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Phosphoramidates: Molecular Packing and Hydrogen Bond Strength in Compounds Having a $P(O)(N)_n(O)_{3-n}$ (n = 1, 2, 3) Skeleton

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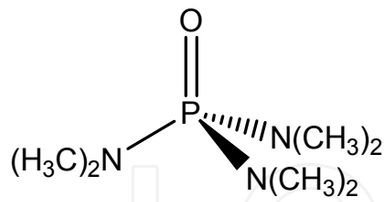
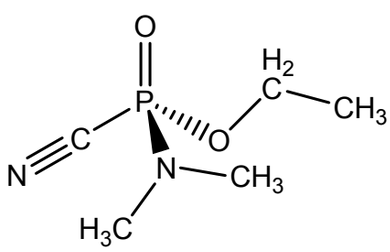
1. Introduction

Compounds containing the $P(O)(N)_n(O)_{3-n}$ (n = 1, 2, 3), $P(O)(N)_m(O)_{2-m}X$ (m = 1, 2, X = C, Cl, F, S etc.) and $P(O)(O)_3$ moieties are among the well-studied inorganic compounds [an interested reader may find many examples of compounds with the mentioned skeletons through a CSD search, [1]]. *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethyl phosphoric triamide (HMPA, Scheme 1) is an important polar aprotic solvent with a high-dielectric constant [2] and an excellent ligand for interaction with hard metal-cations [3].



Scheme 1. *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethyl phosphoric triamide

Tabun, $NCP(O)[N(CH_3)_2][OCH_2CH_3]$ (Scheme 2), Sarin, $FP(O)(CH_3)[OCH(CH_3)_2]$ and Soman, $CH_3P(O)(F)[OCH(CH_3)(C(CH_3)_3)]$ are among the well-known "nerve agents" that act as acetylcholinesterase enzyme (AChE) inhibitors in human body and mammals [4].



Scheme 2. Tabun, a nerve agent

Some researchers focus on decontamination of such compounds under UV-irradiation or in the presence of nano-oxides or nano-photocatalysts under sun-light [5]. The flame retardancy of some phosphoric esters was studied [6] and some phosphoramidates have therapeutic applications in the treatments of HIV and cancer [7]. Some pure chemists have interested to the NMR consideration [8], chemical calculation [9] and crystallography [10] of such compounds. A few bio-inorganic chemists have worked on the prediction of the biological properties of compounds based on their structures, with the related software programs such as PASS [11], and the evaluation of some relationships between structural features and biological activities [12]. In our laboratory, we centralize on the synthesis of new phosphorus-nitrogen and phosphorus-oxygen compounds and on obtaining their suitable single crystals for the X-ray crystallography experiments [13-64].

A schematic classification for the compounds having a $P(O)(N)_n(O)_{3-n}$ (n = 1, 2, 3) skeleton is shown in Scheme 3.

The numbers of the reported crystal structures in each family are presented in Scheme 3. The central box (blue) indicates the overall number of phosphoramidates having a $P(O)(N)_n(O)_{3-n}$ (n = 1, 2, 3) skeleton; the more well-studied categories of phosphoramidates are shown as green boxes in the top and bottom of the central box namely: a) phosphoric triamides (having a P(O)(N)(N)(N) or P(O)(NHC(O))(N)(N) fragment), and b) amidophosphoric acid esters (containing a P(O)(O)(N)(N) or P(O)(O)(O)(N) skeleton).

As a nitrogen bonded H atom is very important in the H-bond pattern consideration, in the sub-categories, the presence or the absence of this H atom is clarified. In the applied notation, for example, the $P(O)(NH)_3$ and $P(O)(N)_3$ denote to the presence of secondary and tertiary nitrogen atoms, respectively. The phosphoramidates containing a $P(O)NH_2$ moiety are distinguished in the left side box directly related to the central box.

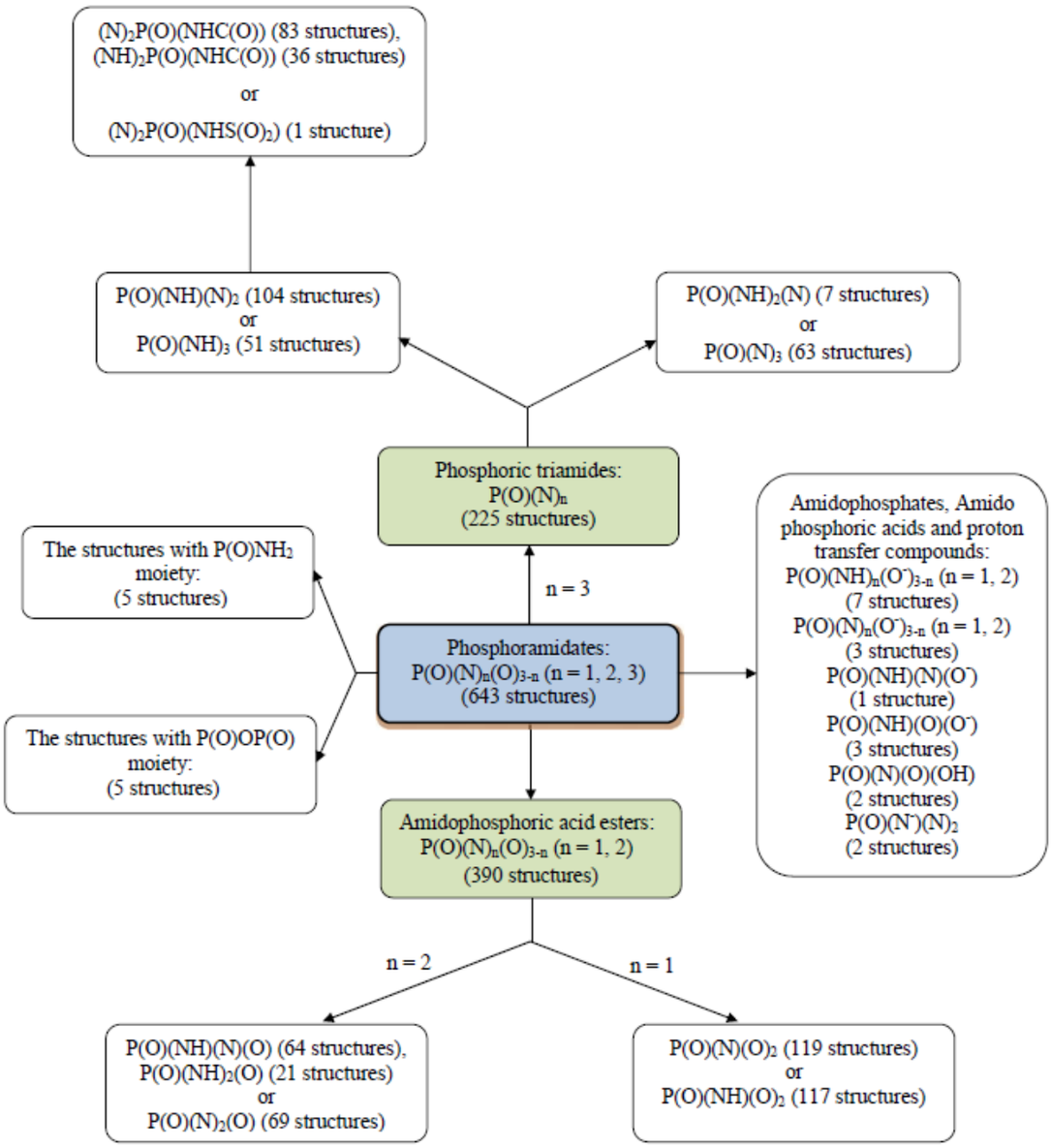
The less-studied (so far) related compounds i.e. c) the proton-transfer and phosphate salts and the acids, and d) the anhydride compounds with a P(O)(O)P(O) skeleton are shown in the right and the left of the central box.

In this flowchart, the skeletons of 643 compounds -which their crystal structures were deposited- have been collected. In this classification, the phosphoramidates containing the phosphorus-carbon and the phosphorus-halogen bonds have not been considered.

2. Synthesis and purification of phosphoramidates and phosphoric acid esters

The reaction of phosphorus(V)-halogen compounds of the type $P(O)X_{3-n}Y_n$ (X = halide, Y = another group such as amide, alkoxide and so on, and n = 0, 1 and 2) with primary or secondary amines leads to the formation of phosphorus(V)-nitrogen compounds. The promotion of this reaction needs to the presence of an excess amount of amine as an HX scavenger or the presence of another acid scavenger such as tertiary amines [61] or pyridine [8] (Scheme 4). In this strategy, removing of the hydrohalide salt of the organic base is a challenging task in the purification process.

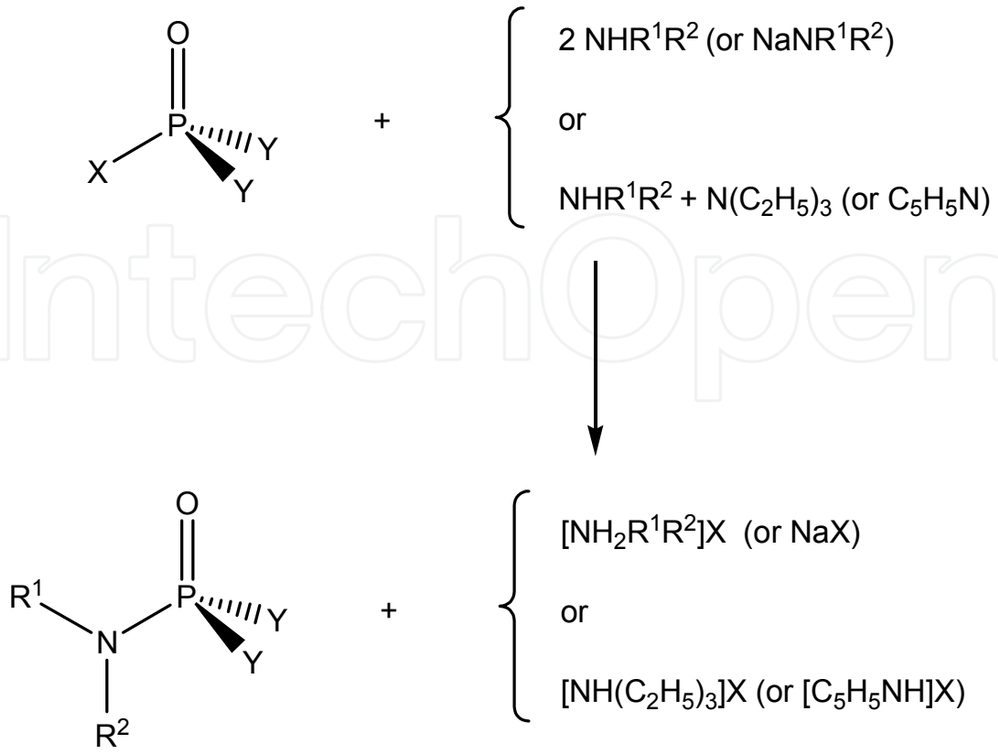
The purification may be performed by stirring the crude product in water to remove the amine hydrohalide or pyridinium halide and/or may be done by selecting the solvent



Scheme 3. The classification of compounds having a $P(O)(N)_n(O)_{3-n}$ (n = 1, 2, 3) skeleton

which the salt is as precipitate (and the product is soluble) and then the filtering off the salt. Moreover, if more than twice mole ratio of amine relative to each P-X bond is used, removing the un-reacted amine should be done in the purification process, too, which may be performed by stirring the crude product in a diluted hydrochloric acid [65].

Setzer and co-workers reported the synthesis of 1,3,2-oxazaphospholane from the reaction between (lR,2R)-(-)-pseudoephedrine, phenyl dichlorophosphate and triethylamine in ethyl acetate. Triethylamine hydrochloride was filtered off and the solvent removed from the filtrate under reduced pressure [66].



Scheme 4. A common route for the synthesis of phosphoramidates

This method may be developed to the reaction between phenols and phosphorus-chlorine compounds. Selecting of a suitable solvent, which triethylamine hydrochloride or the other salt is low-soluble, develops the synthesis of some initial phosphorus-chlorine compounds such as $[(CH_3)(C_6H_{11})N]P(O)Cl_2$ [67], $[4\text{-}CH_3C_6H_4NH]P(O)Cl_2$ [68], $[C_6H_5O][4\text{-}CH_3C_6H_4NH]P(O)Cl$ [69] and so on. For example, *para*-toluidine hydrochloride is relatively insoluble in CH_3CN; so, the reaction of $P(O)Cl_3$ or $[C_6H_5O]P(O)Cl_2$ with $4\text{-}CH_3\text{-}C_6H_4NH_2$ (1:2 mole ratio) respectively leads to the formation of $[4\text{-}CH_3C_6H_4NH]P(O)Cl_2$ [68] and $[C_6H_5O][4\text{-}CH_3C_6H_4NH]P(O)Cl$ [69] which are soluble in acetonitrile, whereas *para*-toluidine hydrochloride is simply filtered off.

Selection of a suitable solvent for such reactions leads to avoid from the time tedious purification methods such as column chromatography. Recently, we are developing this simple strategy for the synthesis of new phosphorus-chlorine compounds such as $[C_6H_5O]P(O)[NHC_6H_{11}]Cl$, $CF_3C(O)NHP(O)[NHC_6H_4(4\text{-}CH_3)]Cl$, $[C_6H_{11}NH]P(O)Cl_2$ and $[(C_6H_5CH_2)_2N]P(O)Cl_2$ [70].

With starting from $P(O)Cl_3$ or PCl_5 as initial phosphorus-chlorine compounds to reaction with an amine, surely a dry solvent is needed. A fully de-watered solvent is obtained by refluxing of a relatively dry solvent in the presence of a very efficient drying agent such as P_2O_5 (for CCl_4 and $CHCl_3$) or sodium (for CH_3OH, C_2H_5OH, C_6H_6 and $C_6H_5CH_3$) and distilling the totally dried solvent. However, it seems that the sensitivity of a $YP(O)Cl_2$ starting material (Y = amide, alkoxy, phenoxy and so on) is very reduced to the moisture and the solvent which was dried with a moderate desiccant (such as $CaCl_2$) is good for the

synthesis. For a bulky amine such as *iso*-propylbenzyl amine or di-cyclohexyl amine as a nucleophile, it seems that a totally-dried solvent is better; of course, it needs to approve with further experiments.

