electronic version of the paper) were observed for $\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}-\text{H}\cdots\text{O}$ and $\text{N}_{\text{amide}}-\text{H}\cdots\text{O}$ hydrogen bonds, respectively. Both types of hydrogen bond were observed in the range 2.80–3.00 Å (central four columns, light brown). Only one $\text{N}_{\text{amide}}-\text{H}\cdots\text{O}$ and one $\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}-\text{H}\cdots\text{O}$ hydrogen bond, respectively, are found in the ranges 2.80–2.85 and 2.95–3.00 Å.

the N atoms of the benzoylamido and the other benzylamido moiety have a practically planar environment. In (III), the environments of all three N atoms are nearly planar. None of these N atoms acts in any hydrogen bond as an acceptor, thus exhibiting low Lewis base character. As expected, the $\text{C}-\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}$ bonds for these structures are shorter than the other $\text{C}-\text{N}_{\text{amide}}$ bonds.

In the structures of (I)–(III), adjacent molecules are linked *via* $\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds and also through two different $\text{N}_{\text{amide}}-\text{H}\cdots\text{O}=\text{P}$ hydrogen bonds involving the same pair of molecules (Tables 2, 4 and 6), building $R_2^2(10)$ rings (Fig. 6*a*) in a linear arrangement, parallel to [010] for (I) and (III) [for example, see Fig. 7 for compound (I)] and parallel to [100] for (II) (Fig. 8). This means that, in each of these structures, the phosphoryl group acts as a double hydrogen-bond acceptor to form a $\text{P}=\text{O}[\cdots\text{H}-\text{N}_{\text{amide}}]_2$ grouping. Another type of $R_2^2(10)$ graph set, forming by co-operation of $\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}-\text{H}\cdots\text{O}(\text{P})$ and $\text{N}_{\text{amide}}-\text{H}\cdots\text{O}(\text{C})$ hydrogen bonds, is observed for diazaphosphorinane $\text{CHCl}_2\text{C}(\text{O})\text{NHP}(\text{O})X$ [$X = \text{HNCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}$; Toghraee *et al.*, 2011] (Fig. 6*b*).

This hydrogen-bond pattern is the opposite of that commonly observed for carbacylamidophosphates, which show a tendency for the phosphoryl group, rather than the carbonyl counterpart, to form hydrogen bonds with the more acidic NH group of the $\text{C}(\text{O})\text{NHP}(\text{O})$ skeleton, whereas the NH group of the NHR' unit is hydrogen bonded to C(O).

Exceptions to this bonding selectivity in these structures may be attributed to kinetic factors controlling the crystal growth (MacDonald & Whitesides, 1994).

A search for phosphoric triamides with a $\text{C}(\text{O})\text{NHP}(\text{O})$ skeleton in the CSD and recently published papers (Pourayoubi, Tarahhomi *et al.*, 2010*a,b*, 2011; Pourayoubi, Rostami Chaijan *et al.*, 2011*a,b*; Pourayoubi & Saneei, 2011; Pourayoubi, Toghraee & Divjakovic, 2011; Raissi Shabari *et al.*, 2011; Tarahhomi *et al.*, 2011; Toghraee *et al.*, 2011) shows that the strongest $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are found for $\text{P}=\text{O}\cdots\text{H}-\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}$ hydrogen bonds, especially in the $R_2^2(8)$ rings of some molecules [in the case of a *syn* orientation of $\text{P}=\text{O}$ *versus* $\text{N}-\text{H}$ which allows the building of the cyclic motif through a pair of $\text{P}=\text{O}\cdots\text{H}-\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}$ hydrogen bonds]. A histogram of the $\text{N}\cdots\text{O}$ distances in these $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds is given in Fig. 9. The strongest (two columns on the left) and weakest (two columns on the right) hydrogen bonds are shown for $\text{N}\cdots\text{O}$ distances in the ranges 2.70–2.80 Å [for $\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}-\text{H}\cdots\text{O}(\text{P})$ hydrogen bonds] and 3.00–3.10 Å [for $\text{N}_{\text{amide}}-\text{H}\cdots\text{O}(\text{C})$ hydrogen bonds], while in the range 2.80–3.00 Å for donor–acceptor distances both types of hydrogen bond are found.

