

Synthesis, spectral characterization and crystal structures of organophosphonic diamides: pyramidal nitrogen centers and hydrogen bonding in $[\text{PhP}(\text{O})(\text{NH}^t\text{Bu})_2]$, $[\text{PhP}(\text{O})(\text{NHDipp})_2]$ (Dipp = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$) and $[\text{BuP}(\text{O})(\text{NH}^i\text{Pr})_2]^\dagger$

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Organophosphonic diamides of general formula $[\text{R}^1\text{P}(\text{O})(\text{NHR}^2)_2]$ (**1–8**; $\text{R}^1 = \text{Ph}$, Cy or ^tBu and $\text{R}^2 = \text{Cy}$, ^iPr , ^tBu or Dipp) have been prepared by the addition of P,P' -dichloro(alkyl/aryl)phosphine oxide, $\text{R}^1\text{P}(\text{O})\text{Cl}_2$, to a solution of primary amine in toluene. The synthesis of $\text{PhP}(\text{O})(\text{NH}^t\text{Bu})_2$ (**1**) in high yield was achieved by slow oxidation of $\text{PhP}(\text{NH}^t\text{Bu})_2$ in air over several days. All new compounds have been characterized by elemental analysis and by IR, EI mass and NMR (^1H and ^{31}P) spectroscopy. The molecular structures of $[\text{PhP}(\text{O})(\text{NH}^t\text{Bu})_2]$ (**1**), $[\text{PhPO}(\text{NHDipp})_2]$ (**2**) and $[\text{BuP}(\text{O})(\text{NH}^i\text{Pr})_2]$ (**7**) have been determined by single crystal X-ray diffraction studies. The amido nitrogen atoms in **1**, **2** and **7** show considerable deviation from the expected trigonal-planar geometry. The observed dihedral angles and the orientation of the nitrogen lone pair (l.p.) in these compounds point to the role of $\text{l.p.}(\text{N}) \rightarrow \sigma^*(\text{P}-\text{X})$ type negative hyperconjugative interactions in $\text{P}-\text{N}$ multiple bonding. Compounds **1** and **7** form interesting polymeric structures in the solid state with the aid of $\text{N}-\text{H} \cdots \text{O}=\text{P}$ hydrogen bonding interactions while the presence of the very bulky Dipp substituent on nitrogen in **2** prevents the participation of the $\text{N}-\text{H}$ protons in hydrogen bonding with phosphoryl oxygen atoms.

Introduction

The discovery of metallocene catalysts for alkene polymerization has received considerable attention owing to their role in stereoselective/specific polymerization.¹ While the use of mixed cyclopentadienyl amide and amidine complexes for catalysis has been reported,² the interest in synthesis and the application of diimide precursors is only just emerging.^{3,4} Since electron deficient, usually d^0 , metal centers are required for efficient catalytic systems, the somewhat poorer donation ability of amide ligands might be expected to offer enhanced activity over the analogous *ansa*-metallocene complexes. In this context, the groups of Brookhart and Gibson have recently prepared complexes based on chelating bis(imido) ligands, which polymerize olefins with excellent activities.⁵ Organophosphonic amides $[\text{R}^1\text{P}(\text{O})(\text{NHR}^2)_2]$ could serve as very useful chelating ligands in this regard and may have a marked influence in the activity of the resulting complex due to the presence of a phosphorus center adjacent to the ligating nitrogen atoms. While Kuchen *et al.* have investigated the coordination chemistry of diorganophosphonic amides $[\text{R}_2^1\text{P}(\text{O})(\text{NHR}^2)]$ in detail and have shown that these ligands stabilize transition metal ions in unusual geometries,⁶ a recent report by Chivers and co-workers has demonstrated the use of $[\text{P}(\text{O})(\text{NHR})_3]$ in synthesizing amido analogs of aluminophosphates (Chart 1).⁷ However, there are no studies on the utilization of $[\text{R}^1\text{P}(\text{O})(\text{NHR}^2)_2]$ as chelating ligands although there have been reports on the synthesis and mechanism of formation of these compounds.^{8,9}

Renewed interest in organophosphonic diamide chemistry is due to the isoelectronic relation of this class of compounds to the extensively investigated organophosphonic acids^{10,11} (Chart 2). In particular, recent work has demonstrated the use of phosphonic acids in the synthesis of several novel cage-like¹⁰ and layered metal phosphonates.¹¹ Similarly, phosphonic diamides are expected to serve as useful ligands in building aggregates that simultaneously contain both $\text{M}-\text{N}-\text{P}$ and $\text{M}-\text{O}-\text{P}$ linkages. In this context, we wish to report herein on the synthesis of a series of organophosphonic diamides and their characterization data. We also report on the first crystal structures of free organophosphonic diamides, establishing the solid-state conformation and hydrogen-bonding pattern in these ligands.

Results and discussion

Synthesis

Although several examples of phosphonic diamides have been described in the literature, they have been poorly characterized, with no spectroscopic or structural studies being

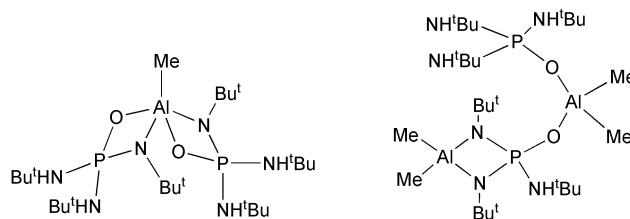


Chart 1

[†] Electronic supplementary information (ESI) available: representative IR and NMR spectra. See <http://www.rsc.org/suppdata/nj/b3/b300035d/>

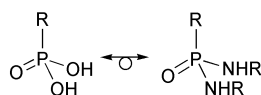


Chart 2

reported.⁸ More importantly, the use of these functional molecules in further reactions to yield metal derivatives has not been studied at all. To investigate these points, the synthesis of a series of phosphonic diamides was carried out by varying the bulkiness and nature of the substituents on both phosphorus and nitrogen atoms.