In the case of *iso*-propylbenzyl amine as nucleophile, the reactions with $[C_6H_5O]P(O)Cl_2$, $[C_6H_5O]_2P(O)Cl$ or 4-F-$C_6H_4C(O)NHP(O)Cl_2$ were not successful to prepare the pure $[C_6H_5O]P(O)[N(CH(CH_3)_2)(CH_2C_6H_5)]_2$, $[C_6H_5O]_2P(O)[N(CH(CH_3)_2)(CH_2C_6H_5)]$ and 4-F-$C_6H_4C(O)NHP(O)[N(CH(CH_3)_2)(CH_2C_6H_5)]_2$; however, the crystal structures of two polymorphs of $[NH_2(CH(CH_3)_2)(CH_2C_6H_5)]Cl$ were obtained [71,72]. With using this amine, the compounds [4-NO_2-$C_6H_4C(O)NH]P(O)[N(CH(CH_3)_2)(CH_2C_6H_5)]_2$ [51], $[NH_2(CH(CH_3)_2)(CH_2C_6H_5)][CCl_3C(O)NHP(O)(O)[OCH_3]]$ [40] and $[NH_2(CH(CH_3)_2)(CH_2C_6H_5)][CF_3C(O)NHP(O)(O)(N(CH(CH_3)_2)(CH_2C_6H_5))]$ [73] were prepared which structurally studied, too.

In the case of $[NH_2(CH(CH_3)_2)(CH_2C_6H_5)][CCl_3C(O)NHP(O)(O)[OCH_3]]$ salt, for example, it seems that the presence of a few amount of H_2O in solvent (or environment) leads to the formation of $CCl_3C(O)NHP(O)(OH)Cl$ which the proton-transfer reaction with the amine produces $[NH_2(CH(CH_3)_2)(CH_2C_6H_5)][CCl_3C(O)NHP(O)(O)Cl]$ and then crystallization in methanol replaces the Cl with OCH_3. Moreover, from the reaction of $P(O)(OC_6H_5)Cl_2$ and $NH(C_6H_{11})_2$, the related pure amido phosphoric acid ester was not achieved; however, the crystal structure of $[(C_6H_{11})_2NH_2]^+Cl^-$ was obtained [74].

We are going to try to synthesize neutral phosphoramidate compounds with this and the other bulky amines. A similar feature was observed for the reaction of $POCl_3$ with *tert*-butyl cyclohexyl amine in $CHCl_3$ under reflux condition, where the salt $[NH_2(tert\text{-}C_4H_9)(C_6H_{11})][PO_2Cl_2]$ was obtained [75].

The moisture led to the formation of some undesirable but interesting products such as $X_2P(O)OP(O)X_2$ (X = $(CH_3)_3CNH$ [76], $C_6H_4(2\text{-}CH_3)NH$ [48] and $C_6H_4(4\text{-}CH_3)NH$ [77]) from the reaction of $P(O)Cl_3$ and corresponding amine (1 to 6 or more mole ratio) , and also formation of [3-F-$C_6H_4C(O)NH][(CH_3)_3CNH]P(O)(O)P(O)[NHC(CH_3)_3][NHC(O)C_6H_4(3\text{-}F)]$ [78] from the reaction of 3-F-$C_6H_4C(O)NHP(O)Cl_2$ and *tert*-butyl amine. Another salt, $[tert\text{-}C_4H_9NH_2][CF_3C(O)NHP(O)(O)NH(tert\text{-}C_4H_9)].0.333CH_3CN.0.333H_2O$, was also obtained [79].

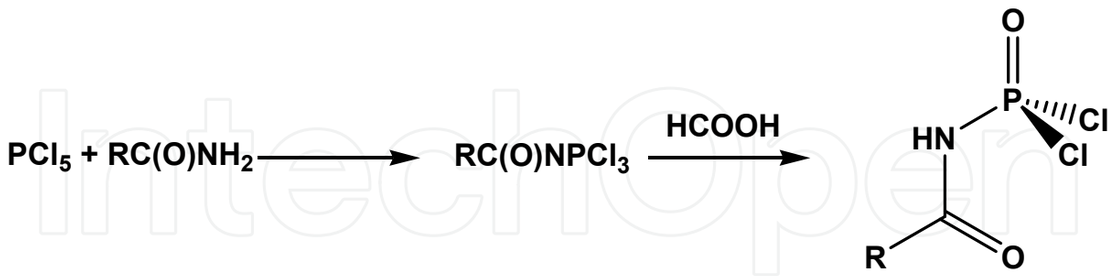
N-methyl cyclohexyl amine showed an interesting feature in some examples which may be accidental needing to further considerations. In the reaction of 4-$CH_3C_6H_4S(O)_2NHP(O)Cl_2$ with an excess amount of $NH(CH_3)(C_6H_{11})$ (1:5 mole ratio), the product is a proton-transfer compound, $[NH_2(CH_3)(C_6H_{11})][4\text{-}CH_3\text{-}C_6H_4S(O)_2NP(O)[N(CH_3)(C_6H_{11})]_2]$ [23]; furthermore, the crystal structures of $[NH_2(CH_3)(C_6H_{11})][CF_3C(O)NP(O)[N(CH_3)(C_6H_{11})]_2]$ [80] and $[NH_2(CH_3)(C_6H_{11})][CCl_3C(O)NP(O)[N(CH_3)(C_6H_{11})]_2]$ [81] were obtained, but in an effort to preparation of their alkaline complexes.

Synthesis of such proton-transfer compounds through stirring a mixture of a few examined amines (NHR^1R^2) and a synthesized phosphoric triamide ($CF_3C(O)NHP(O)[NR^1R^2]_2$) were not successful; however, this also needs to some further experiments.

Another strategy for preparation of phosphoramidate compounds is the application of sodium amide salts which produces sodium halide as a by-product [82] (Scheme 4).

The P-N bond formation between an amide, of the type $RC(O)NH_2$, and a phosphorus(V) site may be performed *via* a two-stages reaction, which is shown for PCl_5 in Scheme 5,

showing the reaction of PCl_5 with an amide and then the treatment of HCOOH. Moreover, a few efforts have been devoted to the synthesis of $RS(O)_2NHP(O)Cl_2$ by a similar procedure [23].

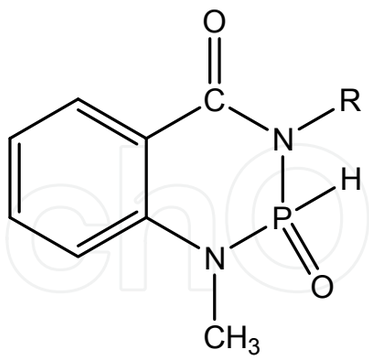


Scheme 5. Synthesis of $RC(O)NHP(O)Cl_2$

The simple mentioned methods for the preparation of phosphoramidates from the reaction of phosphorus-chlorine compounds and amines may be extended to the diamines or amino alcohols to produce cyclic [83] or bridged compounds [61].

The preparation of some compounds containing the P-Cl bonds, such as 4-$CH_3C_6H_4OP(O)Cl_2$ and $[(CH_3)_2N]P(O)Cl_2$, were performed through the reaction between corresponding phenol derivatives or amine hydrochloride salts [for example *para*-cresol or dimethylamine hydrochloride salt for the mentioned phosphorus-chlorine compounds] with an excess amount of $POCl_3$ and then the removal of the remaining $POCl_3$ in a reduced pressure [32,47].

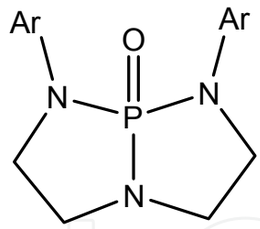
Some compounds were synthesized by the reaction of P-H compounds (such as dimethylphosphine oxide, $(CH_3)_2P(O)H$ and *N*,*N*-disubstituted derivatives of 5,6-benzo-2H-2-oxo-1,3,2λ⁴-diazaphosphorinan-4-one, Scheme 6) with ketones [84].



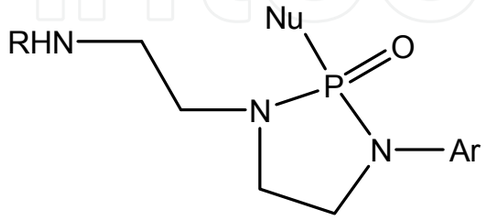
Scheme 6. 5,6-benzo-2H-2-oxo-1,3,2λ⁴-diazaphosphorinan-4-one

Wan and Modro developed the synthesis of a bicyclic phosphoric triamide (Scheme 7) *via* the base-promoted cyclization of the corresponding 3-(2-chloroethyl)-2-oxo-1-aryl-2-arylamino-1,3,2-diazaphospholidine [85].

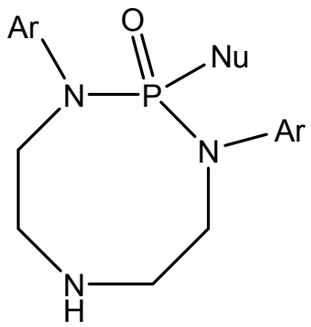
Mbianda and co-workers reported the solvolysis of 1-oxo-2,8-diphenyl-2,5,8-triaza-1 λ⁵-phosphabicyclo[3.3.0]octane under base-promoted alcoholysis and acid-catalyzed alcoholysis. Scheme 8 shows the two different products of such solvolysis reactions [86].



Scheme 7. A bicyclic phosphoric triamide



Base-promoted alcoholysis



Acid-catalyzed alcoholysis

Scheme 8. The obtained products from the solvolysis of 1-oxo-2,8-diphenyl-2,5,8-triaza-1 λ^5-phosphabicyclo[3.3.0]octane under base-promoted alcoholysis and acid-catalyzed alcoholysis

3. Crystallization of phosphoramidates

The convenient solvents for obtaining suitable single crystals for the studied compounds may be $CH_3C(O)CH_3$, $CHCl_3$, $CHCl_3$/n-C_7H_{16}, CH_2Cl_2, CH_3CN, CH_3CN/CH_3OH, $CH_3CN/CHCl_3$, CH_3OH, CH_3OH/H_2O, C_2H_5OH/n-C_6H_{14}, $(CH_3)_2CHOH$/n-C_6H_{14}, $(CH_3)_2NC(O)H/CHCl_3$, $(CH_3)_2NC(O)H/CH_3OH$ and n-C_6H_{14}. The crystal may be obtained at room temperature after slow evaporation of the solvent.

4. General features of phosphoramidate compounds

Compounds with formula $RC(O)NHP(O)[NR^1R^2]_2$ and $RC(O)NHP(O)[NHR^1]_2$

The four different groups linked to the P atom result in a distorted tetrahedral configuration; as one instance, the bond angles around the P atom of $P(O)[NHC(O)CF_3][NHCH_2C_6H_4(2\text{-}Cl)]_2$ range from 102.67(12)° to 117.60(12)° [87]. In the

C(O)NHP(O) moiety, however, the carbonyl and phosphoryl groups are separated from each other with one N-H unit, but the terms *syn*, *gauche* and *anti* were used for the description of the C(O) orientation versus P(O) in the literatures [10,26]. Up to now, both *gauche* and *anti* orientations were found for phosphoric triamide compounds having a C(O)NHP(O) skeleton, respectively in 14 and 98 structures (from the 119 structurally reported compounds, 7 cifs are not available). Among them, for the acyclic compounds of the type $RC(O)NHP(O)[NHR^1]_2$, merely, the *anti* orientation was reported, so far.

Fig. 1. indicates a general view of compounds with formula $CF_3C(O)NHP(O)[NHR]_2$.

In the C(O)NHP(O) moiety, the P—N bond is longer and the O—P—N angle is contracted compared with the respective values in the $[P(O)NHR]_2$ section. For the phosphoramidate compounds, each N atom bonded to phosphorus has a sp^2 character which is reflected in the C—N—P angles of the C(O)NHP(O) or C—NH—P moiety or sum of the surrounding angles around the tertiary nitrogen atom (C—N—C + C—N—P + P—N—C). The deviation of this summation from 360° (to a lower value) has been used to show the deviation of nitrogen atom environment from planarity. This may be also illustrated with the distance between the position of N atom from the plane crossing from the directly attached atoms to nitrogen, i.e. C, C and P. In $[C_6H_5O]_2P(O)[NC_4H_8N]P(O)[OC_6H_5]_2$ (Fig. 2) which belongs to the amidophosphoric acid ester family, the N atom shows some deviation from planarity and it is 0.25(1) Å above (or below) the CCP plane [61]. For the phosphoramidate compounds, the P-N bonds are shorter than the P-N single bond and the P=O bond are longer than the normal P=O bond [88].

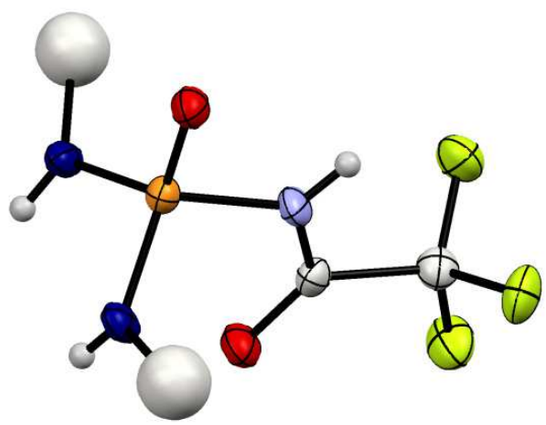


Fig. 1. A typical view for a compound with formula $CF_3C(O)NHP(O)[NHR]_2$ [Color key: O atoms are red, the N atom of C(O)NHP(O) is light blue, the other amido N atoms are dark blue, F atoms are yellowish green., C and H atoms are light grey and P atom is orange]; the R substituents are shown as big balls.

In 1,3-diazaphosphorinane compounds, the P=O bond is placed in an equatorial position and the aliphatic six-membered rings adopt conformation between chair and envelope (Fig. 3).