In (I), besides co-operation in the $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond, the benzamide $\text{N}-\text{H}$ group is involved in an intramolecular $\text{N1}-\text{H1N}\cdots\text{F1}$ hydrogen bond (Table 2). Further stabilization of (I) is produced *via* a weak $\text{C11}-\text{H11A}\cdots\text{F2}^{\text{iii}}$ hydrogen bond and $\text{C}=\text{O1}\cdots\text{F1}^{\text{i}}$ [$\text{O1}\cdots\text{F1}^{\text{i}} = 2.876(3)$ Å; symmetry code: (i) $x, y + 1, z$] and $\text{Cl2}\cdots\text{Cl2}^{\text{iv}}$ [$3.258(1)$ Å; symmetry code: (iv) $-x, -y + 2, -z + 1$] intermolecular interactions.

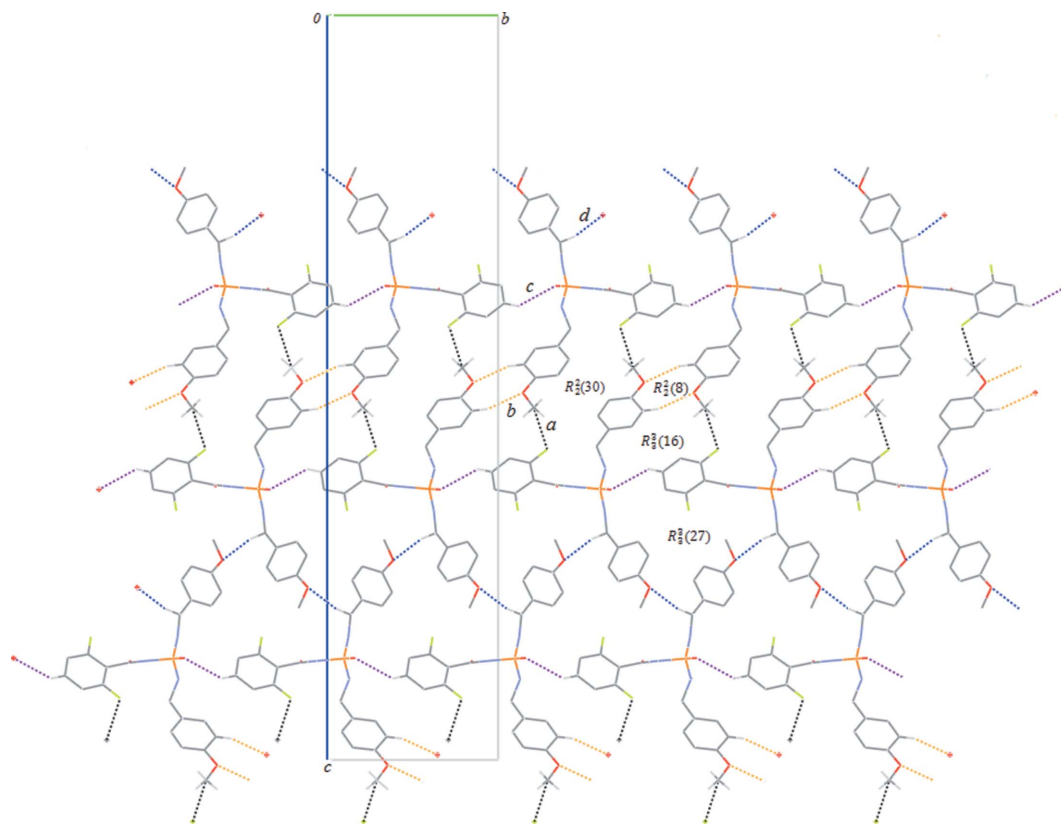


Figure 10

A partial crystal packing diagram for (II), viewed parallel to the bc plane, formed *via* intermolecular C—H \cdots F and C—H \cdots O hydrogen bonds (the N—H \cdots O hydrogen bonds are along the a axis). H atoms involved in contacts are shown as light grey and the other H atoms have been omitted for clarity. The C15_{methoxy}—H15A \cdots F1ⁱⁱⁱ (marked *a*), C13—H13A \cdots O3^{iv}_{methoxy} (marked *b*), C3—H3B \cdots (O2)P1^v (marked *c*) and C16—H16B \cdots O4^{vi}_{methoxy} (marked *d*) hydrogen bonds are shown (colour key for the electronic version of the paper: black, orange, purple and blue dashed lines, respectively). The symmetry codes are as in Table 4.