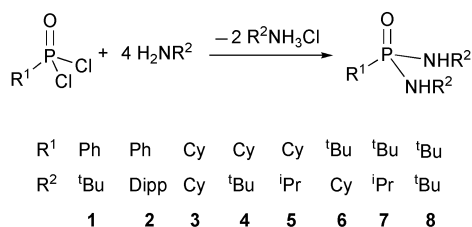
The phosphonic diamides **1–8** have been synthesized essentially by following the reaction procedure shown in Scheme 1 although some variations in reaction conditions were necessary, depending on the relative bulkiness of the amines used. Typically alkyl/arylphosphonic dichlorides $R^1P(O)Cl_2$ ($R = Ph, ^iBu, Cy$) were reacted with 4 equiv. of a primary aliphatic or aromatic amine R^2NH_2 in boiling toluene. For the preparation of $[PhP(O)(NHDipp)_2]$ (**2**), only 2 equiv. of high-boiling DippNH₂ was used while 2 equiv. of Et₃N was added in the reaction mixture as an HCl scavenger. The reaction proceeded with the formation of amine hydrochloride. Since phosphonic amides are freely soluble in toluene, the amine hydrochloride formed was separated by simple filtration.

Synthesis of $[^iBuP(O)(NH^iBu)_2]$ (**8**) could not be accomplished under the conditions described above owing to the presence of bulky *tert*-butyl groups in both reactants. Hence this reaction was carried out under solvothermal conditions in an autoclave at 140 °C using acetonitrile as described by Quast *et al.*^{8a} Work-up in this case was carried out by pouring the reaction mixture into ice-cold water and stirring for 30 min to extract the amine hydrochloride formed. For the synthesis of **1**, compared to following the reaction shown in Scheme 1, crystallization of tervalent phosphorus amide $[PhP(NH^iBu)_2]$ in air over prolonged time from a CH_2Cl_2 –hexane solution results in better yields of $[PhP(O)(NH^iBu)_2]$ (90%). Although there has been some variations in the reaction times (typically 5 to 9 days), this reaction is highly reproducible with high isolated yields of **1**. While air seems to act as a convenient oxidizing agent in the present case, the earlier reported method for the preparation of this compound involves the use of ozone as the oxidizing agent.^{8b}

Characterization

Compounds **1–8** were found to have good solubility in most organic solvents and hence could be purified by repeated crystallization. The isolated yield of analytically pure $[PhP(O)(NHDipp)_2]$ (**2**) is comparatively low due to the substitution of two very bulky DippNH groups at the phosphorus. Characterization of all the compounds was carried out with the aid of IR, mass and NMR (¹H and ³¹P NMR) spectroscopic techniques. Selected analytical and spectroscopic data for the new products are listed in Table 1.

The re-crystallized samples of all new compounds were analytically pure with fairly sharp melting points. The electron impact mass spectra (EI MS) of all compounds yielded peaks



Scheme 1

Table 1 Selected characterization data for **1–8**

Compound	% Yield	M.p./°C	<i>m/z</i> ⁺ (EIMS %)	δ (³¹ P)/ppm
$[PhP(O)(NH^iBu)_2]$ (1)	80	181–182	268 (5)	15.3
$[PhP(O)(DippNH)_2]$ (2)	18 ^a	210–211	476 (5)	9.1
$[CyP(O)(NHCy)_2]$ (3)	67	230–235	326(3)	30.9
$[CyP(O)(NH^iBu)_2]$ (4)	50	236–237	274(2)	28.1
$[CyP(O)(NH^iPr)_2]$ (5)	52	137–138	247(2)	30.1
$[^iBuP(O)(NHCy)_2]$ (6)	58	197–198	300(2)	37.4
$[^iBuP(O)(NH^iPr)_2]$ (7)	90	164–165	221(5)	35.5
$[^iBuP(O)(NH^iBu)_2]$ (8)	65	181–182	249(5)	32.6

^a Yield of the twice re-crystallized sample.

due to the respective molecular ions, even at 70 eV. The fragmentation pattern of the products under EI conditions is consistent with the proposed structures. The IR spectral data of **1–8** display the vibrational bands for all structural linkages expected for these compounds.¹² For example, the characteristic P=O absorption for all compounds was observed around 1200 cm^{−1}. The N–H stretching vibration in **1–8** results in a strong absorption in the range 3200–3300 cm^{−1}.

The ¹H NMR spectral data obtained for **1–8** are suggestive of the expected structure of these molecules. A description of the spectrum of $[PhP(O)(NHDipp)_2]$ (**2**) is presented here as a representative example. Compound **2** shows two doublets (δ 0.9 and 1.1 ppm) of equal intensity (³*J*_{HH} = 6.96 Hz) corresponding to the methyl groups of two inequivalent isopropyl groups and a septet for the methine protons at δ 3.3 ppm. The resonance appearing at δ 4.1 ppm (doublet) is due to the N–H protons. This resonance could be interpreted either as two separate peaks for two non-equivalent N–H protons or as a phosphorus-coupled doublet (²*J*_{PH} = 10 Hz). This ambiguity could, however, be resolved by recording the spectrum at three different spectral frequencies (60, 300, and 400 MHz), which clearly showed that this resonance is a phosphorus-coupled doublet. This strong coupling of phosphorus to the N–H protons can be attributed to the presence of fairly strong N–H bonds in **2** due to the absence of hydrogen bonding involving these protons (*vide infra*).