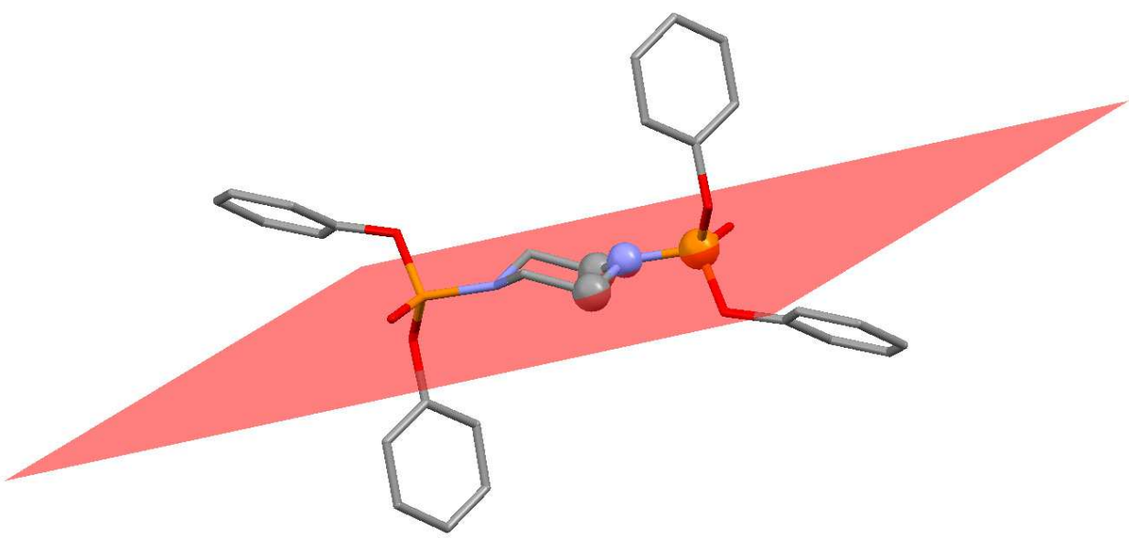


Fig. 2. A view of the PCC mean plane which is crossed from the phosphorus and carbon atoms shown as balls in the right-side $[C_6H_5O]_2P(O)(NC_2H_4)$ moiety of $[C_6H_5O]_2P(O)[NC_4H_8N]P(O)[OC_6H_5]_2$ (the molecule is organized around an inversion center located at the centre of the piperazine ring), the N atom environment shows some deviation from planarity. The balls representation denote to the P (orange), N (blue) and C (grey) atoms.

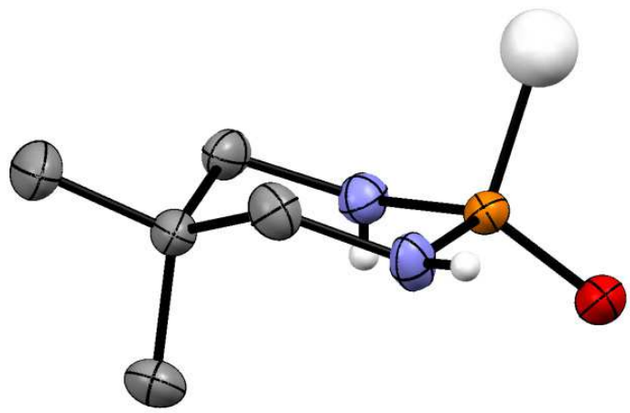
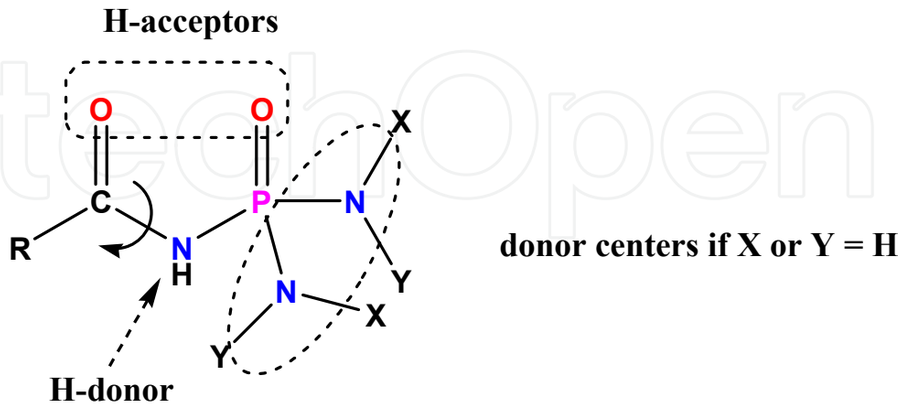


Fig. 3. A general view of a 1,3-diazaphosphorinane, a six-membered ring heterocyclic phosphorus compound (the carbon-bonded H atoms were omitted for clarity). The grey big ball in the figure may be RC(O)NH, RNH or the other moieties.

The hydrogen bond pattern of compounds having the $C(O)NHP(O)(N)_2$ and $C(O)NHP(O)(NH)_2$ skeletons may be predictable with considering the following "empirical rules":

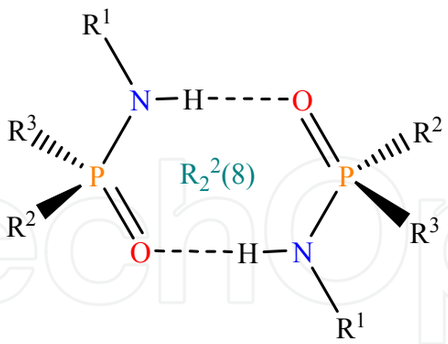
1. In the reported compounds, the nitrogen atoms bonded to P don't involve in hydrogen bonding interaction as an acceptor (due to their low Lewis base characteristic). Scheme 9 illustrates the possible H-donor sites and H-acceptor centers in the structure of compounds having the $C(O)NHP(O)(N)_2$ and $C(O)NHP(O)(NH)_2$ skeletons.



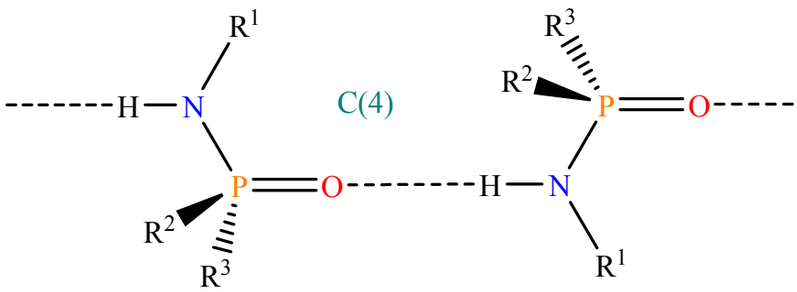
Usually the N atoms don't involve in hydrogen bonding as an acceptor

Scheme 9. The possible H-donor sites and H-acceptor centers in the $C(O)NHP(O)(N)_2$ and $C(O)NHP(O)(NH)_2$ skeletons (the R, X or Y groups may also be contained the additional H-donor or H-acceptor sites in their structures which may be involved in the H-bond pattern, the curved arrow shows that the orientation of C=O versus P=O may change)

2. The P=O is a better H-acceptor than the C=O counterpart.
3. In compounds having a $C(O)NHP(O)(N)_2$ skeleton, i.e. with formula $RC(O)NHP(O)[NR'R'']_2$, both *gauche* and *anti* orientations of P=O *versus* C=O have been found, so, two kinds of packing are expectable which are seen: a) a 1-D chain for a *gauche* orientation, and b) a dimeric aggregate (as an $R_2^2(8)$ loop; for H-bond motifs of phosphoric triamide, see: ref. [10]) with C_i or C_1 symmetry for *anti*. The unique NH proton interacts with the oxygen atom of PO, whereas the CO does not cooperate in HB. Such H-bond patterns may also be expectable for the other phosphoramidate compounds having a P(O)NH group, Scheme 10; however, the other H-bond patterns have also been observed in the other sub-categories with a P(O)NH moiety which will be noted, later.
4. In compounds having a $C(O)NHP(O)(NH)_2$ skeleton, only an *anti* situation has been found in acyclic molecules; however, in diazaphosphorinane molecules both conformations were found.
5. In the crystal packing of acyclic compounds having a $C(O)NHP(O)(NH)_2$ skeleton, adjacent molecules are often linked *via* $N_{C(O)NHP(O)}—H…O=P$ and $N—H…O=C$ (or $(N—H)_2…O=C$) hydrogen bonds, building $R_2^2(8)$ and $R_2^2(12)$ rings (or $R_2^2(8)$ and $R_2^2(12)/R_2^1(6)$) in a linear arrangement (Scheme 11). However, the existence of a PO…HNR interaction has been observed for a few compounds as tri-centered $PO[…H_{C(O)NHP(O)}N][…HNR]$ and PO[…HNR][…HNR] hydrogen bonding, where the oxygen atom of the phosphoryl group acts as a double H-acceptor (for a definition of a double-H bond acceptor, see: ref. [89]).

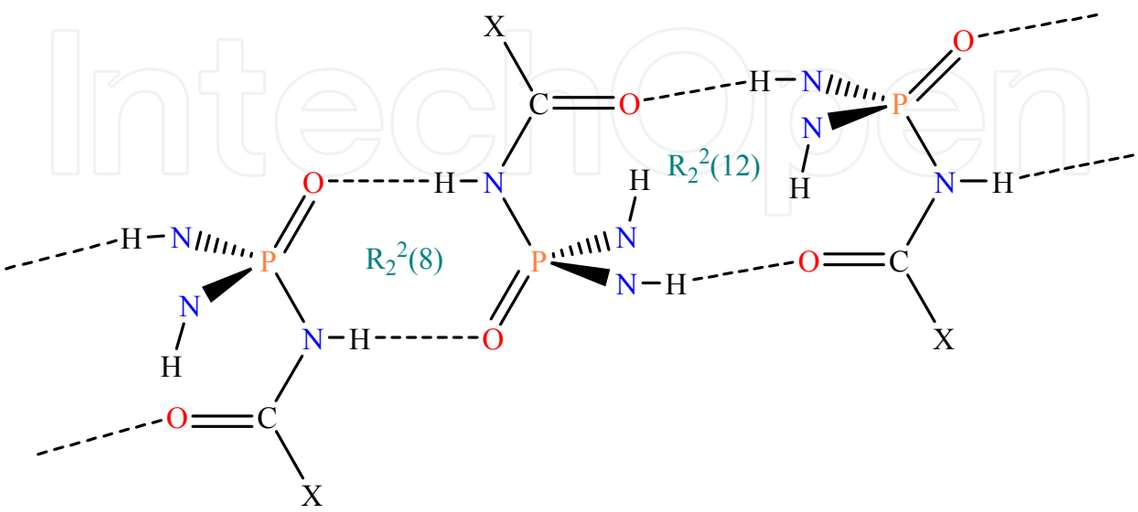


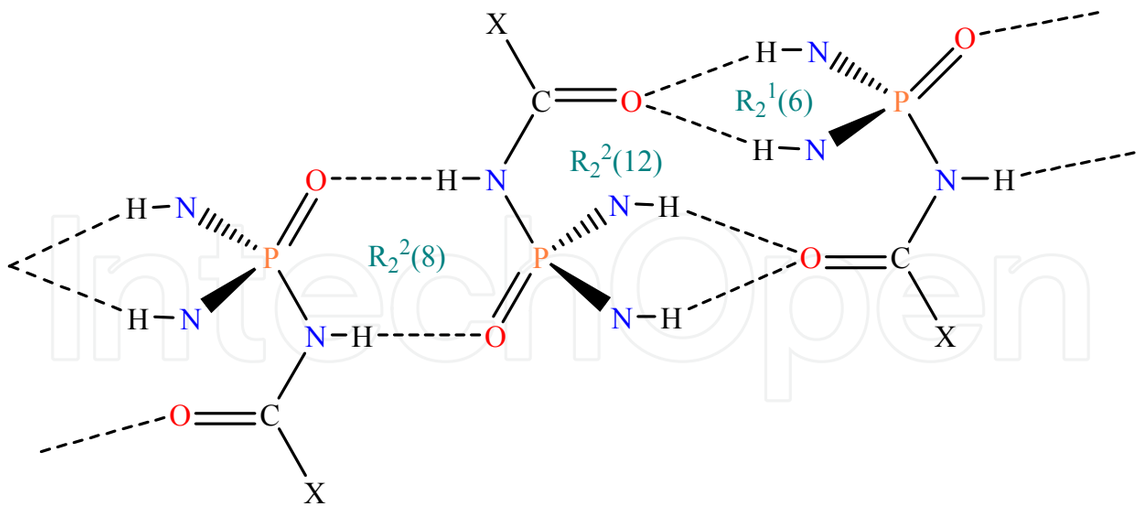
R^1 = alkyl, aryl or C(O)R'
R^2 and R^3 = OR, NR'R"



R^1 = alkyl, aryl or C(O)R, R^2 = OR or NR'R", R^3 = OR, NHR' or NR"R'"

Scheme 10. The observed hydrogen bond patterns in compounds having a P(O)NH skeleton (such as $C(O)NHP(O)[N]_2$)