The hydrogen-bond pattern in (II) is complicated. A pair of C15_{methoxy}—H15A \cdots F1ⁱⁱⁱ hydrogen bonds make an $R_2^2(30)$ ring, whereas a combination of one C13—H13A \cdots O3^{iv}_{methoxy}, one C_{methoxy}—H \cdots F and one C3—H3B \cdots (O2)P1^v hydrogen bond forms $R_3^3(16)$ rings. Moreover, the cyclic dimer motif is composed of a pair of intermolecular C—H \cdots O_{methoxy} hydrogen bonds forming a centrosymmetric $R_2^2(8)$ ring (Fig. 10). Also, a trimer motif, *viz.* an $R_3^3(27)$ ring (Fig. 10), is formed through a combination of two intermolecular C16—H16B \cdots O4^{vi}_{methoxy} and one C—H \cdots (O)P hydrogen bond. These hydrogen bonds expand the crystal structure of (II) into a three-dimensional arrangement. A weak C7=O1 \cdots F1ⁱ [O1 \cdots F1ⁱ = 2.986 (2) Å; symmetry code: (i) $x + 1, y, z$] interaction is also found in the crystal packing. The crystal packing of (III) does not show any C—H \cdots X ($X = O, F$ or Cl) interactions.

In a paper by Tarahhomi *et al.* (2011), the effect of lowering the $N_{C(O)NHP(O)}-H$ vibrational frequency by strong $N_{C(O)NHP(O)}-H\cdots O=P$ hydrogen bonds was discussed, so that a compound with a stronger N—H \cdots O hydrogen bond showed a lower N—H vibrational frequency. Moreover, the $N_{C(O)NHP(O)}-H$ stretching mode appeared at a lower frequency than that of $N_{amide}-H$.

The differences in the N—H regions in the IR spectroscopic data of (I)–(III) from those of previously reported analogous

compounds may be a result of these different hydrogen-bond patterns. For example, in the compounds 2-NO₂-C₆H₄-C(O)NHP(O)[N(C₂H₅)₂]₂ (Gholivand *et al.*, 2010) and Cl₃CC(O)NHP(O)[NHC(CH₃)₃]₂ (Gholivand & Pourayoubi, 2004), the $N_{C(O)NHP(O)}-H$ stretching frequencies, which are involved in the $N_{C(O)NHP(O)}-H\cdots O(P)$ hydrogen bond, appear at 3030 and 3045 cm⁻¹, respectively, while no absorption bands for N—H stretching frequencies are observed below 3180 cm⁻¹ in any of (I)–(III). In (I), three absorption bands are revealed at 3204, 3262 and 3345 cm⁻¹, while for (II), with hydrogen bonds of fairly similar strengths, the N—H stretching modes overlap and only one absorption band appears at 3263 cm⁻¹. For (III), the absorption bands at 3260 and 3183 cm⁻¹ are assigned to the N—H stretching modes.

Experimental

2,6-F₂-C₆H₃C(O)NHP(O)Cl₂ and CClF₂C(O)NHP(O)Cl₂ were prepared according to the literature methods reported by Pourayoubi, Tarahhomi *et al.* (2010a) and Iriarte *et al.* (2008), respectively.

Compound (I) was synthesized from the reaction of 2,6-F₂-C₆H₃C(O)NHP(O)Cl₂ (0.35 g, 1.28 mmol) and 2-chlorobenzylamine (0.725 g, 5.12 mmol) in dry chloroform (30 ml). After stirring for 6 h, the solvent was evaporated and the product was washed with distilled water and recrystallized from a 1:2 (v/v) mixture of methanol and

chloroform at room temperature. IR (KBr, ν , cm^{-1}): 3345 (NH), 3262 (NH), 3204 (NH), 2925, 1668 (C=O), 1623, 1470, 1426, 1287, 1236, 1205, 1127, 1090, 1049, 1041, 1011, 902, 817, 769, 753, 694, 584, 510, 578.

Compound (II) was synthesized by a similar method to (I), but using 4-methoxybenzylamine (0.598 g, 4.36 mmol) instead of 2-chlorobenzylamine [2,6-F₂-C₆H₃C(O)NHP(O)Cl₂: 0.30 g, 1.09 mmol]. Single crystals suitable for X-ray crystallography were obtained after recrystallization from a 1:2 (v/v) mixture of methanol and chloroform at room temperature. IR (KBr, ν , cm^{-1}): 3263 (NH), 3003, 2958, 1668 (C=O), 1623, 1589, 1515, 1466, 1441, 1303, 1253, 1197, 1078, 1042, 1007, 923, 813, 788, 764, 698, 588, 523, 478.