The observed ³¹P NMR chemical shift values for all the compounds fall in the range δ 9.1 to 37.4 ppm (Table 1). The nature of the R¹ group attached directly to phosphorus has a more pronounced effect on the observed chemical shift than the R² group on the nitrogen atoms. For example, the *tert*-butyl phosphonic amides show resonances in the range δ 32.6 to 37.4 ppm while the chemical shifts of cyclohexyl phosphonic amides fall in the range δ 28.1 to 30.9 ppm. The most upfield shifts are observed for the phenyl phosphonic diamides **1** and **2**. In particular, the presence of the bulky Dipp group on the nitrogen in **2** causes the highest upfield shift among the phosphonic diamides reported herein (δ 9.1 ppm).

Molecular structures

The relative disposition of the acidic N–H protons (Chart 3) in phosphonic diamides is of interest for their subsequent reactions with metal precursors to generate metallophosphonamides. The predominance of one of the forms over other forms shown in Chart 3 will be dictated by both the bulkiness of the substituents R¹ and R² and the maximization of P–N multiple bonding effects. Hence, in order to glean structural insights into the conformations of these molecules, single crystal X-ray diffraction studies were carried out for the representative examples **1**, **2**, and **7**.¹³

The ORTEP of the final refined structures of compound **1**, **2** and **7** are shown in Fig. 1. Selected bond lengths, bond angles and dihedral angles found in these compounds are listed in Tables 2–4, respectively. A comparison of the key structural

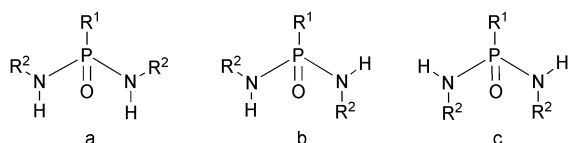


Chart 3

features is presented in Table 5. It has been possible to locate the N–H hydrogen atoms in each of the three compounds from the difference Fourier maps and subsequently refine them to convergence.¹⁴ This allows a meaningful interpretation of the nature of the bonding and conformations around the imino nitrogen atoms. Compounds **1** and **7** form interesting polymeric structures in the solid state with the aid of N–H···O=P hydrogen-bonding interactions (Fig. 2). Although both **1** and **7**

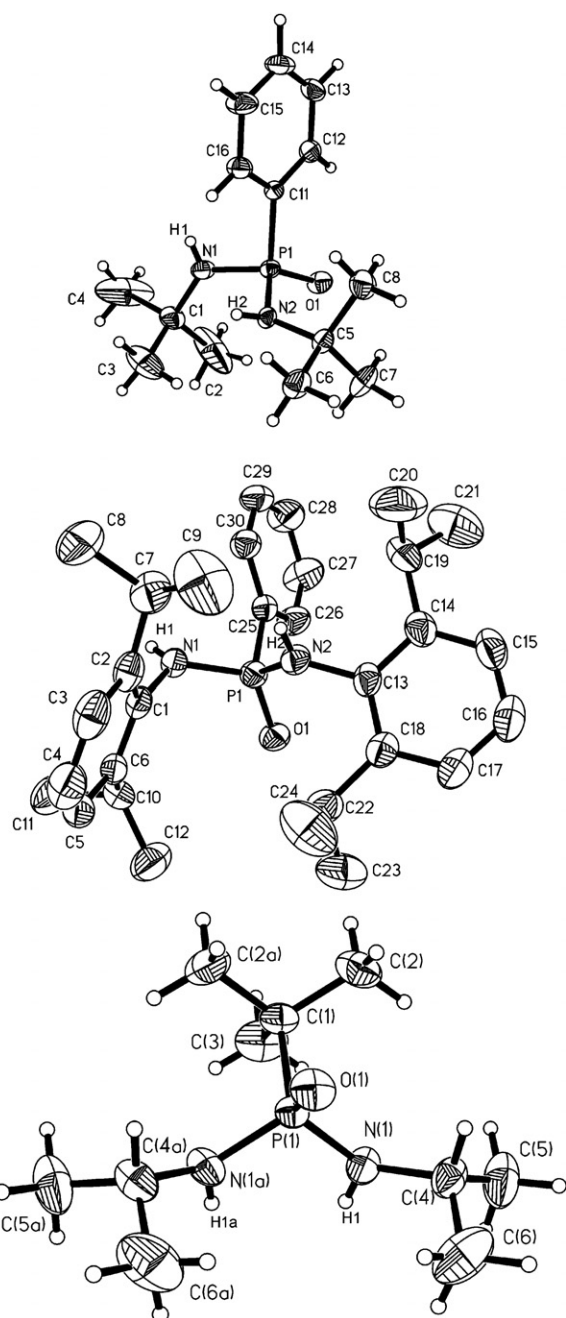


Fig. 1 ORTEP plots (50% probability level) of [PhP(O)(NH'Bu)₂] (**1**) (top), [PhP(O)(NHDipp)₂] (**2**) (middle) and [tBuP(O)(NH'Pr)₂] (**7**) (bottom). The hydrogen atoms on carbon atoms in **2** are omitted for clarity.