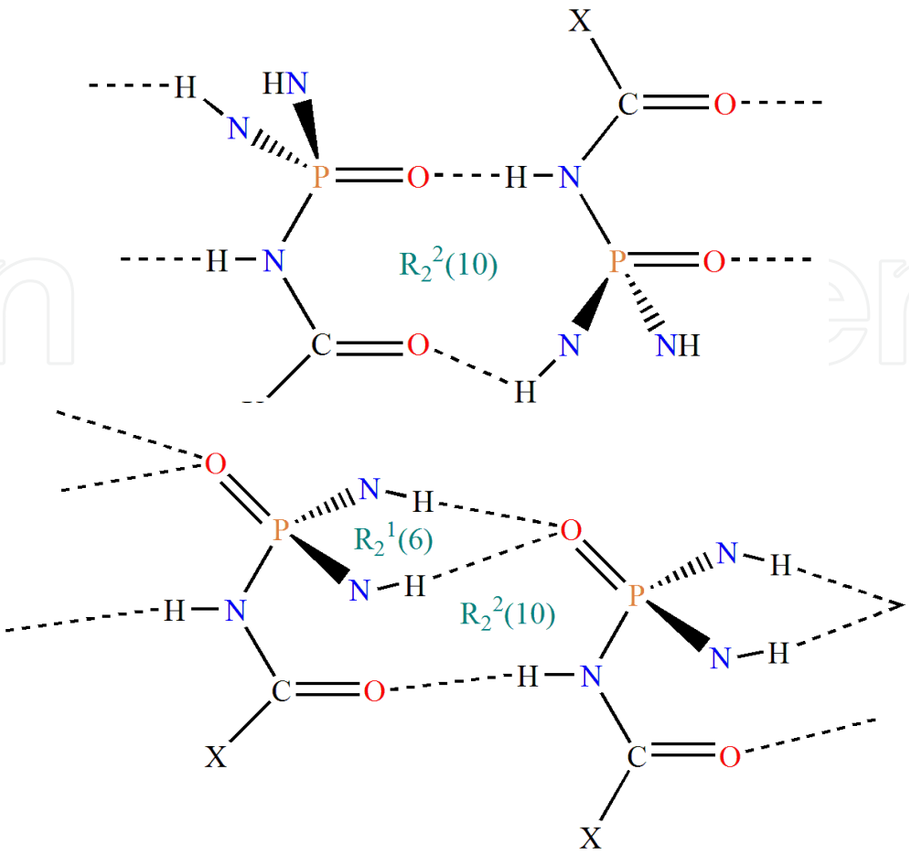




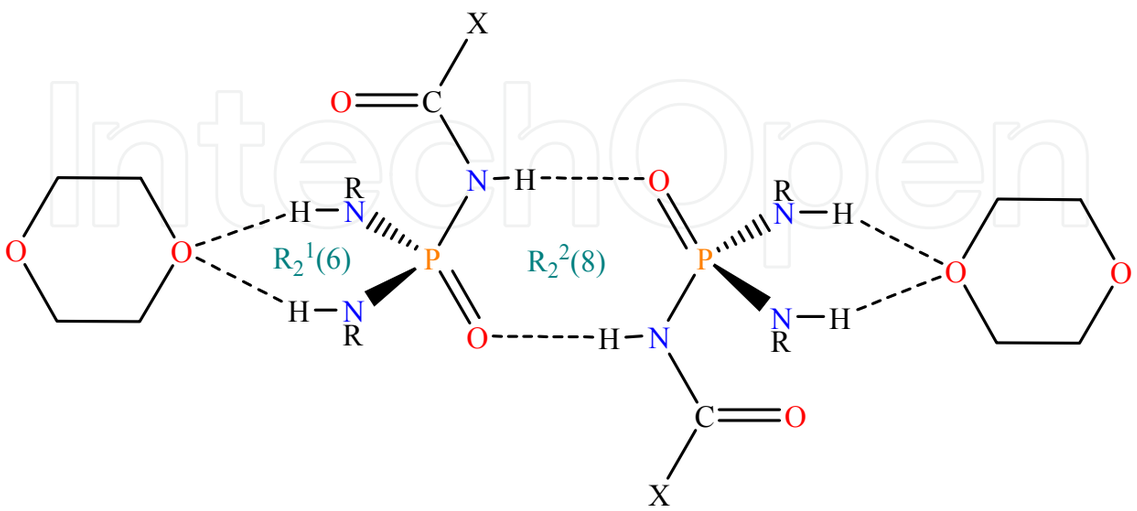
Scheme 11. A sequence of $R_2^2(8)$ and $R_2^2(12)$ (top), a sequence of $R_2^2(8)$ and $R_2^2(12)/R_2^1(6)$ (bottom) rings in compounds having a $C(O)NHP(O)(NH)_2$ skeleton: in these H-bond patterns, the P=O…H-$N_{C(O)NHP(O)}$ and C=O…H-N or C=O…$(H-N)_2$ exist

In most cases of compounds having a $C(O)NHP(O)(NH)_2$ skeleton (containing two H-acceptors–three H-donors), the HBs lead to a 1-D chain. Different 1-D ladder arrangements with tetramer motifs and a linear arrangement with two different kinds of motifs (dimer and tetramer) were also observed. Therefore, two H-donor sites ($HN_{C(O)NHP(O)}$ and one of the HNR) participate with two O atoms in the intermolecular HBs, the other HNR may act as the three following manners: (a) in an intramolecular HB with C(O), (b) in a weaker HB with P(O) as the above mentioned tri-centered HB and (c) without cooperation in any HB.

6. A sequence of $R_2^2(10)$ (or $R_2^2(10)/R_2^1(6)$ or $R_2^2(10)/S_6$) may be expected when the C=O is hydrogen-bonded to the $N_{C(O)NHP(O)}$-H unit and the P=O interacts with the N_{amide}-H unit. If the remaining N_{amide}-H unit is involved in an intramolecular hydrogen bond with the oxygen of carbonyl, the $R_2^2(10)/S_6$- graph-set is formed, in this case the oxygen atom of carbonyl acts as a double-H acceptor. In the case of involving this N-H unit in the H-bonding interaction with the oxygen of phosphoryl, the $R_2^2(10)/R_2^1(6)$ is formed (Scheme 12).
7. In a solvated molecule [90], the hydrogen-bond pattern may not be predictable, but some previously mentioned rules may be beneficial, Scheme 13.
8. The investigation for the phosphoric triamide containing a $C(O)NHP(O)(NH)_2$ skeleton shows that in eleven structures the carbonyl oxygen atom acts as a double-H acceptor *via* C(O)...(H—N)(H—N) grouping (in the $R_2^2(12)/R_2^1(6)$ motifs) and in ten structures the phosphoryl oxygen atom acts as a double-H acceptor *via* P(O)…(H—N)(H—N) or P(O)…(H—N)(H—$N_{C(O)NHP(O)}$) groups in the $R_2^2(12)/R_2^1(6)$ rings or $R_2^2(10)/R_2^1(6)$ ring or in the 1-D ladder arrangement). In the other such phosphoramidate compounds the remaining N—H unit doesn't cooperate in H-bonding interaction. The unique found structure of phosphoramidate with a $C(O)NHP(O)Cl_2$ skeleton is $CF_3C(O)NHP(O)Cl_2$ [91].



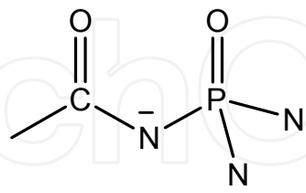
Scheme 12. A sequence of $R_2^2(10)$ (top) and $R_2^2(10)/R_2^1(6)$ rings (bottom) in compounds having a $C(O)NHP(O)(NH)_2$ skeleton; in the existing examples of $R_2^2(10)/S_6$, the N-H…O angle is less than 110°



Scheme 13. A four-component cluster in the solvated molecule $CCl_3C(O)NHP(O)[NHC_6H_{11}]_2.C_4H_8O_2$(X = CCl_3, R = C_6H_{11})

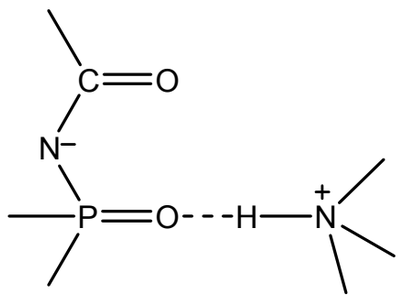
Proton transfer compounds

In the proton transfer compounds containing a $\{[C(O)NP(O)][N]_2\}^-$ skeleton (Scheme 14), the P-N bond in the [C(O)NP(O)] fragment is shorter than the two other P-N bonds, one example for such compounds is $[C_6H_{11}NH_2CH_3][CF_3C(O)NP(O)[N(CH_3)(C_6H_{11})]_2]$ in which the phosphoryl and carbonyl groups are staggered [O-P-N-C = 64.8(3)°] [80].



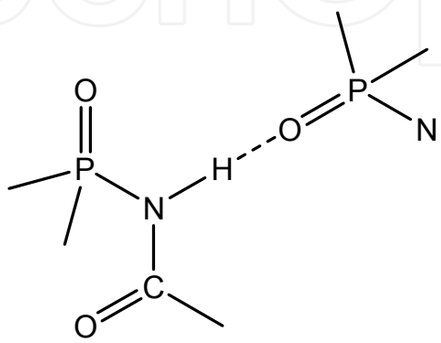
Scheme 14. The $\{[C(O)NP(O)][N]_2\}^-$ skeleton

The hydrogen bonds (Scheme 15) in such compounds, of the type charge-assisted and also polarization-assisted HBs [92], are strong, reflecting in the distances between the donor and acceptor atoms. Scheme 16 shows a polarization-assisted hydrogen bond in a neutral phosphoramidate, for comparison.



Scheme 15. Contribution of two factors in strengthening of hydrogen bonds (charge and polarization) in the proton-transfer compounds: charge and polarization-assisted hydrogen bonds

Two reported crystal structures of this category, $[C_6H_{11}NH_2CH_3][CF_3C(O)NP(O)[N(CH_3)(C_6H_{11})]_2]$ [80] and $[C_6H_{11}NH_2CH_3][4\text{-}CH_3\text{-}C_6H_4S(O)_2NP(O)[N(CH_3)(C_6H_{11})]_2]$ [20], have a similar HB pattern as a centrosymmetric four-component cluster involving two anions and two cations which interact through N—H…O hydrogen bonds (Fig. 4).



Scheme 16. A polarization-assisted hydrogen bond in a neutral phosphorus compound

Compounds with formula $[R^1R^2N][R^3R^4N][R^5R^6N]P(O)$, $[RNH][R^1R^2N][R^3R^4N]P(O)$, $[R^1NH][R^2NH][R^3R^4N]P(O)$, $[R^1NH][R^2NH][R^3NH]P(O)$ or more complicated phosphoric triamide compounds

Tris-alkyl (aryl) amido phosphates of the formula $[R^1R^2N]_3P(O)$, with three equal amido substituents linked to the P atom, are easily prepared from a one-pot reaction between phosphoryl chloride and corresponding amine. The single crystal X-ray determinations were performed for $[R^1R^2N]$ = $NHCH_3$ (KABVAL) [93], $N(CH_3)_2$ (POTJAJ) [94], $NHC(CH_3)_3$ (KABVEP) [93], NHC_6H_5 (KEQLUO) [95], $NHCH_2C_6H_5$ (TOKXIB) [96] and $NHC_6H_4(4\text{-}OCH_3)$ (WAWNIS) [97] and also for the substituents shown in Scheme 17 [98-105]. Moreover, a few other phosphoramide compounds which each contains a triamido moiety (like for example compounds with refcodes EDEVAK [106] and NUVSEC [107] (Schemes 18 and 19) and some co-crystal compounds (for example BARHMP [108] and VAFRIE [109], see Schemes 20 and 21) were reported.

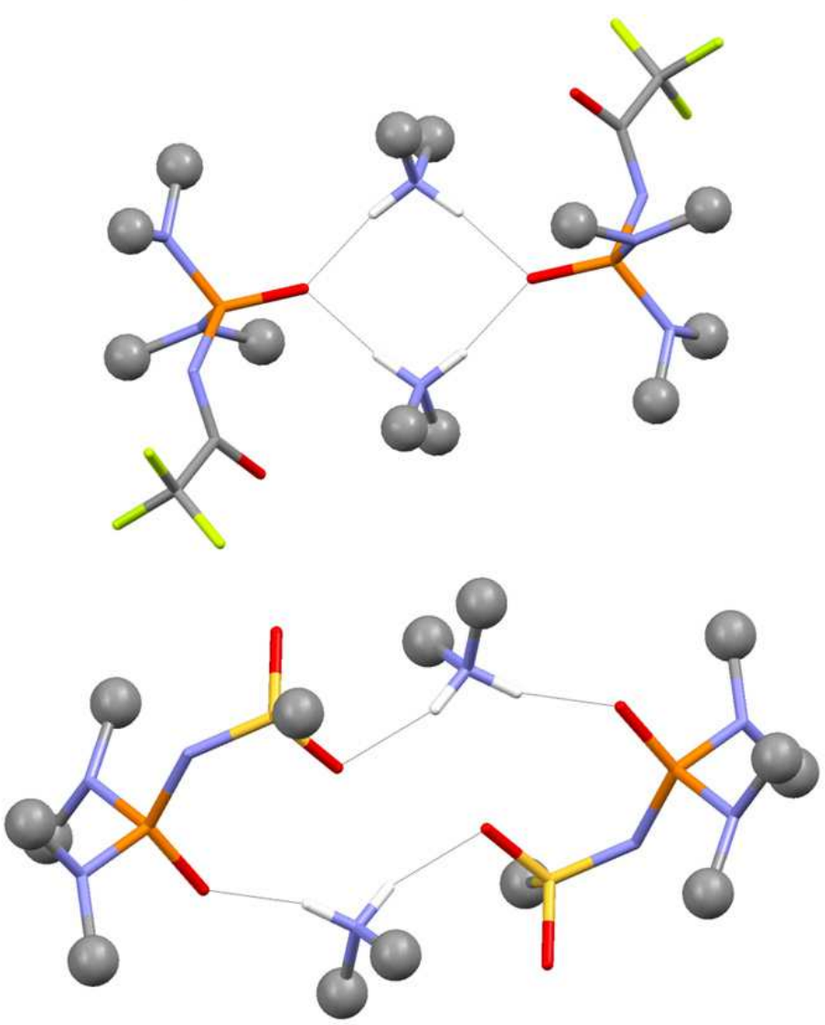
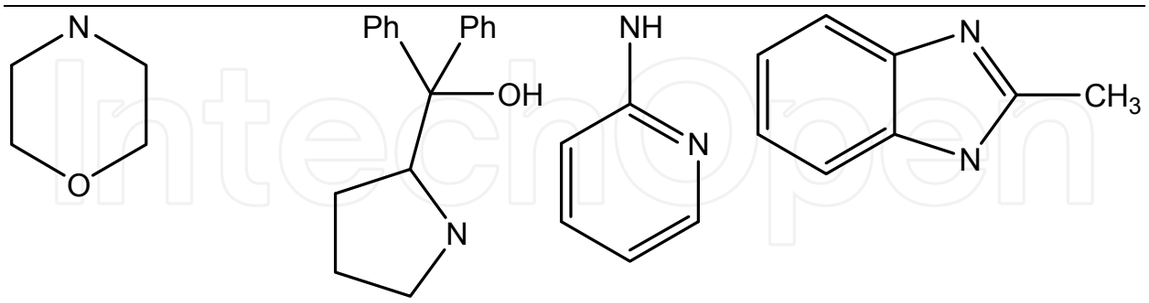
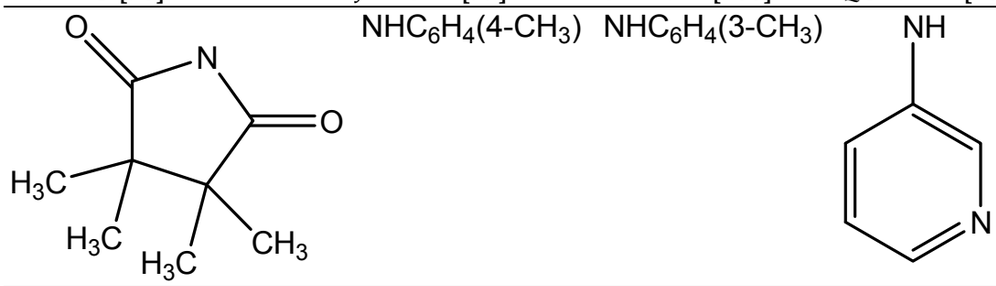


Fig. 4. A view of the H-bonded centrosymmetric four-component cluster in the crystal packing of $\{C_6H_{11}NH_2CH_3\}^+\{CF_3C(O)NP(O)[N(CH_3)(C_6H_{11})]_2\}^-$ (top) and $\{C_6H_{11}NH_2CH_3\}^+\{4\text{-}CH_3C_6H_4S(O)_2NP(O)[N(CH_3)(C_6H_{11})]_2\}^-$ (bottom); the N—H···O hydrogen bonds are shown

as dotted lines. The H atoms not involved in hydrogen bonding have been omitted for the sake of clarity and the 4-CH_3-C_6H_4 (bottom) and C_6H_{11} and CH_3 substituents are shown as balls (the N…O distances are 2.771(3) & 2.804(3) Å and 2.648(4) & 2.864(4) Å, respectively).



