

Synthesis and Spectroscopic Study of Some New Phosphoramidates, Crystal Structures of N-Benzoyl-N',N''-bis(azetidinyl)phosphoric Triamide and N-Benzoyl-N',N''-bis(hexamethylenyl)phosphoric Triamide

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Abstract. Some new N-carbonyl, phosphoramidates with formula $C_6H_5C(O)N(H)P(O)R_2$ ($R = NC_3H_6$ (**1**), NC_6H_{12} (**2**), $NHCH_2CH=CH_2$ (**3**), $N(C_3H_7)_2$ (**4**)) and $CCl_3C(O)N(H)P(O)R'_2$ ($R' = NC_3H_6$ (**5**), $NHCH_2CH=CH_2$ (**6**)) were synthesized and characterized by 1H , ^{13}C , ^{31}P NMR and IR spectroscopy and elemental analysis. The structures were determined for compounds **1** and **2**. Compound **1** exists as two crystallographically independent molecules in crystal lattice. Both compounds **1** and **2** produced dimeric aggregates via intermolecular $-P=O...H-N-$ hydrogen

bonds, which in compound **2** is a centrosymmetric dimer. In compounds with four-membered ring amine groups, $^3J(P,C) > ^2J(P,C)$, in agreement with our previous studies about five-membered ring amine groups. Also, $^3J(P,C)$ values in compounds **1** and **5** are greater than in compounds with five-, six- and seven-membered ring amine groups.

Keywords: Phosphoric triamide; NMR spectroscopy; Crystal structure

Introduction

Research on compounds with $RC(O)N(H)P(O)$ moiety are of interest based on their complexation reactions [1–3] and the inhibition of urease enzyme [4]. In previous studies, we considered the conformational forms of phosphoramidates in solution, solid state and calculation of the stabilization energies [5–8]. Also, we discussed on the disordered forms and on the presence of independent molecules (in crystal lattice) of phosphorus compounds containing five- and six-membered ring amine groups, pyrrolidiny, piperidiny, 4-methyl piperidiny rings, and cyclohexyl-*tert*-butyl amine [7–10]. The effect of various substituents on the structural parameters [11, 12] and on near-range P–C spin–spin couplings in phosphoramidates and phosphoramidic acid esters were considered [13–15]. Furthermore, we compared two and three bond distances P–C coupling constants in compounds containing acyclic and cyclic amine groups (with five- and six-membered rings) [13]. In this work, we synthesized some new compounds of these series (containing $RC(O)N(H)P(O)$ moiety with four and seven-membered ring amine groups and other aliphatic amines) and discuss on $^{2,3}J(P,C)$ coupling constants. Besides, we consider the crystal structures of N-benzoyl, N',N''-bis(azetidinyl) phosphoric triamide (containing two crystallographically independent molecules due to the conformational forms of four-membered ring amine group) and N-benzoyl, N',N''-bis(hexamethylenyl) phosphoric triamide.

Results and Discussion

Syntheses of phosphoramidates **1–6** were performed by the reaction of N-benzoyl [16] and N-trichloroacetyl [17] phosphoramidic dichloride with the corresponding amines.

NMR Study

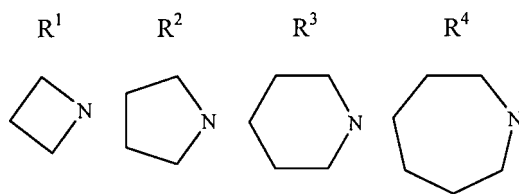
Phosphorus chemical shifts in compounds **1–6** were observed in the range of 4.65 ppm (in **5**) to 14.79 ppm (in **4**). $^2J(PNH)_{amide}$ coupling constant appears in compounds **1**, (**5.4** Hz), **2** (**3.8** Hz), **3** (**6.1** Hz) and **6** (**4.8** Hz). This coupling constant did not appear in previously studied compounds with formula $C_6H_5C(O)N(H)P(O)R_2$ ($R =$ five- and six-membered ring amine groups) [13]. Compounds **1–6** indicate $^3J(PNCH)$ coupling constant, too.