Table 2 Selected bond lengths (Å), bond angles and dihedral angles (°) in **1**

P(1)–O(1)	1.477(2)	P(1)–N(1)	1.646(2)
P(1)–N(2)	1.644(2)	P(1)–C(11)	1.811(2)
N(1)–H(1)	0.71(3)	N(1)–H(2)	0.78(3)
O(1)–P(1)–N(1)	117.8(1)	N(1)–P(1)–N(2)	104.6(1)
O(1)–P(1)–N(2)	111.7(1)	O(1)–P(1)–C(11)	110.5(1)
N(1)–P(1)–C(11)	100.2(1)	N(2)–P(1)–C(11)	111.3(1)
P(1)–N(1)–C(1)	129.8(2)	P(1)–N(2)–C(5)	125.7(2)
P(1)–N(1)–H(1)	112(3)	C(5)–N(2)–H(2)	111(2)
C(1)–N(1)–H(1)	117(3)	P(1)–N(2)–H(2)	114(2)
C(1)–N(1)–P(1)–O(1)	–59.8(3)	C(5)–N(2)–P(1)–O(1)	–43.4(2)
C(1)–N(1)–P(1)–N(2)	65.0(2)	C(5)–N(2)–P(1)–C(11)	80.7(2)
C(1)–N(1)–P(1)–C(11)	–179.6(2)	C(5)–N(2)–P(1)–N(1)	–171.9(2)
H(1)–N(1)–P(1)–N(2)	–124(3)	H(2)–N(2)–P(1)–O(1)	173(2)
H(1)–N(1)–P(1)–O(1)	111(3)	H(2)–N(2)–P(1)–N(1)	45(2)
H(1)–N(1)–P(1)–C(11)	–9(3)	H(2)–N(2)–P(1)–C(11)	–63(2)

form a one-dimensional polymeric chain through N–H···O=P interactions, in the case of **1** only one of the N–H groups participates in polymer formation. On the other hand, the presence of a mirror symmetry running through the P=O axis in **7** imposes the participation of both the N–H groups in hydrogen bonding, thus forming PN₂H₂O rings along the polymeric chain (Fig. 2). However, in both the cases, no inter-chain hydrogen bonds are observed. On the other hand, the presence of the very bulky Dipp groups on nitrogen in **2** does not allow the formation of hydrogen bonds by this compound and the molecules of **2** are largely held in the crystal through van der Waals forces.

The observed P=O and P–N distances are consistent with the expected values for these linkages.¹⁵ The angles observed around the central phosphorus are largely tetrahedral. The most interesting structural feature observed for these molecules is the presence of significantly pyramidalized nitrogen atoms (Table 5). Barring a few exceptions, a tricoordinate nitrogen atom that is attached to a phosphorus¹⁶ (or silicon¹⁷) is expected to exhibit a perfect trigonal-planar geometry. The literature examples with non-planar nitrogen atoms attached to a phosphorus center were proven to be a result of geometric constraints (*e.g.*, an aziridinyl phosphazene,¹⁸ a chelate complex of a λ³-cyclotriphosphazene¹⁶ or a bridging nitrogen atom of a bicyclophephazene,¹⁹ *etc.*) rather than electronic effects. These well-known exceptions to planar nitrogen atoms in the literature are normally from constrained cyclic systems of the above type and are not commonplace among acyclic P–NR₂ type compounds. Hence the observed pyramidal geometry for the nitrogen centers of unconstrained acyclic phosphonic diamides **1**, **2** and **7** is quite unique.

It is important to note, however, that in spite of the appreciable pyramidalization of the nitrogen atoms, the observed P–N distances (1.64–1.65 Å) are shorter than the corresponding distances found in acyclic and cyclic phosphazanes that contain

Table 3 Selected bond lengths (Å), bond angles and dihedral angles (°) in **2**

P(1)–O(1)	1.476(2)	P(1)–N(1)	1.658(2)
P(1)–N(2)	1.653(2)	P(1)–C(25)	1.799(3)
N(1)–H(1)	0.82(3)	N(1)–H(2)	0.77(2)
O(1)–P(1)–N(1)	121.1(1)	N(1)–P(1)–N(2)	100.4(1)
O(1)–P(1)–N(2)	111.1(1)	O(1)–P(1)–C(25)	111.1(1)
N(1)–P(1)–C(25)	101.7(1)	N(2)–P(1)–C(25)	110.7(1)
P(1)–N(1)–C(1)	123.2(2)	P(1)–N(2)–C(13)	128.0(2)
P(1)–N(1)–H(1)	114(2)	P(1)–N(2)–H(2)	114(2)
C(1)–N(1)–H(1)	118(2)	C(13)–N(2)–H(2)	114(2)
O(1)–P(1)–N(1)–C(1)	–64.6(2)	O(1)–P(1)–N(2)–C(13)	–32.6(3)
N(2)–P(1)–N(1)–C(1)	58.0(2)	N(1)–P(1)–N(2)–C(13)	–161.9(2)
C(25)–P(1)–N(1)–C(1)	171.8(2)	C(25)–P(1)–N(2)–C(13)	91.3(2)
O(1)–P(1)–N(1)–H(1)	91(2)	O(1)–P(1)–N(2)–H(2)	169(2)
N(2)–P(1)–N(1)–H(1)	–147(2)	N(1)–P(1)–N(2)–H(2)	40(2)
C(25)–P(1)–N(1)–H(1)	–33(2)	C(25)–P(1)–N(2)–H(2)	67(2)