Compound (III) was synthesized from the reaction of CCl₄-F₂C(O)NHP(O)Cl₂ (0.40 g, 1.6 mmol) in dry CHCl₃ and a solution of *p*-toluidine (0.343 g, 3.2 mmol) and triethylamine (0.324 g, 3.2 mmol) in dry CHCl₃ at 273 K. After stirring for 4 h, the solvent was evaporated at room temperature. The solid product was washed with water. Single crystals suitable for X-ray crystallography were recrystallized from a 4:1 (v/v) mixture of methanol and acetonitrile by slow evaporation at room temperature. IR (KBr, ν , cm^{-1}): 3260 (NH), 3183 (NH), 2927, 1717 (C=O), 1620, 1517, 1466, 1383, 1281, 1225, 1163, 1133, 963, 863, 813, 697.

Compound (I)

Crystal data

C ₂₁ H ₁₈ Cl ₂ F ₂ N ₃ O ₂ P	$V = 2058.2$ (4) Å ³
$M_r = 484.25$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 19.643$ (3) Å	$\mu = 0.44$ mm ⁻¹
$b = 4.9874$ (6) Å	$T = 100$ K
$c = 21.482$ (3) Å	$0.25 \times 0.10 \times 0.10$ mm
$\beta = 102.056$ (2)°	

Table 1

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

P1—O2	1.475 (2)	O1—C7	1.227 (3)
P1—N2	1.616 (2)	N1—C7	1.355 (4)
P1—N3	1.632 (2)	N2—C8	1.457 (4)
P1—N1	1.707 (2)	N3—C15	1.465 (4)
O2—P1—N2	115.79 (12)	N3—P1—N1	108.83 (12)
O2—P1—N3	116.04 (12)	C7—N1—P1	123.5 (2)
N2—P1—N3	102.33 (13)	C8—N2—P1	123.93 (19)
O2—P1—N1	104.51 (11)	C15—N3—P1	120.01 (19)
N2—P1—N1	109.20 (12)	O1—C7—N1	121.7 (2)
O2—P1—N1—C7	173.6 (2)	N3—P1—N1—C7	49.1 (3)
N2—P1—N1—C7	-61.9 (3)	P1—N1—C7—O1	2.6 (4)

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 (2)	2.04 (2)	2.858 (3)	162 (3)
N1—H1N \cdots F1	0.85 (2)	2.44 (3)	2.881 (3)	113 (2)
N2—H2N \cdots O2 ⁱⁱ	0.83 (2)	2.32 (2)	3.092 (3)	154 (3)
N3—H3N \cdots O2 ⁱⁱ	0.83 (2)	2.08 (2)	2.869 (3)	161 (3)

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

Table 3

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

P1—O2	1.4804 (12)	O1—C7	1.225 (2)
P1—N3	1.6141 (14)	N1—C7	1.355 (2)
P1—N2	1.6263 (14)	N2—C8	1.465 (2)
P1—N1	1.7084 (14)	N3—C16	1.461 (2)
O2—P1—N3	114.12 (7)	N2—P1—N1	106.75 (7)
O2—P1—N2	117.74 (7)	C7—N1—P1	125.50 (11)
N3—P1—N2	103.24 (7)	C8—N2—P1	121.68 (12)
O2—P1—N1	102.89 (7)	C16—N3—P1	124.33 (12)
N3—P1—N1	112.12 (7)	O1—C7—N1	123.24 (15)
O2—P1—N1—C7	-178.00 (13)	N2—P1—N1—C7	-53.42 (15)
N3—P1—N1—C7	58.94 (15)	P1—N1—C7—O1	-7.4 (2)

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	0.84 (1)	2.07 (2)	2.8958 (18)	169 (2)
N2—H2N \cdots O2 ⁱⁱ	0.83 (2)	2.04 (2)	2.8414 (18)	163 (2)
N3—H3N \cdots O2 ⁱⁱ	0.83 (2)	2.15 (2)	2.9173 (18)	153 (2)
C3—H3B \cdots O2 ^v	0.95	2.61	3.293 (2)	129
C13—H13A \cdots O3 ^{iv}	0.95	2.49	3.390 (3)	158
C15—H15A \cdots F1 ⁱⁱⁱ	0.98	2.76	3.156 (2)	105
C16—H16B \cdots O4 ^{vi}	0.99	2.68	3.581 (2)	151