BIVYAG [98] JEKLER [99] LAFNAI [100] QONBEB [101]



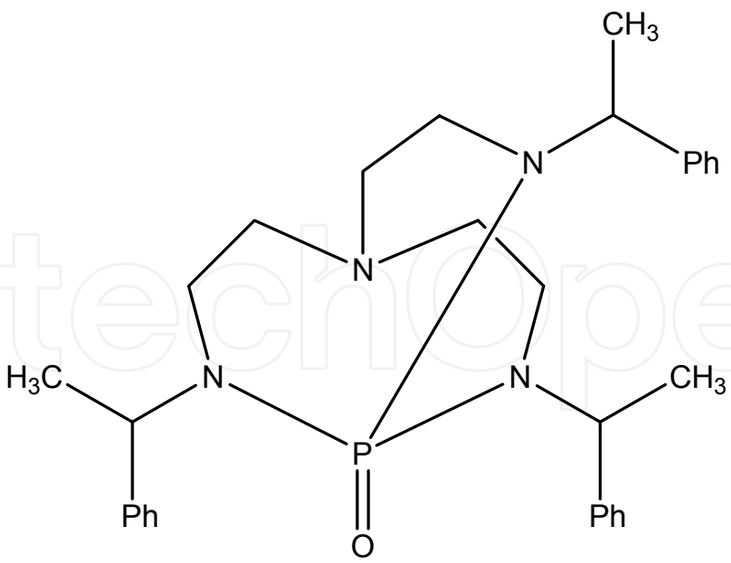
[1]QUFJIL [102] [2]TAZPOX [103] [3]TOLZPO [104] [4]OLOCEY [105]

[1]There is the hydrogen-bonded amide molecule in the structure, i.e. the formula is $C_{24}H_{36}N_3O_7P_1$,$C_8H_{13}N_1O_2$. [2]There is the solvent C_2H_5OH molecule in the structure, i.e. the formula is $C_{21}H_{24}N_3O_1P_1$,$C_2H_6O_1$. [3]The formula is $C_{21}H_{24}N_3O_1P_1$,2($C_7H_{10}N_1^{1+}$),2(Cl_1^{1-}). [4]The formula is $C_{15}H_{15}N_6O_1P_1$,H_2O_1.

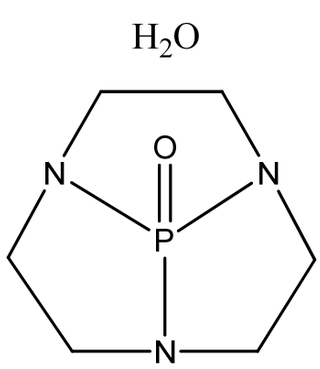
Scheme 17. The structurally investigated compounds of the formula $[R^1R^2N]_3P(O)$ or $[R^1R^2N]_3P(O).B$, where B is a hydrogen-bonded species to phosphoric triamide (the related amido moieties and the CSD refcode are presented)

In the crystal packing of molecules having a $P(O)(NH)_3$ skeleton, hydrogen bonded 1-D chain, 1-D ladder, 2-D layer and 3-D arrangements were found. Three different types of 1-D arrangement are formed respectively through a P=O…$(H\text{-}N)_3$ or P=O…$(H\text{-}N)_2$ groups or *via* the P=O…H-N hydrogen bond. In the two latter cases, respectively one and two N-H units don't cooperate in the hydrogen bond interaction. One example of a linear arrangement, involving the N—H···O and N—H···N HBs, is also found in the structure of $P(O)(NH—C_5H_4N)_3$ (LAFNAI) [100] in which the pyridine nitrogen atom is involving in the HB pattern as an acceptor, too. As, the phosphoryl oxygen atom may cooperate in H-bonding interaction as a double- or a triple- acceptor, some examples of 2-D and 3-D arrangements have also been found in this class of compounds.

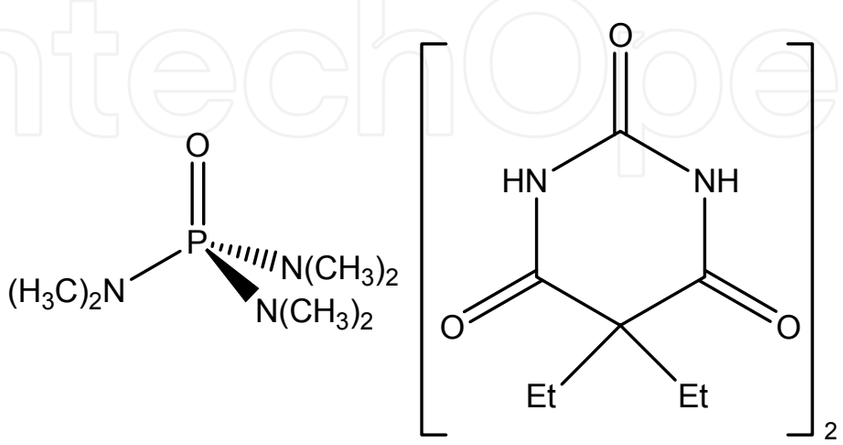
Some phosphoric triamides $[R^1R^2N][R^3R^4N][R^5R^6N]P(O)$ (where merely tertiary nitrogen atoms exist in the structure of molecule) have been reported (for example see: Scheme 22 [110]). Structures with a $P(O)(N)_3$ skeleton, where "N" is a tertiary nitrogen atom, do not show any classical (normal) hydrogen bonding in their crystal packing if the substituent involving the N atom doesn't contain the hydrogen linked to an electronegative atom.



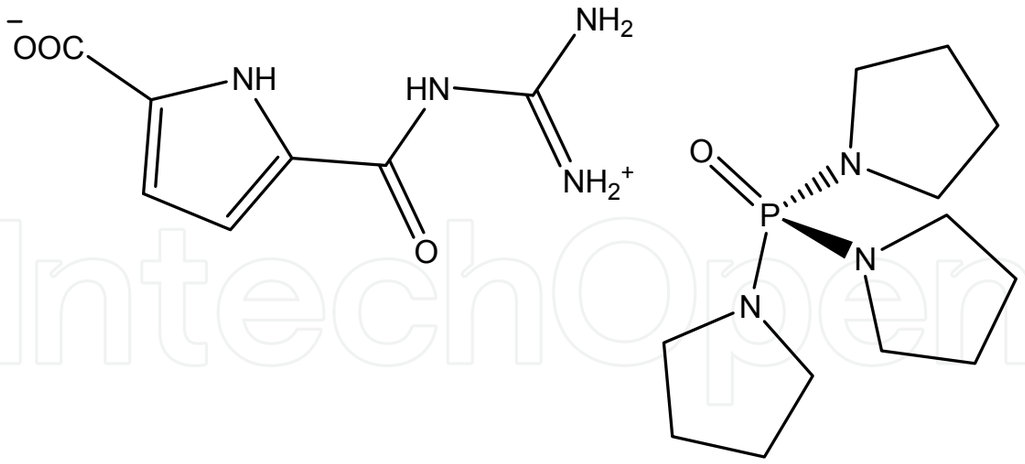
Scheme 18. 4,6,9-Tris(1-phenylethyl)-1,4,6,9-tetraaza-5-phosphabicyclo(3.3.3) undecane P-oxide (refcode: EDEVAK [106])



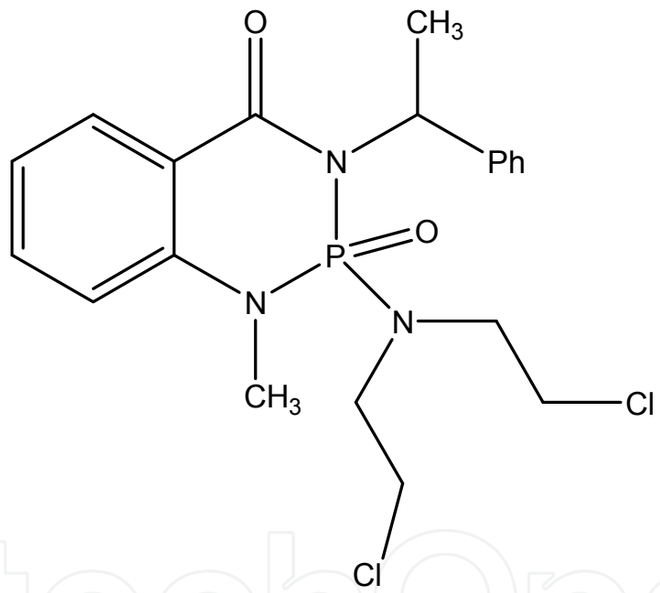
Scheme 19. 10-Oxo-10-phospha-1,4,7-triazatricyclo(5.2.1.$0^{4,10}$)decane monohydrate (NUVSEC [107])



Scheme 20. Bis(barbital)-hexamethylphosphoramide complex (BARHMP [108])



Scheme 21. 5-(Guanidiniocarbonyl)pyrrole-2-carboxylate tris(pyrrolidino)phosphine oxide solvate (VAFRIE [109])

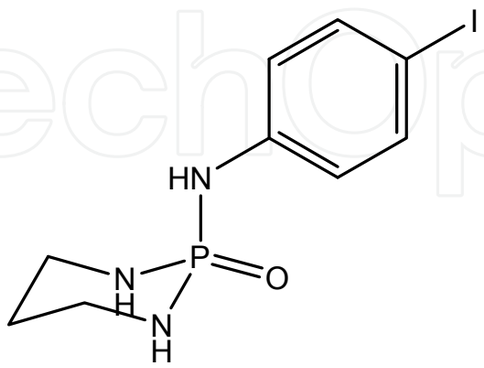


Scheme 22. Refcode BEJNEJ [110]

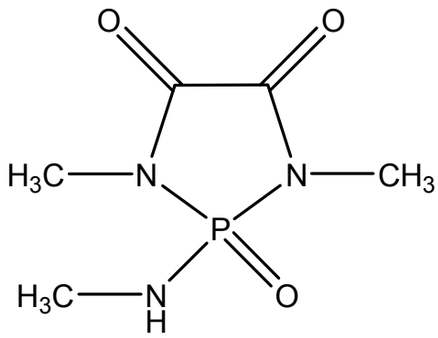
A search on the CSD shows that the nitrogen atoms bound to phosphorus in phosphoramidate compounds aren't involved in normal H-bonding interaction as an acceptor due to the deviation of each N atom environment from pyramidality after binding to P and decreasing its Lewis base character with respect to the initial amine; so that, merely one example (refcode: HESCEO [111], Scheme 23), belonging to the diazaphosphorinane family, is observed so far with the donor…acceptor (N…N) distance of 3.258(8) Å in which it may be considered as a weak N—H…N—P hydrogen bond.

In compounds having a $P(O)(NH)(N)_2$ skeleton, only the P(O)NH unit cooperates in a HB interaction; so, two expectable HB patterns are the H-bonded dimer (with C_i symmetry; a dimer with C_1 symmetry has not reported, so far) and the 1-D chain (Scheme 10). Usually,

an H-bonded dimer forms when the P(O) group and the N—H unit have a *syn* orientation with respect to one another. However, in one structure (refcode: DIYMED [112], Scheme 24) with the *syn* orientation of P(O) *versus* N—H, the molecules are aggregated as a one dimensional H-bonded chain.