Table 4 Selected bond lengths (Å), bond angles and dihedral angles (°) in **7**

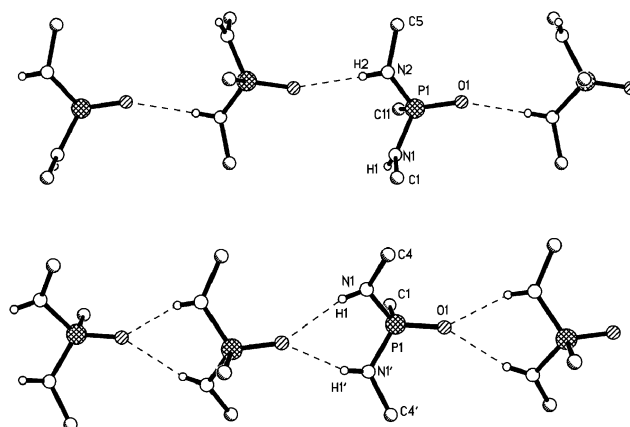
P(1)–O(1)	1.489(2)	P(1)–N(1)	1.641(1)
P(1)–C(1)	1.823(2)	N(1)–H(1)	0.80(3)
O(1)–P(1)–N(1)	114.3(1)	O(1)–P(1)–C(1)	109.0(1)
N(1)–P(1)–C(1)	107.0(1)	N(1)–P(1)–N(1)a	104.7(1)
P(1)–N(1)–C(4)	123.5(1)	P(1)–N(1)–H(1)	114(2)
C(4)–N(1)–H(1)	116(1)		
O(1)–P(1)–N(1)–C(4)	–13.9(2)	C(1)–P(1)–N(1)–C(4)	106.8(1)
N(1)a–P(1)–N(1)–C(4)	–139.8(1)	O(1)–P(1)–N(1)–H(1)	137(2)
C(1)–P(1)–N(1)–H(1)	–103(2)	N(1)a–P(1)–N(1)–H(1)	11(2)

perfectly planar nitrogen atoms.¹⁵ The short P–N distances, largely planar nitrogen coordination and poor amine basicity have been attributed for a long time to the involvement of the nitrogen lone pair in multiple bonding with the phosphorus atom through $p\pi \rightarrow d\pi$ interactions.¹⁷ The importance of this mode of multiple bonding has been questioned both from a theoretical and experimental standpoint for the last two decades.²⁰ It is now believed that the P–N multiple bonding in these kinds of systems involve $\text{l.p.}(N) \rightarrow \sigma^*(P-X)$ negative hyperconjugation rather than $\text{l.p.}(N) \rightarrow d(P)$ interactions.²¹ Application of the $\text{l.p.}(N) \rightarrow \sigma^*(P-X)$ model to compounds **1**, **2**, and **7** would require a knowledge of the dihedral angles involved in the core. For example, if these interactions are really indeed responsible for the short P–N bonds, then either the C–P–N–H or O–P–N–H dihedral angle should be close to 90° (Chart 4), since only such arrangements would allow the nitrogen lone pair to align itself parallel to the P–O or P–C σ^* orbital. The observed dihedral angles listed in Tables 2–5 indeed show that this is true in all three molecules. For example, the observed O–P–N–H angles in both **1** and **2** (111° and 91°, respectively) indicate that the lone pair on N1 is involved in multiple bonding through interaction with the P–O σ^* orbital while the C–P–N–H dihedral angles involving N2 (–63° and –67°, respectively) are indicative of this nitrogen interacting with the P–C σ^* orbital. In **7**, the lone pairs of both nitrogen atoms are almost parallel to the P–C bonds. Hence, it appears that, in spite of the small pyramidalization, the nitrogen lone pairs in these molecules prefer a P–X σ^* orbital to a $d\pi$ -orbital.

Another structural feature of interest in these molecules is the relative disposition of the N–H protons (Fig. 3), which is likely to have an influence on the reactivity of these molecules with metal alkyls and halides. The $\text{H} \cdots \text{H}$ distance between the two N–H protons provides useful information on whether the molecule has an approximate cis or trans orientation or a twisted conformation. The calculated $\text{H} \cdots \text{H}$ distances (Table 5) indicate that the N–H proton in **7** is in a cis conformation (2.251 Å) while a considerable twist is observed in the relative N–H orientation in compounds **1** and **2** (3.071 and 3.221 Å, respectively). The molecular core of **1**, **2** and **7** viewed along the C–P axis (Fig. 3) also clearly shows the observed disposition of the N–H groups as discussed above. Interestingly, as Fig. 3 also shows, the N–H protons prefer to orient themselves

Table 5 Comparison of structural features of phosphonic diamides **1**, **2** and **7**

	1	2	7
P–O/Å	1.477(2)	1.476(2)	1.489(2)
P–N/Å	1.645(2)	1.656(2)	1.641(1)
$\sum \angle \text{N}/^\circ$	358.8	355.2	353.5
	350.7	356.0	
O(1)–P(1)–N(1)–H(1)/°	111(3)	91(2)	137(2)
O(1)–P(1)–N(2)–H(2)/°	173(2)	169(2)	–
H \cdots H/Å	3.017	3.221	2.251

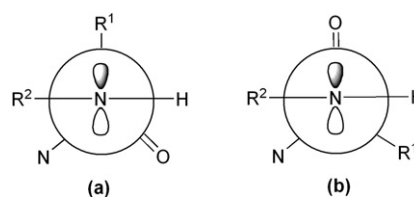
**Fig. 2** Ball-and-stick model showing the hydrogen bonding in [PhP(O)(NH^tBu)₂] (**1**) (top) and [tBuP(O)(NH^tPr)₂] (**7**) (bottom). Only core atoms are shown for the sake of clarity.

trans to the P=O group. Thus, there appears to be a large flexibility for P–N bond rotation in these molecules in spite of the geometrical constraints posed by the maximization of negative hyperconjugative interactions. Hence these compounds should prove to be useful multidentate and chelate ligands after deprotonation of the N–H groups.