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $-x, -y + 1, -z + 1$; (iv) $-x, -y + 2, -z + 1$; (v) $x, y - 1, z$; (vi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection

Bruker APEXII CCD area-detector diffractometer	25048 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)	4821 independent reflections
$T_{\min} = 0.899, T_{\max} = 0.958$	3463 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.128$
 $S = 1.03$
 4821 reflections
 289 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.65$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³

Compound (II)

Crystal data

C ₂₃ H ₂₄ F ₂ N ₃ O ₄ P	$V = 2249.7$ (5) Å ³
$M_r = 475.42$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 4.8252$ (6) Å	$\mu = 0.17$ mm ⁻¹
$b = 10.3456$ (12) Å	$T = 100$ K
$c = 45.068$ (5) Å	$0.22 \times 0.10 \times 0.10$ mm
$\beta = 90.530$ (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	18537 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)	5131 independent reflections
$T_{\min} = 0.963, T_{\max} = 0.983$	4200 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.042$

Table 5
Selected geometric parameters (Å, °) for (III).

P1—O2	1.475 (4)	F1—C2	1.330 (6)
P1—N2	1.615 (5)	O1—C1	1.233 (6)
P1—N3	1.622 (4)	N1—C1	1.339 (7)
P1—N1	1.707 (5)	N2—C3	1.410 (7)
O2—P1—N2	116.7 (2)	N3—P1—N1	107.9 (2)
O2—P1—N3	117.1 (2)	C1—N1—P1	123.4 (4)
N2—P1—N3	102.1 (2)	C3—N2—P1	126.5 (4)
O2—P1—N1	104.2 (2)	C10—N3—P1	120.9 (3)
N2—P1—N1	108.5 (2)	O1—C1—N1	124.8 (5)
O2—P1—N1—C1	176.1 (4)	N3—P1—N1—C1	51.0 (5)
N2—P1—N1—C1	−58.9 (5)	P1—N1—C1—O1	3.3 (8)

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O1 ⁱ	0.86 (2)	2.05 (3)	2.877 (6)	163 (5)
N2—H2...O2 ⁱⁱ	0.85 (2)	2.19 (3)	2.986 (6)	158 (5)
N3—H3...O2 ⁱⁱ	0.84 (2)	2.20 (3)	2.972 (5)	153 (5)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.101$

$S = 1.05$

5131 reflections

309 parameters

3 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.41 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$

Compound (III)

Crystal data

 $C_{16}H_{17}ClF_2N_3O_2P$ $M_r = 387.75$ Monoclinic, $C2/c$ $a = 21.164 (5) \text{ Å}$ $b = 5.0011 (12) \text{ Å}$ $c = 33.635 (8) \text{ Å}$ $\beta = 95.149 (5)^\circ$ $V = 3545.7 (15) \text{ Å}^3$ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.34 \text{ mm}^{-1}$ $T = 120 \text{ K}$ $0.40 \times 0.25 \times 0.15 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1998)

$T_{\min} = 0.903, T_{\max} = 0.950$

16802 measured reflections

3058 independent reflections

1614 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.111$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.076$

$wR(F^2) = 0.197$

$S = 1.00$

3058 reflections

237 parameters

3 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.54 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.44 \text{ e } \text{Å}^{-3}$

length restraint of $0.85 (2) \text{ Å}$ and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The positions of H atoms bound to C atoms were calculated and refined as isotropic using an appropriate riding model; for compounds (I) and (II), bond distances were 0.95, 0.99 and 0.98 Å for CH, CH₂ and CH₃ groups, respectively, with riding constraints of $1.2U_{\text{eq}}(\text{C})$ for CH and CH₂ groups, and $1.5U_{\text{eq}}(\text{C})$ for CH₃ groups. For compound (III), the distance values were 0.93 and 0.96 Å for CH and CH₃ groups, respectively, with $U_{\text{iso}}(\text{H}) = 1.2$ and $1.5U_{\text{eq}}(\text{C})$, respectively.

Data collection: APEX2 (Bruker, 2005) for (I) and (II); SMART (Bruker, 1998) for (III). Cell refinement: SAINT (Bruker, 2005) for (I) and (II); SAINT-Plus (Bruker, 1998) for (III). Data reduction: SAINT for (I) and (II); SAINT-Plus for (III). For all compounds, program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXTL and enCIFer (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: YP3002). Services for accessing these data are described at the back of the journal.

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