Compounds **1**, **3** and **6** do not show two bond distances P–C coupling constant, whereas compounds **1** and **5** with four-membered ring amine groups have high value $^3J(P,C_{aliphatic})$ coupling constants (18.0 Hz) that are greater than in compounds with five-, six- and seven-membered ring amine groups (Table 1). Also, in these compounds $^3J(P,C_{aliphatic}) > ^2J(P,C_{aliphatic})$ is in agreement with our previous study about five-membered ring amine groups [13]. In opposite to compounds with four- and five-membered ring amine groups, compounds **2** (seven-membered ring amine) and **4** (acyclic aliphatic amine), show $^2J(P,C_{aliphatic}) > ^3J(P,C_{aliphatic})$, which is similar to previously reported acyclic aliphatic amine groups. It seems that the ring strain (in four- and five-membered rings) cause high value $^3J(P,C_{aliphatic})$ coupling constant (see also compounds **7** and **13** in Table 1). Carbon-13 chemical shifts of C=O groups in compounds **5** and **6** (with $CCl_3C(O)N(H)P(O)$ moiety) appear in upfield (162.21 and 162.99 ppm, respectively) relative to the values in compounds **1–4** (containing $C_6H_5C(O)N(H)P(O)$ moiety) that

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Table 1 J(P,C) coupling constants in compounds **1-13**.

No.	Compound	$^2J(\text{P,C}_{\text{aliphatic}})$	$^3J(\text{P,C}_{\text{aliphatic}})$	$^3J(\text{P,C}_{\text{aromatic}})$
1	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^1_2$	0.0 (CH ₂)	18.0 (CH ₂)	8.7 (benzamide)
2	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^4_2$	4.7 (CH ₂)	4.2 (CH ₂)	8.7 (benzamide)
3	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{NHCH}_2\text{CH}=\text{CH}_2]_2$	0.0 (CH ₂)	--	8.0 (benzamide)
4	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{N}(\text{C}_2\text{H}_5)_2]_2$	4.7 (CH ₂)	2.5 (CH ₂)	8.7 (benzamide)
5	$\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^1_2$	1.5 (CH ₂)	18.0 (CH ₂) 9.2 (CCl ₃)	--
6	$\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{NHCH}_2\text{CH}=\text{CH}_2]_2$	0.0 (CH ₂)	9.6 (CCl ₃)	--
a7	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^2_2$	5.5 (CH ₂)	8.6 (CH ₂)	8.7 (benzamide)
a8	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})[\text{N}(\text{C}_2\text{H}_5)_2]_2$	5.3 (CH ₂)	2.6 (CH ₃)	8.6 (benzamide)
b9	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^3_2$	2.7 (CH ₂)	4.7 (CH ₂)	8.5 (benzamide)
a10	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{NHP}(\text{O})[\text{N}(\text{C}_2\text{H}_5)_2]_2$	4.5 (CH ₂)	2.0 (CH ₃)	6.7 (C _{ortho})
a11	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{NHP}(\text{O})\text{R}^4_2$	3.9 (CH ₂)	3.9 (CH ₂)	6.8 (C _{ortho})
a12	$(4\text{-CH}_3\text{-C}_6\text{H}_4\text{O})_2\text{P}(\text{O})\text{R}^4_2$	4.3 (CH ₂)	1.6 (CH ₃)	6.7 (C _{ortho})
a13	$(4\text{-CH}_3\text{-C}_6\text{H}_4\text{O})_2\text{P}(\text{O})\text{R}^2_2$	4.8 (CH ₂)	9.6 (CH ₂)	6.5 (C _{ortho})



^{a,b} The data of these compounds are given in Refs. [13] and [8], respectively.

are in the range of 167.87-169.62 ppm. This effect is due to the more electronegativity of CCl₃ than the C₆H₅C(O) group that cause the strengthen of C=O bond and shielding of carbon atoms in **5** and **6** relative to compounds **1 - 4**. This phenomenon is confirmed by IR spectra which will discussed in IR section.

IR spectroscopy

The C=O vibrational bands of compounds **1 - 4** (with C₆H₅C(O)N(H)P(O) moiety) appear in the range of 1640-1667 cm⁻¹ and those of compounds **5** and **6** (containing CCl₃C(O)N(H)P(O) moiety) are at 1710 and 1697 cm⁻¹,

Table 2 Crystallographic data for compounds **1** and **2**.