Conclusion

It has been shown in this contribution that organophosphonic diamides, which have an isoelectronic relationship with organophosphonic acids, can be synthesized in good yields using a simple synthetic methodology. Although the bulkiness of the amines used in the present study has a marked effect on the reaction conditions employed to synthesize the phosphonic amides, the resultant molecules essentially have common structural features such as short P–N bonds and appreciably pyramidalized nitrogen atoms. It appears that the pyramidalization of the nitrogen atoms is not driven by the packing effects in the solid state since this phenomenon is observed in all three compounds **1**, **2** and **7**, which have nitrogen substituents of varying sizes. Even the alternative explanation that the pyramidal coordination can be observed in the presence of a low inversion barrier because of the lower steric congestion cannot be applied to these systems bearing bulky R² groups. Since the magnitude of the pyramidalization in the present molecules is relatively low, the observed non-planar nitrogen coordination can be accounted for in terms of minimized inductive effects due to the presence of just one phosphorus substituent on nitrogen.

The presence of two N–H groups and one P=O linkage and the observed flexibility of the P–N bonds make these systems very attractive chelating and bridging ligands for metal amido chemistry. Our current work in this area is concentrated in developing medium to large cluster molecules based on these ligands that will have structural similarities to those reported for organophosphonic acids.

**Chart 4**

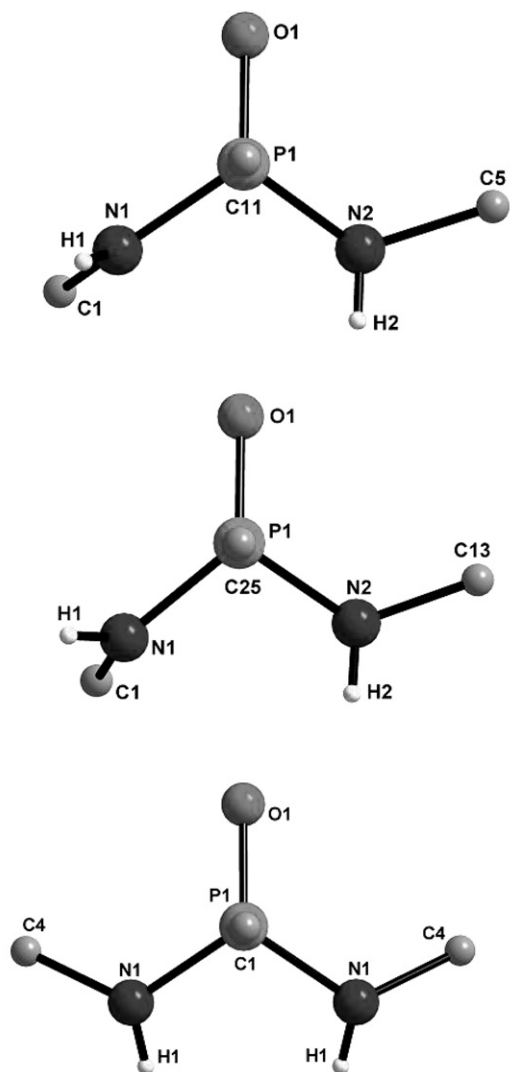


Fig. 3 The molecular core of phosphonic amides **1** (top), **2** (middle) and **7** (bottom) viewed along the C–P axis showing the relative disposition of N–H groups with respect to the phosphoryl oxygen.

Experimental

Materials and methods

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk line techniques. Manipulations of all compounds were carried out in a M-Braun glove box. Elemental analyses were performed on a Carlo Erba (Italy) Model 1106 Elemental Analyzer at IIT-Bombay. The EI-MS data for all compounds were obtained on a Perkin-Elmer GC-MS system. All other spectral measurements were carried out as described previously.²²

Dichloromethane, petroleum ether, acetonitrile, and toluene were purified and dried by conventional procedures and freshly distilled prior to use. PCl_3 (Thomas Baker), $t\text{-BuOH}$ (SRL), conc. HCl (Merck), AlCl_3 (S.D. Fine), $t\text{-BuNH}_2$ (Merck), $i\text{-PrNH}_2$ (Merck), cyclohexylamine (S.D. Fine), PhP(O)Cl_2 (Lancaster), CyP(O)Cl_2 (Aldrich) and 2,6-diisopropylaniline (Aldrich) were obtained from commercial sources. $t\text{-BuP(O)Cl}_2$ was prepared using a previously reported procedure.²³

Syntheses

[PhP(O)(NH $t\text{-Bu}$) $_2$] (1). *Route 1:* To a solution of $t\text{-BuNH}_2$ (20 mL, 190 mmol) in toluene (30 mL), PhP(O)Cl_2 (5 g, 26 mmol) in toluene (50 mL) was added through a dropping funnel. The reaction mixture was heated under reflux for 24 h and filtered.

Toluene from the filtrate was completely removed *in vacuo* and the resulting material was crystallized from a petroleum ether– CH_2Cl_2 mixture (1:1). Yield: 1.0 g (12%).

Route 2: PhPCl_2 (6.4 g, 36 mmol) in benzene (25 mL) was added dropwise, with stirring, to *tert*-butylamine (17.4 g, 238 mmol) in benzene (400 mL) under a stream of nitrogen at 0 °C. The amine hydrochloride was removed by filtration under nitrogen. Removal of benzene by distillation left a viscous yellow oil of $[\text{PhP}(\text{NH}^t\text{Bu})_2]$. This oil was dissolved in benzene and left for crystallization in air. After a week, the precipitated white solid of **1** was crystallized from a petroleum ether– CH_2Cl_2 mixture (1:1). Yield: 8.6 g (90%).