Scheme 23. One N atom of the diazaphosphorinane ring cooperates in hydrogen bonding interaction as an H-acceptor [111]

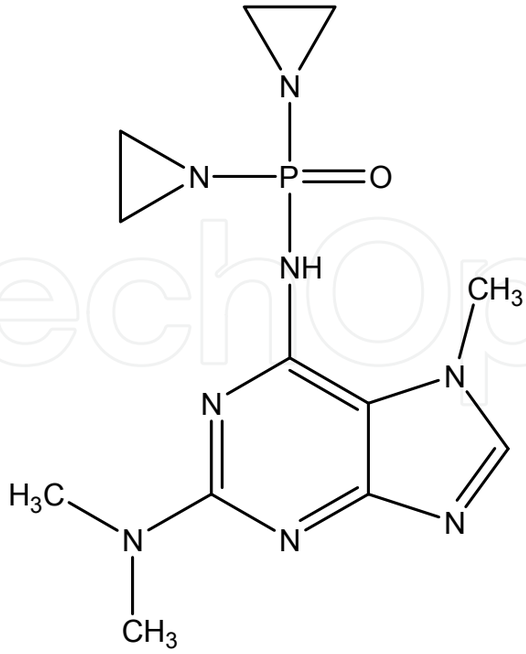


Scheme 24. Refcode DIYMED [112]

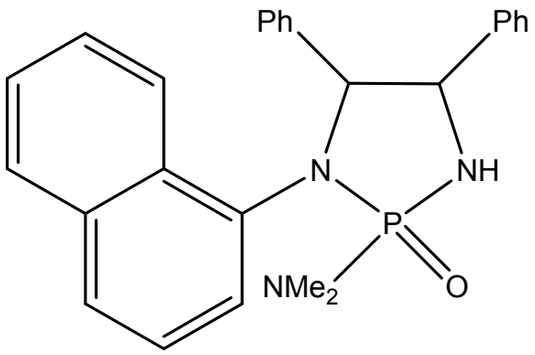
If the P(O) adopts an *anti* orientation *versus* NH, an extended 1-D chain arrangement is expectable through the intermolecular PO···HN hydrogen bond which is found for the most of reported compounds. One example without any N—H···O HB (BIFDUP [113], Scheme 25) and one example as H-bonded tetramer (XAVXEY, Scheme 26) were also found.

In compounds having an $(N)P(O)(NH)_2$ skeleton, three different linear arrangements were observed: a) through P(O)···H—N hydrogen bonds in which one N—H unit doesn't cooperate in H-bonding (NUVROL [107], Scheme 27 and HIVLII [67], Scheme 28), b) through $R_2^1(6)$ (in $[(CH_3)_2N]P(O)[NHC_6H_5]_2$ [52] and the compound with refcode MIFYIJ [114], Scheme 29 (top)) and c) through $R_2^2(8)$ rings ($[(CH_3)_2N]P(O)[NHC_5H_9]_2$ [62] and the compound with refcode IKASAP [47], Scheme 29 (bottom)), two latter cases *via* P(O)···(H—N)(H—N) grouping in which the phosphoryl oxygen atom acts as a double-H acceptor.

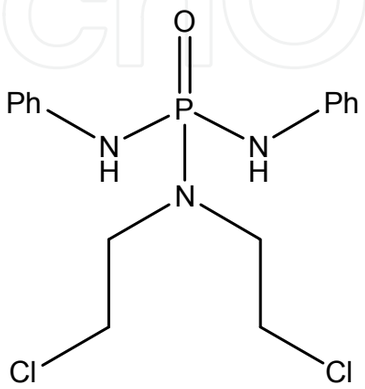
In this series, some other H-bond motifs were observed in compounds having an NH_2 moiety instead of NHR moiety (BIXFOE [115], GOMDOB [116]), Scheme 30.



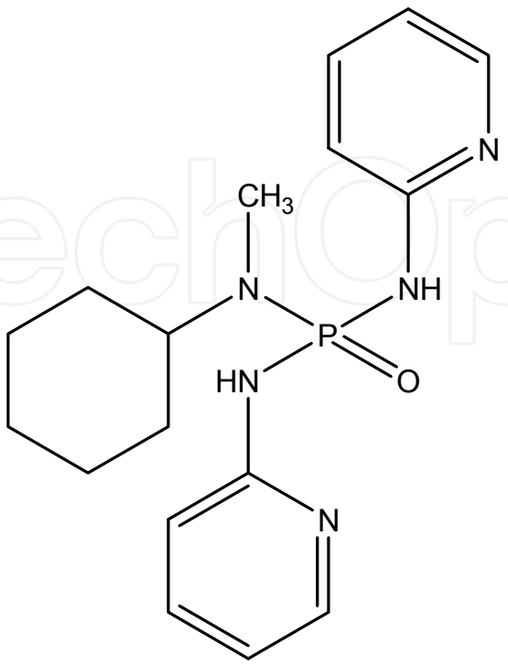
Scheme 25. Refcode BIFDUP [113]



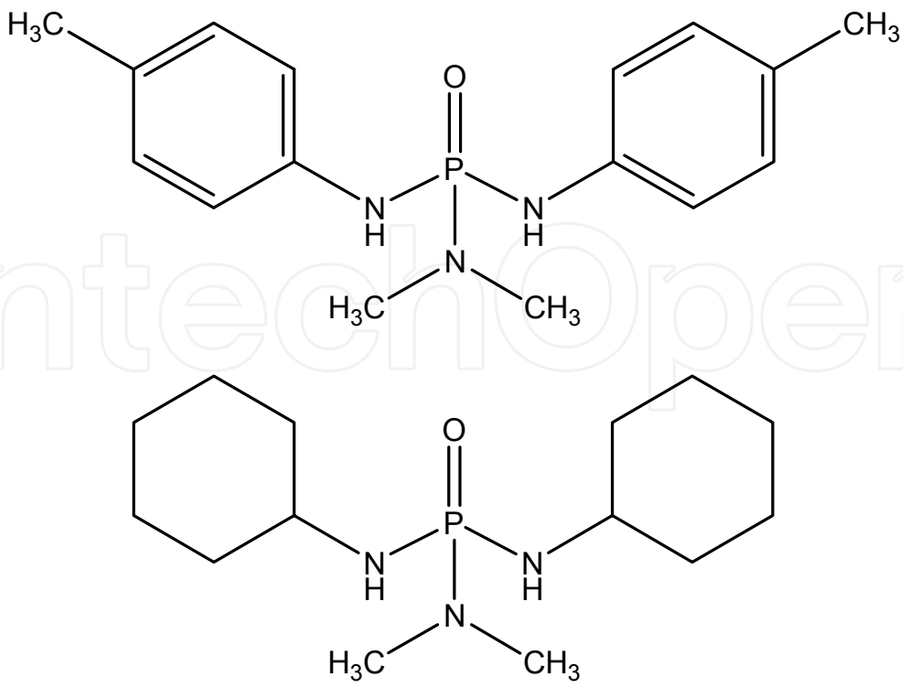
Scheme 26. Refcode XAVXEY (any reference to a journal, book and so on was not found for this structure)



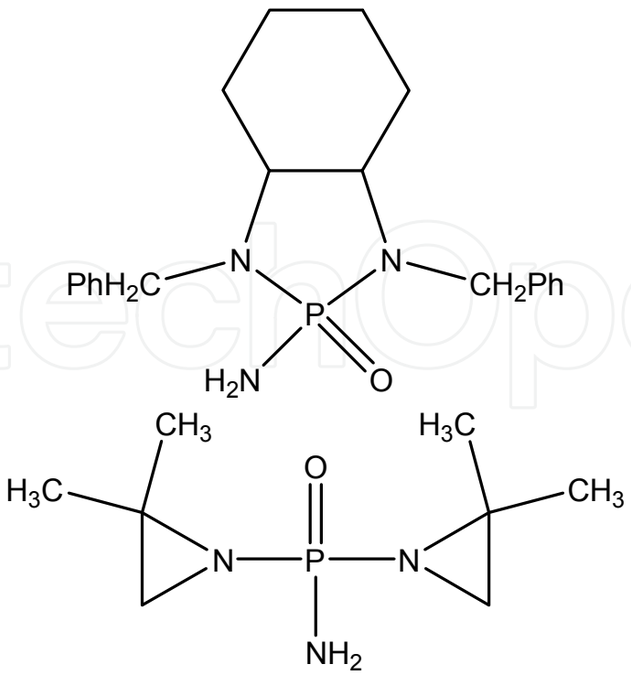
Scheme 27. Refcode NUVROL [107]



Scheme 28. Refcode HIVLII [67]



Scheme 29. Refcodes MIFYIJ (top) [114] and IKASAP (bottom) [47]



Scheme 30. Refcodes BIXFOE (top) [115] and GOMDOB (bottom) [116]

Compounds with formula $(R^1O)(R^2O)(R^3R^4N)P(O)$, $(R^1O)(R^2O)(R^3NH)P(O)$, $(R^1O)(R^2R^3N)(R^4R^5N)P(O)$, $(R^1O)(R^2NH)(R^3R^4N)P(O)$ *and* $(R^1O)(R^2NH)(R^3NH)P(O)$

The tetrahedral configuration of phosphorus atom is significantly distorted as it has been noted for the other phosphoramides and their chalco-derivatives [117]. For example, the bond angles around the P atom of $(4\text{-}CH_3\text{-}C_6H_4O)(C_6H_{11}NH)_2P(O)$ [116] vary in the range from 101.48(10)° [for $O_{phenoxy}—P—N1$ angle] to 118.58(9)° [for $O_{phosphoryl}—P—N2$ angle]. The C—O—P angle is 123.52(15)°. A general view of a compound with formula $(4\text{-}CH_3\text{-}C_6H_4O)(RNH)_2P(O)$ is shown in Fig. 5.

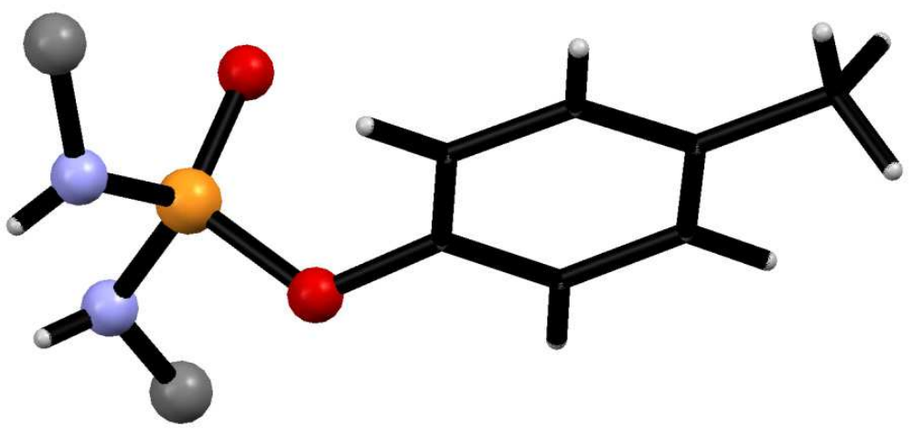


Fig. 5. A general view of a compound with formula $(4\text{-}CH_3\text{-}C_6H_4O)(RNH)_2P(O)$, the R moieties are shown as grey balls.

Similar to the other phosphoramidates, each N atom bonded to phosphorus doesn't involve in any HB as an acceptor, showing its low Lewis-base character. In most cases, it has a nearly planar environment [26]. Of course, the nitrogen atom' environment of some substituents, such as aziridinyl, like for example in the compound with refcode GOMDOB [118] (Scheme 30 (bottom)) shows some deviation from planarity, but such N atom doesn't cooperate in hydrogen bonding interaction, too. Moreover, the oxygen atom of the phenoxy or alkoxy groups in the 47 structures with an (O)P(=O)(NH)(N) skeleton (like for example in $4\text{-}CH_3\text{-}C_6H_4OP(O)[N(CH_3)_2][NHC(CH_3)_3]$, GUDGIW: [119]) doesn't cooperate in the HB interaction, as it can not compete with the phosphoryl oxygen atom for H-accepting from the unique H-donor site in the molecule. Furthermore, among the 106 deposited structures with an (O)(O)P(=O)(NH) skeleton, only the structure of $[CH_3O]_2P(O)[NHCH(CH(CH_3)(OC(O)CH_3))(C(O)(C(NN)(COOC_2H_5)))]$ (IJUMAB: [120]) shows N-H...O(CH_3) not N-H...O(P) hydrogen bond (in this consideration, some structures with unavailable cifs were not enumerated). So, such compounds [if the substituents linked to the N or/and O atoms don't contain any H-acceptor or H-donor centers] may be almost always considered as compounds with "one H-acceptor (the oxygen of phosphoryl) and one H-donor sites", both in the P(O)NH group.

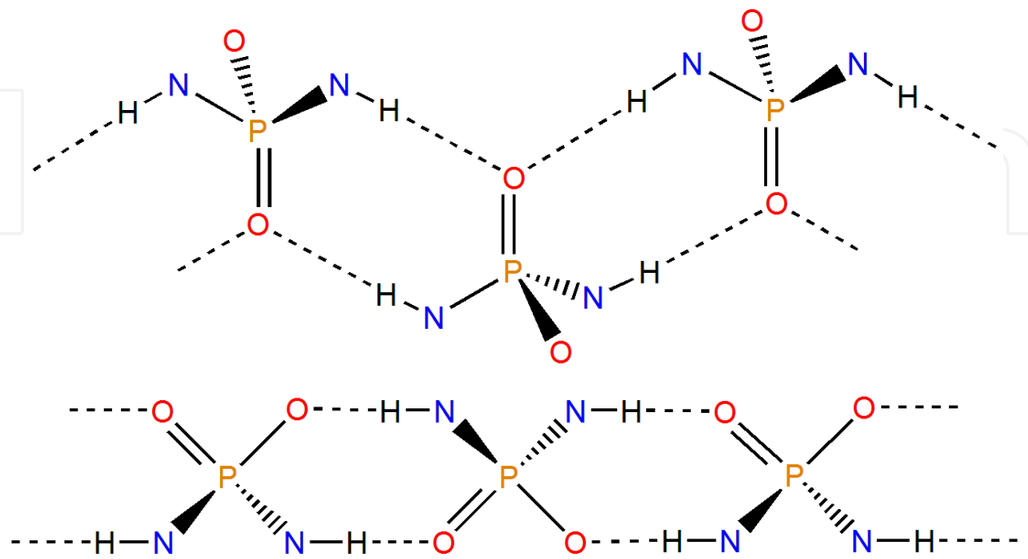
The oxygen atom of OR moiety in some examples of compounds with a higher H-donor sites, such as compounds containing an (O)P(=O)(NH)(NH) skeleton, however, it has a lower H-acceptability than the phosphoryl oxygen atom, is enforced to involve in the HB interaction ($[4\text{-}CH_3\text{-}C_6H_4O]P(O)[NHC_6H_4(4\text{-}CH_3)]_2$: MUBPIJ, [36]). The better H-acceptability of the phosphoryl O atom than that of the RO moiety, in some cases for example in $[C_6H_5O]P(O)[NHC_6H_{11}][NHC_6H_4(4\text{-}CH_3)]$ (ERUFIH: [69]), leads to act it as a double-H acceptor. In the molecular packing of $[C_6H_5O]P(O)[NHC_6H_{11}]_2.CH_3OH$ (HIVLOO, [67]), a linear arrangement is formed through a P(O)[...H—O][…H—N] grouping, where, the P(O) group acts as a double H-acceptor, the OH unit belongs to the solvent methanol.