	1	2
Empirical formula	C ₁₃ H ₁₈ N ₃ O ₂ P	C ₁₉ H ₃₀ N ₃ O ₂ P
Formula weight	279.27	363.43
Temperature (K)	120(2)	120(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	triclinic, <i>P</i> $\bar{1}$	monoclinic, C2/c
Unit cell dimensions	a = 10.7685(16) Å b = 10.9779(16) Å c = 13.0476(19) Å α = 106.356(3)° β = 95.505(3)° γ = 104.420°	a = 22.270(8) Å b = 9.274(3) Å c = 20.525(8) Å β = 114.531(13)°
V (Å ³)	1410.3(4)	3857(2)
Z, Calculated density	4, 1.315 Mg.m ⁻³	8, 1.252 Mg.m ⁻³
Absorption coefficient	0.197 mm ⁻¹	0.160 mm ⁻¹
F(000)	592	1568
Crystal size	0.29 × 0.23 × 0.21 mm ³	0.35 × 0.20 × 0.20 mm ³
θ range for data collection	1.98 to 29.00°	2.18 to 28.00°
Limiting indices	-14 ≤ h ≤ 14 -14 ≤ k ≤ 14 -17 ≤ l ≤ 17	-28 ≤ h ≤ 26 -10 ≤ k ≤ 12 -27 ≤ l ≤ 27
Reflections collected / unique	15919 / 7455 [R(int) = 0.0351]	12771 / 4552 [R(int) = 0.0244]
Completeness to theta	99.5 %	97.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	7455/0/351	4552/0/230
Goodness-of-fit on F ²	1.008	1.072
Final R indices	R1 = 0.0510, wR2 = 0.0942	R1 = 0.0498, wR2 = 0.1204
R indices (all data)	R1 = 0.0820, wR2 = 0.1020	R1 = 0.0620, wR2 = 0.1279
Largest diff. peak and hole	0.850 and -0.398 e.Å ⁻³	0.547 and -0.255 e.Å ⁻³

respectively (due to more electronegativity of CCl_3 than C_6H_5).

X-ray crystallography

Single crystals of both compounds **1** and **2** were obtained from a mixture of chloroform-heptane after a slow evaporation at room temperature. The crystal data and the details of X-ray analysis are given in Table 2. Selected bond lengths and angles are listed in Tables 3 and 4. Molecular structures of these compounds are shown in Figures 1 and 2.

Compound **1** exists as two crystallographically independent molecules in crystalline lattice. The difference is described by comparison of corresponding torsion angles in two molecules. Torsion angles $\text{N}(3)\text{-P}(1)\text{-N}(2)\text{-C}(11)$ and $\text{O}(1)\text{-P}(1)\text{-N}(2)\text{-C}(11)$ are $-173.0(2)^\circ$ and $-55.5(2)^\circ$ whereas $\text{N}(3')\text{-P}(1')\text{-N}(2')\text{-C}(11')$ and $\text{O}(1')\text{-P}(1')\text{-N}(2')\text{-C}(11')$ are $-78.5(2)^\circ$ and $160.8(2)^\circ$, respectively. Both compounds **1** and **2** contain one amidic hydrogen atom and form dimeric aggregates via intermolecular $\text{-P=O}\cdots\text{H-N}$ -hydrogen bonds, which in compound **2** is a centrosymmetric dimer. The dimeric aggregate in compound **1** is formed between two symmetrically different molecules via two various intermolecular $\text{-P=O}\cdots\text{H-N}$ -hydrogen bonds. The bond distances between donor and acceptor in compound **1** are $2.817(1)\text{ \AA}$ and $2.815(1)\text{ \AA}$ for $\text{N}3\cdots\text{O}1'$ and $\text{N}3'\cdots\text{O}1$ distances, respectively, and in compound **2** is $2.816(3)\text{ \AA}$ for $\text{N}1\cdots\text{O}1$ bond distance. $\text{P}(1)\text{-N}(1)$, $\text{P}(1)\text{-N}(2)$, $\text{P}(1')\text{-N}(1')$ and $\text{P}(1')\text{-N}(2')$ bond lengths, in compound **1**, and $\text{P}(1)\text{-N}(2)$ and $\text{P}(1)\text{-N}(3)$ in compound **2**, are lower than the P-

N bonds of C(O)N(H)P(O) moieties, Tables 3 and 4. All of these bonds are shorter than the P-N single bond (1.77 \AA) [18]. The sum of the surrounding angles around N(2) and N(3) atoms in compound **2** are 360.01° and 359.28° , corresponding to the sp^2 angles. In compound **1**, the environment of the nitrogen atoms show some deviations from planarity. The angles $\text{P}(1)\text{-N}(1)\text{-C}(10)$, $\text{C}(8)\text{-N}(1)\text{-P}(1)$ and $\text{C}(10)\text{-N}(1)\text{-C}(8)$ are $130.7(2)^\circ$, $125.31(5)^\circ$ and $91.9(2)^\circ$ with the average 116.97° . For N(1'), N(2) and N(2') the average are 113.5° , 114.43° and 119.32° , respectively. The $\text{P}(1)\text{-O}(1)$ and $\text{P}(1')\text{-O}(1')$ bond lengths in compound **1** ($1.484(2)$ and $1.484(1)\text{ \AA}$) and $\text{P}(1)\text{-O}(1)$ bond length in compound **2** ($1.488(1)\text{ \AA}$) are slightly longer than the PO double bond length (1.45 \AA) [18]. The phosphorus atoms of **1** and **2** are slightly distorted from tetrahedral configuration. The bond angles around P(1) and P(1') in compound **1** and P(1) in compound **2** are in the range of $119.44^\circ\text{-}101.79^\circ$, $118.66^\circ\text{-}102.63^\circ$ and $113.88^\circ\text{-}106.83^\circ$, respectively.