Data for **1**: m.p. 181–182 °C. Anal. calcd: C, 62.66; H, 9.39; N, 10.44%; found: C, 62.6; H, 9.4; N, 10.5%. IR (KBr, cm^{-1}): 3237 s, 2973 s, 2924 m, 2868 m, 1432 w, 1387 m, 1235 s, 1196 s, 1123 m, 1245 s, 1196 s, 1123 w, 1012 s, 873 w, 709 m. ^1H NMR (60 MHz, CDCl_3) δ 1.3 (s, $t\text{-Bu}$, 18H), 7.4 (m, Ph, 5H) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 15.3 ppm. EI-MS (70 eV): m/z (%): 268 (M^+ , 5), 57 ($t\text{-Bu}$, 100).

[PhP(O)(NHDipp)] $_2$ (2). To a solution of DippNH_2 (7.5 mL, 40 mmol) and Et_3N (5.6 mL, 40 mmol) in toluene (70 mL), PhP(O)Cl_2 (2.8 mL, 20 mmol) in toluene (30 mL) was added through a dropping funnel. The reaction mixture was heated under reflux for 3 days and filtered through filter paper. Toluene from the filtrate was completely removed *in vacuo* and the resulting solid material was twice crystallized from a petroleum ether– CH_2Cl_2 mixture (5:2). Yield: 1.7 g (18%). M.p. 210–211 °C. Anal. calcd: C, 75.60; H, 8.67; N, 5.88%; found: C, 74.9; H, 8.5; N, 5.4%. IR (KBr, cm^{-1}): 3412 s, 3353 s, 2954 vs, 2927 vs, 2866 s, 1461 m, 1440 m, 1360 s, 1333 m, 1253 w, 1220 s, 928 m, 910 m, 795 m, 743 m, 695 m. ^1H NMR (300 MHz, CDCl_3) δ 0.9 (d, Me, 12H), 1.1 (d, Me, 12H), 3.3 (sep, CH, 4H), 4.1 (d, NH, 2H), 7.0–8.1 (m, Ph, 11H) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 9.1 ppm. EI-MS (70 eV): m/z (%): 476 (M^+ , 5), 177 (DippNH_2 , 100).

Preparation of 3–7. Compounds **3–7** were prepared by following essentially the same experimental procedure. In a typical experiment, to a solution of R^2NH_2 (175 mmol) in toluene (50 mL), $\text{R}^1\text{P(O)Cl}_2$ (25 mmol) in toluene (50 mL) was added through dropping funnel. The reaction mixture was heated under reflux for 24 h and filtered. The volume of the solution was reduced *in vacuo* and the compound was crystallized from toluene at room temperature.

[CyP(O)(NHCy)] $_2$ (3). Yield: 5.5 g (67%). M.p. 230–235 °C. Anal. calcd: C, 66.22; H, 10.81; N, 8.58%; found: C, 61.1; H, 11.0; N, 7.5%. IR (KBr, cm^{-1}): 3210 s, 2921 s, 2855 s, 1460 s, 1163 s, 1131 s, 1032 m, 933 w, 900 w. ^1H NMR (300 MHz, CDCl_3) δ 1.0–2.0 (m, Cy) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 30.9 ppm. EI-MS (70 eV): m/z (%): 326 (M^+ , 3), 98 (CyNH, 100).

[CyP(O)(NH $t\text{-Bu}$) $_2$] (4). Yield: 3.4 g (50%). M.p. 236–237 °C. Anal. calcd: C, 61.28; H, 11.39; N, 10.21%; found: C, 61.3; H, 11.5; N, 8.5%. IR (KBr, cm^{-1}): 3237 s, 2967 s, 2927 s, 2855 s, 1453 m, 1394 m, 1242 m, 1170 s, 1012 s, 861 m. ^1H NMR (300 MHz, CDCl_3) δ 1.3 (s, $t\text{-Bu}$, 18H), 1.0–2.1 (m, Cy, 11H) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 28.1 ppm. EI-MS (70 eV): m/z (%): 274 (M^+ , 1), 58 ($t\text{-BuH}$, 100).

[CyP(O)(NH $i\text{-Pr}$) $_2$] (5). Yield: 3.2 g (52%). M.p. 137–138 °C. Anal. calcd: C, 58.51; H, 11.05; N, 11.37%; found: C, 56.6; H, 11.0; N, 10.1%. IR (KBr, cm^{-1}): 3233 s, 2967 s, 2927 s, 2861 m, 2730 m, 1473 m, 1440 m, 1381 w, 1163 s, 1012 m, 908 m. ^1H NMR (300 MHz, CDCl_3) δ 1.1 (d, Me, 6H), 1.2 (d, Me, 6H), 1.3–1.9 (m, Cy, 11H), 3.4 (sep, CH, 2H) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 30.1 ppm. EI-MS (70 eV): m/z (%): 247 (M^+ , 2), 106 ($\text{P(O)(NH}^i\text{Pr)}$, 100).