In the 2-D H-bonded arrangement for diazaphosphorinane $4\text{-}CH_3C_6H_4OP(O)X$ [X = $NHCH_2CH_2CH_2NH$ (KIVXIX)] and $C_6H_5OP(O)Y$ [Y = $NHCH_2C(CH_3)_2CH_2NH$ (KIVXOD)], the P(O) functions as a double-H acceptor [121]. In the other cases, both O atoms are involved in the HB interactions with two N—H units (or the other H-donor site(s) in the molecule or in the crystal), in which the P(O) forms a stronger HB. Typically, in the crystal packing of $[4\text{-}CH_3\text{-}C_6H_4O]P(O)[NHC_6H_4(4\text{-}CH_3)]_2$ (MUBPIJ, [36]), the N...O(P) = 2.805(2) Å & N...O(C_6H_4-4-CH_3) = 3.068(2) Å and of $C_6H_5OP(O)[NHC_6H_4(4\text{-}CH_3)][NHCH_2C_6H_5]$, in a recently published paper by Pourayoubi *et al.*, 2011 [43], these distances are 2.761(3) Å & 3.127(3) Å, respectively.

Scheme 31 illustrates the contribution of P(O) as a double-H atom acceptor (top) and cooperation of both oxygen atoms (bottom) in hydrogen bond pattern in compounds having a P(O)(O)(NH)(NH) moiety.

In the crystal packing of compounds with the general formula $(R^1O)P(O)[NHR^2]_2$, both linear and 2-D hydrogen-bonded arrangements were observed; for example, $C_6H_5OP(O)[NHC_6H_{11}]_2.CH_3OH$ (HIVLOO [67]), $4\text{-}CH_3\text{-}C_6H_4OP(O)[NHC_6H_4\text{-}4\text{-}CH_3]_2$ (MUBPIJ [36]), $4\text{-}CH_3\text{-}C_6H_4OP(O)[NHC_6H_4\text{-}2\text{-}CH_3]_2$ (YUPVEL [32]) and $4\text{-}CH_3\text{-}C_6H_4OP(O)X$ (X = $NHCH_2C(CH_3)_2CH_2NH$, NIBNOC [83]-a) exist as a linear H-bonded arrangement, whereas a 2-D array is found for instance in each of $4\text{-}CH_3—C_6H_4OP(O)X$ (X =

$NHCH_2CH_2CH_2NH$, KIVXIX [121]), $C_6H_5OP(O)X$ (X = $NHCH_2C(CH_3)_2CH_2NH$, KIVXOD [83]-a), $C_6H_5OP(O)(NH_2)_2$ (PPOSAM [122]) and $C_6H_5OP(O)X$ (X = $NHNHP(O)(OC_6H_5)NHNH$ (FIMVUS [123])).



Scheme 31. A view of contribution of phosphoryl oxygen atom as a double-H acceptor (top) and a view of contribution of both oxygen atoms (bottom) in hydrogen bond pattern of compounds having a P(O)(O)(NH)(NH) skeleton

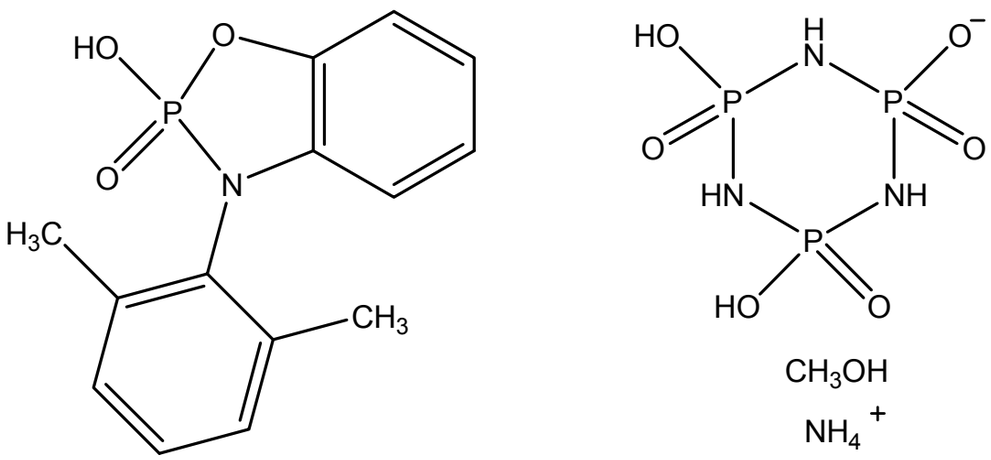
In summary, the cif files of all published compounds with the $(O)P(=O)(NH)_2$, $(O)_2P(=O)(NH)$ and (O)P(=O)(NH)(N) skeletons were investigated and the following "empirical rules" were obtained:

1. In none of the reported structures, the nitrogen atom doesn't cooperate in HB interaction as an acceptor.
2. Almost in all of the compounds having the $(O)_2P(=O)(NH)$ and (O)P(=O)(NH)(N) skeletons, the oxygen atom of the phenoxy (or alkoxy) group doesn't cooperate in the HB interaction, as it can't compete with the phosphoryl oxygen atom to H-accepting from the unique H-donor site in the molecule. There is only one example of hydrogen bond of the type N—H...O(R) in this family of compounds in one compound containing some H-acceptor centers in addition to one phosphoryl group.
3. The oxygen atom of OR moiety in some examples of compounds with a higher number of H-donor sites relative to the H-acceptor centers, such as compounds containing an $(O)P(=O)(NH)_2$ skeleton, however, it has a lower H-acceptability than the phosphoryl oxygen atom, is enforced to involve in the HB interaction.
4. In compounds having an $(O)P(=O)(NH)_2$ skeleton, the better H-acceptability of the phosphoryl O atom than that of the RO moiety, in some cases, leads to act it as a double-H acceptor.

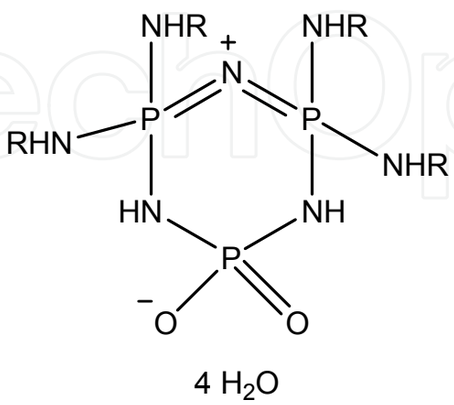
Amidophosphoric acid and amido phosphate compounds

Compounds with refcodes PHOXBP (Scheme 32, left) [124] and TMPMET (Scheme 32, right) [125] are respectively the examples of an acid and a solvated acidic-salt belonging to the

phosphorus-nitrogen compounds' family. The crystal packing of the latter compound contains some various HBs such as two very strong homo-conjugated $[O-H\ldots O]^-$ hydrogen bonds (O…O = 2.43 & 2.50 Å) and relatively strong hetero-conjugated $[N-H\ldots O]^{\delta+}$ hydrogen bond (N…O = 2.93 Å). In the hydrated zwitterionic compound shown in Scheme 33 (refcode: GAHFUS) [126], the N^+ which is lack of the lone electron pair doesn't involve in H-bonding interaction; whereas, the $[P(O)(O)]^-$ unit cooperates in some N—H…O and O—H…O hydrogen bonds (Fig. 6). Compounds with refcodes IGASUF (Scheme 34) [127] and WIYFAL (Scheme 35) [128] are respectively a simple phosphate salt and an HCl-water absorbed phosphorus-nitrogen compound in which the Cl^- ion is hydrogen-bonded to the N—H units of two-neighboring phosphoramidates.



Scheme 32. Refcodes PHOXBP (left) [124] and TMPMET (right) [125]



Scheme 33. Refcode GAHFUS, R = cyclo-hexyl [126]

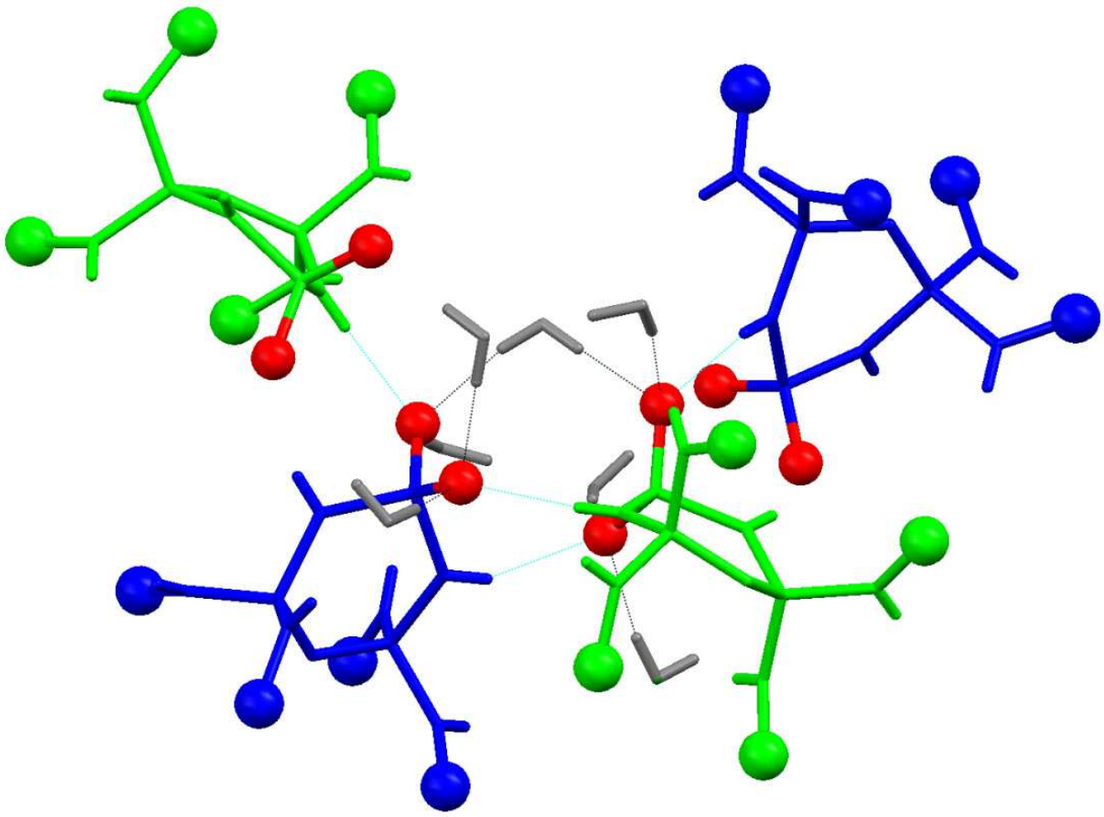
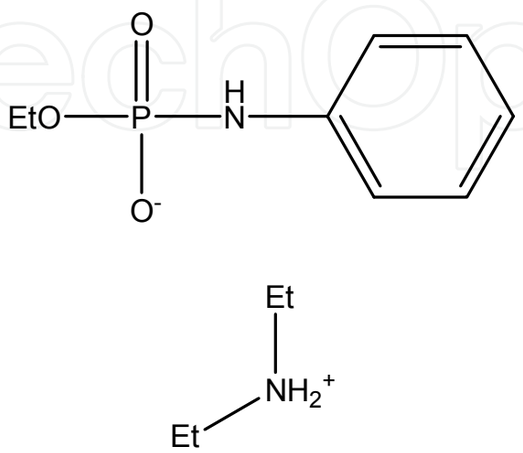
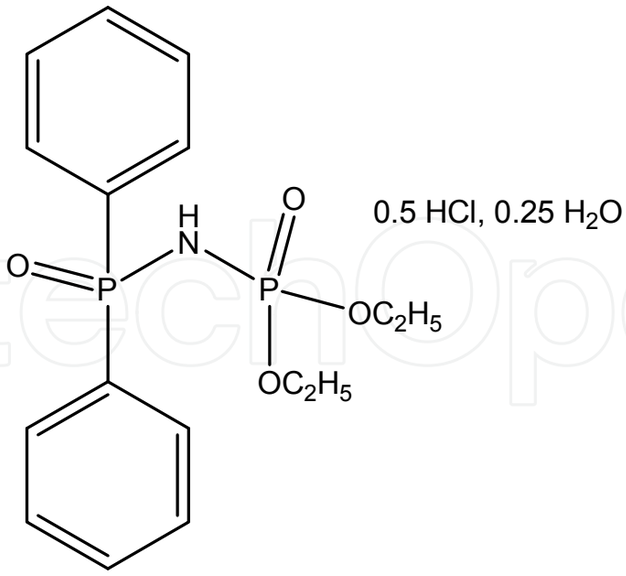


Fig. 6. Fragment of the crystal packing of the hydrated zwitterionic compound with refcode GAHFUS [126] showing the involvement of $[P(O)(O)]^-$ units in N—H…O (blue dotted lines) and O—H…O (black dotted lines) hydrogen bonds, two symmetrically independent zwitterionic compounds in the structure are shown as blue and green apart the oxygen atoms of $[P(O)(O)]^-$ units which are shown as red balls, the water molecules are represented with grey color. The cyclohexyl groups are shown as balls (green and blue).