Experimental Section

X-ray measurements

X-ray data were collected on a Bruker SMART 1000 CCD single crystal diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$). The structures were refined with SHELXL-97 [19] by a full-matrix least-squares procedure on F^2 . The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed for compounds **1** and **2** using the SADABS program [20]. Crystallographic data for the structures in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 259340 ($\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_2\text{P}_1$) and 259341 ($\text{C}_{19}\text{H}_{30}\text{N}_3\text{O}_2\text{P}_1$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Spectroscopic measurements

^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to internal TMS, ^{31}P chemical shifts relative to 85% H_3PO_4 as external standard. Infrared (IR) spectra were recorded on a Shi-

Table 3 Selected bond lengths/ \AA and angles/ $^\circ$ for compound **1**.

P(1)-O(1)	1.484(2)	P(1')-O(1')	1.484(1)
P(1)-N(3)	1.681(2)	P(1')-N(3')	1.682(2)
P(1)-N(2)	1.634(2)	P(1')-N(2')	1.614(2)
P(1)-N(1)	1.624(2)	P(1')-N(1')	1.639(2)
N(1)-C(8)	1.484(3)	N(1')-C(8')	1.488(3)
N(1)-C(10)	1.497(3)	N(1')-C(10')	1.487(3)
C(1)-O(2)	1.215(2)	C(1')-O(2')	1.221(2)
C(1)-N(3)	1.380(3)	C(1')-N(3')	1.370(3)
N(2)-C(11)	1.483(3)	N(2')-C(11')	1.483(3)
N(2)-C(13)	1.483(3)	N(2')-C(13')	1.482(3)
C(1)-C(2)	1.505(3)	C(1')-C(2')	1.498(3)
C(12)-C(13)	1.540(3)	C(12')-C(13')	1.541(3)
O(1)-P(1)-N(1)	109.29(9)	O(1')-P(1')-N(1')	118.66(9)
O(1)-P(1)-N(2)	119.44(9)	O(1')-P(1')-N(2')	111.41(9)
N(1)-P(1)-N(2)	103.49(9)	N(1')-P(1')-N(2')	102.63(9)
O(1)-P(1)-N(3)	107.05(9)	O(1')-P(1')-N(3')	105.99(9)
N(1)-P(1)-N(3)	116.10(9)	N(1')-P(1')-N(3')	103.09(9)
N(2)-P(1)-N(3)	101.79(9)	N(2')-P(1')-N(3')	115.19(9)
C(8)-N(1)-C(10)	91.9(2)	C(8')-N(1')-C(10')	92.1(2)
C(8)-N(1)-P(1)	125.3(2)	C(8')-N(1')-P(1')	124.3(2)
C(10)-N(1)-P(1)	130.7(2)	C(10')-N(1')-P(1')	124.1(4)
O(2)-C(1)-N(3)	123.4(2)	O(2')-C(1')-N(3')	123.0(2)
O(2)-C(1)-C(2)	120.7(2)	O(2')-C(1')-C(2')	120.9(2)
N(3)-C(1)-C(2)	115.9(2)	N(3')-C(1')-C(2')	116.1(2)
C(11)-N(2)-C(13)	91.8(2)	C(11')-N(2')-C(13')	92.2(2)
C(11)-N(2)-P(1)	126.1(1)	C(11')-N(2')-P(1')	133.8(1)
C(13)-N(2)-P(1)	125.3(2)	C(13')-N(2')-P(1')	131.9(1)
C(1)-N(3)-P(1)	127.4(2)	C(1')-N(3')-P(1')	127.3(2)
N(1)-C(8)-C(9)	88.9(2)	N(1')-C(8')-C(9')	89.0(2)
N(1)-C(10)-C(9)	88.1(2)	N(1')-C(10')-C(9')	89.2(2)
N(2)-C(11)-C(12)	89.3(2)	N(2')-C(11')-C(12')	88.0(2)
N(2)-C(13)-C(12)	89.1(2)	N(2')-C(13')-C(12')	88.0(2)

Table 4 Selected bond lengths/ \AA and angles/ $^\circ$ for compound **2**.