[$t\text{-BuP(O)(NHCy)}_2$] (6). Yield: 5.0 g (58%). M.p. 197–198 °C. Anal. calcd: C, 63.96; H, 11.92; N, 9.32%; found: C, 64.2; H, 11.2; N, 10.7%. IR (KBr, cm^{-1}): 3289 s, 2934 s,

2861 m, 1479 m, 1453 m, 1216 s, 1111 s, 940 s, 834 m, 670 s. ^1H NMR (300 MHz, CDCl_3) δ 1.2 (d, ^tBu , 9H), 1.4 (d, CH, 2H), 1.6 (d, CH, 2H), 1.7 (d, CH, 2H), 2.0 (d, CH, 2H), 2.1 (d, CH, 2H), 2.3 (s, CH, H) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 37.4 ppm. EI-MS (70 eV): m/z (%): 300 (M^+ , 2), 98 (C_2NH , 100). [$^t\text{BuP}(\text{O})(\text{NH}^t\text{Pr})_2$] (**7**). Yield: 5.8 g (90%). M.p. 164–165 °C. Anal. calcd: C, 54.52; H, 11.44; N, 12.72%; found: C, 53.8; H, 11.3; N, 11.7%. IR (KBr, cm^{-1}): 3256 s, 2973 s, 2920 m, 2661 m, 1420 m, 1301 m, 1189 s, 1137 s, 887 s. ^1H NMR (300 MHz, CDCl_3) δ 1.1 (d, Me, 12H), 1.2 (s, Me, 9H), 3.5 (sept, CH, 2H) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 35.5 ppm. EI-MS (70 eV): m/z (%): 221 (M^+ , 5), 106 ($^t\text{Bu-P}(\text{O})\text{H}_2$, 100).

[$^t\text{BuP}(\text{O})(\text{NH}^t\text{Bu})_2$] (**8**). $^t\text{BuNH}_2$ (20 mL, 189 mmol) was added to an autoclave containing $^t\text{BuP}(\text{O})\text{Cl}_2$ (5 g, 28.6 mmol) in acetonitrile (50 mL). Then the closed autoclave was kept in an oven at 140 °C for 24 h. After the reaction was completed, ice cold water (100 mL) was added at room temperature. The reaction mixture was stirred for 1 h, then filtered. The precipitate was washed with 40 mL of ice cold water. The precipitate was recovered and crystallized from petroleum ether. Yield: 4.5 g (65%). M.p. 181–182 °C. Anal. calcd: C, 58.03; H, 11.77; N, 11.28%; found: C, 58.0; H, 12.1; N, 11.9. IR (KBr, cm^{-1}): 3289 s, 2967 s, 2900 m, 2868 m, 1486 w, 1387 m, 1368 m, 1249 s, 1178 s, 999 s, 841 s. ^1H NMR (60 MHz, CDCl_3) δ 1.2 (d, ^tBu , 9H), 1.4 (s, ^tBu , 18H), 1.9 (m, NH, 1H) ppm. ^{31}P NMR (120 MHz, CDCl_3) δ 32.6 ppm. EI-MS (70 eV): m/z (%): 249 (M^+ , 5), 57 (^tBu , 100).

X-Ray structure determination

Single crystals of **1** and **2** for X-ray structure analysis were obtained from a petroleum ether– CH_2Cl_2 solution. Single crystals of **7** for X-ray structure analysis were obtained from toluene solution by slow evaporation over a period of 5 days. A suitable crystal of each compound was used for the diffraction studies (Siemens STOE AED2 diffractometer for **1** and **7** and Nonius MACH-3 diffractometer for **7**). The cell parameters were derived from well-centered reflections chosen over a wide 2θ range. The structure solution was achieved by direct methods as implemented in SHELXS-97.²⁴ The final refinement of the structures was carried using full-matrix least-squares methods on F^2 using SHELXL-97.²⁵ The positions of hydrogen atoms attached to nitrogen atoms were identified from the successive difference Fourier maps and were included in further calculations and refinement. All non-hydrogen

atoms were refined anisotropically and the hydrogen atoms isotropically. Other details pertaining to data collection, structure solution, and refinement are given in Table 6.

CCDC reference number 200563–200565. See <http://www.rsc.org/suppdata/nj/b3/b300035d/> for crystallographic files in CIF or other electronic format.

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- Although it has been possible to obtain X-ray quality crystals for all the compounds, examples **1**, **2**, **7** were chosen for diffraction studies in view of the different bulkiness of the R^2 group in the molecules. Diffraction data for **4** were also obtained; however, the structure of this compound could not be refined to a satisfactory level due to a 3-fold rotational disorder between the cyclohexyl and *tert*-butyl groups about the $\text{P}=\text{O}$ axis.
- At the convergence of refinement, all hydrogen atoms attached to nitrogen atoms displayed acceptable N–H distances and very good thermal (U_{iso}) parameters.
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Table 6 Crystal data and experimental details for **1**, **2** and **7**

	1	2	7
Empirical formula	$\text{C}_{14}\text{H}_{25}\text{N}_2\text{OP}$	$\text{C}_{30}\text{H}_{41}\text{N}_2\text{OP}$	$\text{C}_{10}\text{H}_{25}\text{N}_2\text{OP}$
Formula weight	268.33	476.62	220.30
T/K	200(2)	293(2)	200(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$Pnma$
$a/\text{\AA}$	8.268(1)	12.7979(6)	9.642(2)
$b/\text{\AA}$	10.527(1)	11.285(1)	15.934(3)
$c/\text{\AA}$	18.297(3)	20.121(1)	8.982(2)
$\beta/^\circ$	98.20(1)	99.745(4)	—
$U/\text{\AA}^3$	1576.3(4)	2864.0(4)	1380(1)
Z	4	4	4
μ/mm^{-1}	0.167	0.119	0.177
Total reflections	2873	5183	2007
Unique reflections	2777	5033	1267
R_{int}	0.0368	0.0328	0.0443
$R1 [I > 2\sigma(I)]$	0.0507	0.0494	0.0366
$wR2 [I > 2\sigma(I)]$	0.1288	0.1015	0.0980

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