Scheme 34. Refcode IGASUF [127]



Scheme 35. Refcode WIYFAL [128]

5. Crystallographically independent molecules and ions

Different orientations resulting from non-rigid units in some molecules and ions and the presence of different H-bonds or the other short contacts may result in two or more conformers (or symmetrically independent molecules (or ions)) in solid state. Compound $C_6H_5C(O)NHP(O)[NH(tert\text{-}C_4H_9)]_2$, exists as two conformers in crystalline lattice (which are detectable in solution, too by NMR experiment) [27]. They are due to different spatial orientations of *tert*-butyl amido groups. One of the two conformers has two NH units (of *tert*-butyl amido moieties) which are *syn*, but not in the other. Another example is the presence of disorder in the cyclic amido moiety. For example, $C_6H_5C(O)NHP(O)[NC_4H_8]_2$ appears as two crystallographically independent molecules [55]. This is based on the conformational forms of the pyrrolidinyl groups and the orientation of the phenyl ring. The dimmeric aggregate in this case, between two independent molecules, is not centrosymmetric. The structure of $[NH_2(C_6H_{11})(tert\text{-}C_4H_9)][PO_2Cl_2]$ consists of two symmetrically independent dichlorophosphate anions as well as cyclohexyl-*tert*-butylammonium cations [75]. In the crystal structure of $[tert\text{-}C_4H_9NH_3][CF_3C(O)NHP(O)(O)(tert\text{-}C_4H_9NH)].0.333CH_3CN.0.333H_2O$ [79], there are three symmetrically independent trifluoroacetyl-N-(*tert*-butylamino) phosphate anions and three independent cations of *tert*-butyl- ammonium; one of the anion indicates disorder in the *tert*-C_4H_9 moiety. There are some other examples of disordered components for the groups such as *tert*-C_4H_9, cyclopentyl and cyclohexyl etc. in the deposited cifs.

6. Hydrogen bond strengths in phosphoramidates

Histogram of the N…O distances in the N—H…O hydrogen bonds in compounds having a $P(O)(N)_n(O)_{3-n}$ (n = 1, 2, 3) skeleton is given in Fig. 7. In this figure, the distribution of H-bond strength in different families of phosphoramidates are shown with different colored columns: compounds having a $P(O)(NH)_n(N)_m(O)_{3-(n+m)}$ skeleton (n = 1, 2; n+m < 3) as black

columns, $C(O)NHP(O)(NH)_2$ and $C(O)NHP(O)(N)_2$ as blue and $P(O)(NH)_x(N)_{3-x}$ (x = 1, 2, 3) as red columns.

In phosphoramidates having a $P(O)(NH)_n(N)_m(O)_{3-(n+m)}$ skeleton (balck), the strongest and weakest N—H…O hydrogen bonds are found for hydrogen bonds in the range of 2.65 to 2.75 Å and 3.20 to 3.30 Å.

In compounds containing a $P(O)(NH)_x(N)_{3-x}$ skeleton, the strongest N—H…O hydrogen bonds are seen for the HBs in the range of 2.70 to 2.80 Å. The phosphoryl group' involvement in a multi-centered $P(O)\cdots[H—N]_n$ (n = 2 & 3) grouping may lead to some weak H-bonds; for example in $P(O)[NHC(CH_3)_3]_3$ (KABVEP [93]), N…O distances & N—H…O angles are 3.255(4) Å & 111.1(2)°, 3.294(4) Å & 93.4(2)° and 3.159(4) Å & 123.0(2)°, and in $P(O)[NH(C_6H_5)]_3$ (KEQLUO [95]) these parameters are 3.06 Å & 110° and 3.06 Å & 108°; this weakening of H-bond strength is attributed to the *anti*-cooperativity effect [89].

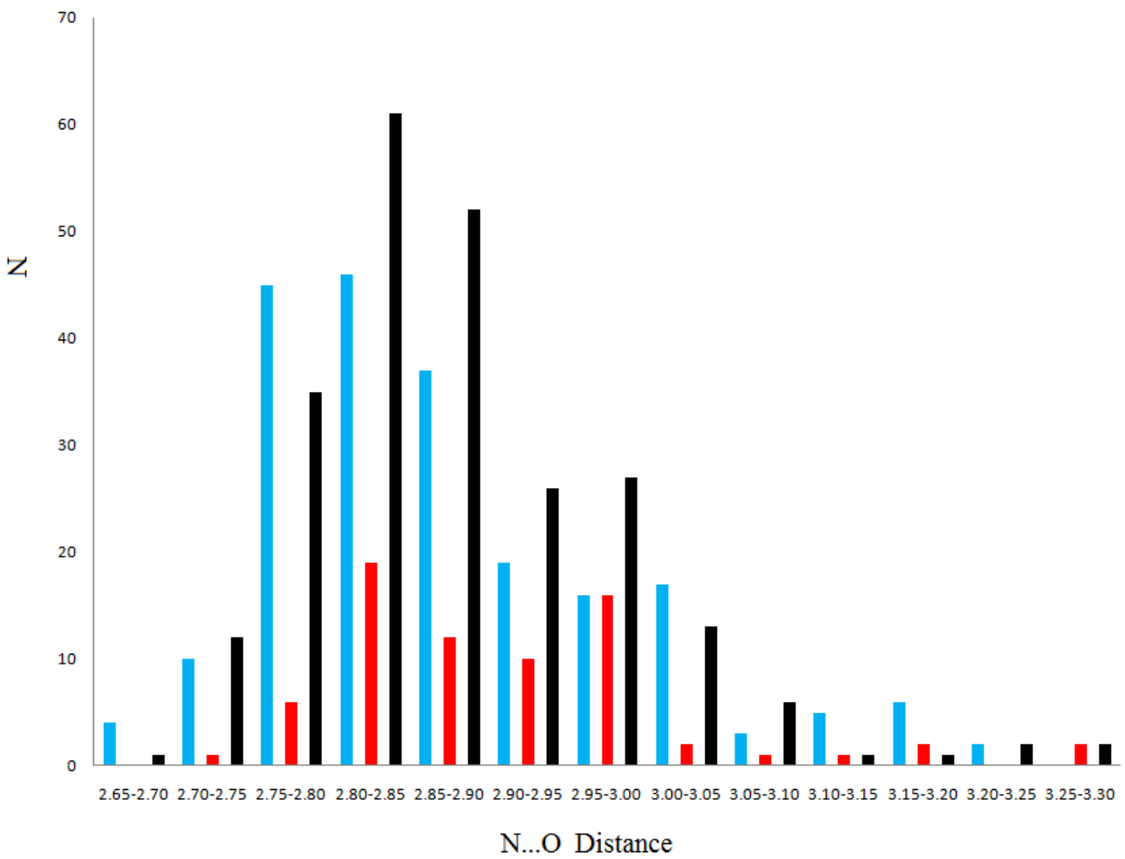


Fig. 7. Histogram of the N…O distances in the N—H…O hydrogen bonds in compounds having $P(O)(NH)_n(N)_m(O)_{3-(n+m)}$ (n = 1, 2; n+m < 3) (black), $C(O)NHP(O)(NH)_2$ and $C(O)NHP(O)(N)_2$ (blue), and $P(O)(NH)_x(N)_{3-x}$ (x = 1, 2, 3) (red) skeletons (the co-crystals and solvated compounds and the compounds having a disorder in the sites involving HB interaction were not enumerated).

In this family, a long donor···acceptor distance (3.477(2) Å) is observed with a relatively linear N—H…O angle (171 (2)°) for the N—H···O(CH_3) hydrogen bond in the packing of $P(O)[NHC_6H_4(4\text{-}OCH_3)]_3$ (WAWNIS [97]).

In compounds having a C(O)NHP(O) fragment, the strongest N—H…O hydrogen bonds are found for the P═O…H—$N_{C(O)NHP(O)}$ hydrogen bonds, especially in the $R_2^2(8)$ rings of some molecules [in the case of a *syn* orientation of P═O versus N—H which allows the building of the cyclic motif through a pair of P═O…H—$N_{C(O)NHP(O)}$ hydrogen bonds]. In this sub-category of compounds, the strongest and weakest hydrogen bonds are observed for the N…O distances in the ranges 2.70–2.80 Å [for $N_{C(O)NHP(O)}$—H…O hydrogen bonds] and 3.00–3.25 Å [for N_{amide}—H…O hydrogen bonds], while in the range 2.80–3.00 Å for donor–acceptor distances both types of hydrogen bonds are found. In a recently published structure [129] with a $NHC(O)NHP(O)[NH]_2$ skeleton, the intramolecular N—H…O hydrogen bonds are found in the range 2.65-2.70 Å (Fig. 7). The asymmetric unit contains four independent molecules and the hydrogen bond pattern is different from all phosphoric triamides having a $C(O)NHP(O)[NH]_2$ fragment.

7. Some future aims and proposals

Phosphorus has a very deep and widespread chemistry and understanding its nature in the compounds is noticeable interest. This may be achieved through the study on collective behaviors of phosphorus compounds in point of view of their different aspects.

The structural investigations and the study on the hydrogen-bond patterns may help to predict the molecular packing from the molecular structure. Moreover, as the biological activity of phosphorus compounds is very important, finding a relationship between the structure and a biological property is beneficial. For example, as well-known, a biological property may be related to the three important factors: lipophilicity, electronic and steric parameters. Probably, part of these factors could be well-understand by considering the crystal structure' study of such compounds; the electronic parameters may be related to the nature of chemical bonds or to the electron density or valence bond in different parts of the molecule. It is believed that, in the first step of interaction with acetylcholinesterase, the phosphoryl group is involving with the enzyme active site through a non-covalent bond; so, considering the non-covalent interaction of phosphoryl group with different atoms such as hydrogen helps to understand that the molecule how much could close to the enzyme active site. The steric parameters may be elucidated from the volume of molecule or considering the V(volume of unit cell)/Z(number of molecules in the unit cell). This may be in fact the practical volume which the molecule has, as the molecule usually cannot be closer to the neighboring molecules from this frontier boundary.

The solubility of molecules in different solvents must be checked in the crystal growth process; so, elucidation of lipophilicity is easy; however, the best method for measuring of this parameter is using of the spectrophotometer. And finally, the steric parameters can simply accessible through a structural study.

Preparation of phosphorus acids of the formula $RP(O)(OH)_2$ may develop the synthesis of the functionalized nano-phosphate materials and also polyoxometalate-based organic/inorganic hybrid compounds in which the phosphorus atom is trapping between

the R group from one side and a cluster containing metal-oxygen framework in the other side. These acids may develop the extraction process of cations, too.

Application of phosphoryl donor ligands in preparation of oxo-centered clusters, in which their terminal ligands are replaced by phosphorus compounds, may be interesting for consideration. Preparation of single- enantiomer phosphoramidates by using a chiral primary or secondary amine is easy; it may extend the strategies for the synthesis of chiral phosphoramidates, phosphoric acids, nano-phosphates and so on.

Synthesis of phosphoramidate-based hybrid compounds by using polyoxoanions may be valuable for spending the time on its consideration and experiment. Some of the well-known hybrids contain the molecule-cation components of the type $[B—H…B]^+$, where the B may be a base such as amide. Designing of such molecule-cation pairs with phosphoramidates, $[PO—H…OP]^+$, may extend the experimental data about the ^{31}P-^{31}P coupling constant through the hydrogen-bond.

The NMR experiments on phosphoramidate-based compounds may develop the study on coupling constants of phosphorus and the other atoms, such as $^2J(^{31}P$-$^{127}Tl)$ or $^2J(^{31}P$-$^{39}K)$. These values may apply to evaluate the strengths of P=O—Tl or P=O—K bonds in their complexes.

We wish to develop the spectroscopic features and chemical calculations on phosphorus compounds, preparation of N-deuterated compounds in order to a good assignment of IR and Raman absorption bands, collecting the NMR data such as chemical shifts and short and long-range coupling constants, and finally chemical calculations on hydrogen-bonded molecules in the crystals.

8. Conclusion

In this chapter, the common methods for the synthesis and crystallization of phosphoramidates, their molecular structural features and the hydrogen-bond patterns and strengths were reviewed; the important structural aspects may be classified as follows:

1. The four different groups linked to the P atom result in a distorted tetrahedral configuration.
2. In the C(O)NHP(O) unit, the P=O is a better H-acceptor than the C=O counterpart, moreover, the *anti* orientation of P=O versus C=O is more common than the *gauche* orientation; in acyclic compounds with formula $RC(O)NHP(O)[NHR']_2$, a *gauche* situation has not been reported, so far. In the $C(O)NHP(O)[N]_2$ fragment, the P—N bond of the C(O)NHP(O) moiety is longer than the two other P—N bonds; whereas, in the $[C(O)NP(O)[N]_2]^-$ fragment, similar P—N bond are shorter than the two others.
3. The nitrogen atom of the P(O)N unit has a sp^2 character and virtually doesn't involve in hydrogen-bond pattern as an H-acceptor.
4. In the C—O—P(=O) fragment, the oxygen of phosphoryl is a better H-acceptor than the other oxygen atom; the C—O—P angle is about 120^o.
5. In the diazaphosphorinane ring, the P=O bond is placed in an equatorial position.
6. The hydrogen bond in a neutral phosphoramidate is of the type polarization-assisted hydrogen bond; whereas, in the proton-transfer and phosphate compounds two factors help to strength of hydrogen bond: polarization-assisted and charge-assisted.

7. In the multi-centered hydrogen-bond of the type $P=O[\ldots H\text{-}N]_n$ (n = 2 & 3) the hydrogen-bond is weak due to the anticooperativity effect.

We wish to collect more structural data about this class of compounds and study the collective behavior of this family in the other domains such as spectroscopy and chemical calculations.

9. Acknowledgements

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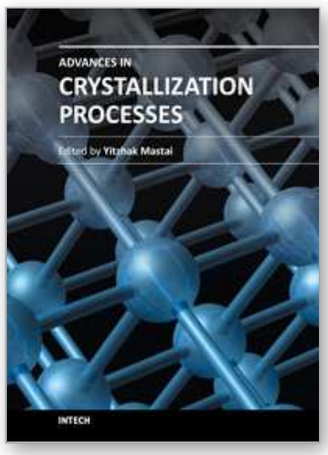

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Crystallization is used at some stage in nearly all process industries as a method of production, purification or recovery of solid materials. In recent years, a number of new applications have also come to rely on crystallization processes such as the crystallization of nano and amorphous materials. The articles for this book have been contributed by the most respected researchers in this area and cover the frontier areas of research and developments in crystallization processes. Divided into five parts this book provides the latest research developments in many aspects of crystallization including: chiral crystallization, crystallization of nanomaterials and the crystallization of amorphous and glassy materials. This book is of interest to both fundamental research and also to practicing scientists and will prove invaluable to all chemical engineers and industrial chemists in the process industries as well as crystallization workers and students in industry and academia.

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