P(1)-O(1)	1.488(1)	N(2)-C(8)	1.472(2)
P(1)-N(3)	1.635(2)	N(2)-C(13)	1.473(2)
P(1)-N(2)	1.637(2)	N(3)-C(14)	1.467(2)
P(1)-N(1)	1.692(2)	N(3)-C(19)	1.474(2)
O(2)-C(1)	1.227(2)	C(1)-C(2)	1.511(2)
N(1)-C(1)	1.377(2)	C(18)-C(19)	1.506(3)
O(1)-P(1)-N(3)	111.62(8)	C(14)-N(3)-C(19)	115.7(1)
O(1)-P(1)-N(2)	113.88(8)	C(14)-N(3)-P(1)	125.7(1)
N(3)-P(1)-N(2)	108.34(8)	C(19)-N(3)-P(1)	117.8(1)
O(1)-P(1)-N(1)	107.33(8)	O(2)-C(1)-N(1)	121.9(2)
N(3)-P(1)-N(1)	108.61(8)	O(2)-C(1)-C(2)	120.5(2)
N(2)-P(1)-N(1)	106.83(8)	N(1)-C(1)-C(2)	117.6(2)
C(1)-N(1)-P(1)	126.6(1)	N(2)-C(8)-C(9)	113.5(2)
C(8)-N(2)-C(13)	116.0(2)	N(2)-C(13)-C(12)	114.7(2)
C(8)-N(2)-P(1)	119.1(1)	N(3)-C(14)-C(15)	113.7(2)
C(13)-N(2)-P(1)	124.9(1)	N(3)-C(19)-C(18)	113.7(2)

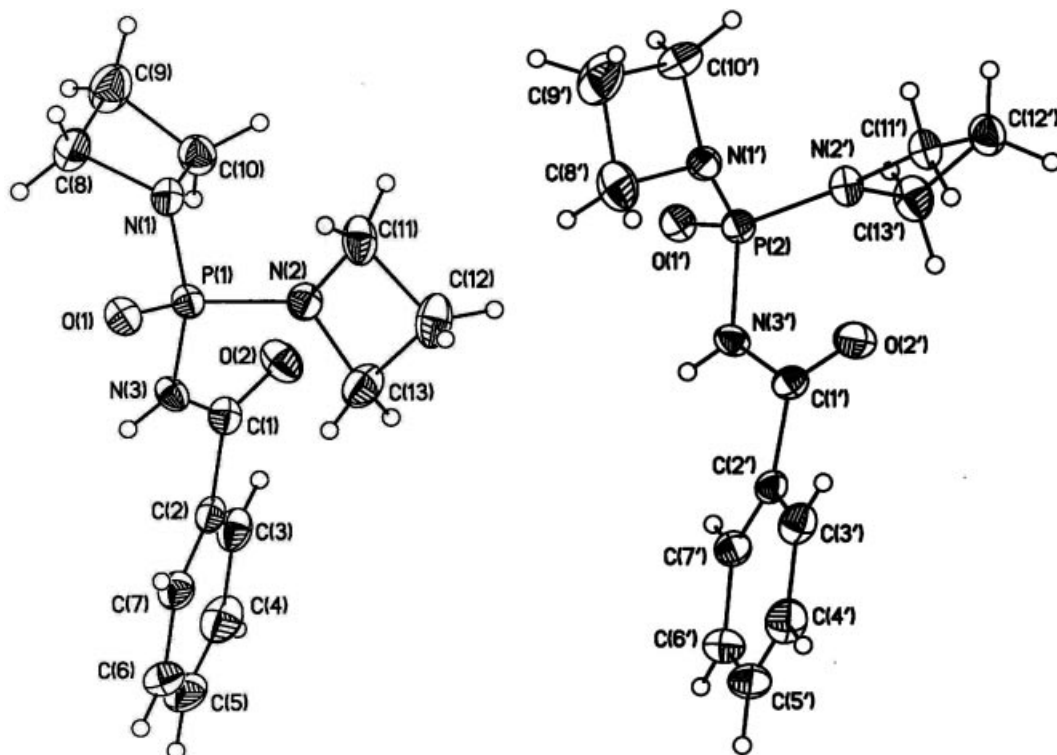


Figure 1 Molecular structure of $C_6H_5C(O)N(H)P(O)(NC_3H_6)_2$ (containing two independent molecules) showing the atom-labeling scheme and 50 % probability level displacement ellipsoids.

madzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

Syntheses

N-Benzoyl-*N',N''*-bis(azetidinyl) phosphoric triamide (1): Azetidine (0.228 g, 4 mmol) was added to a solution of *N*-benzoyl

phosphoramidic dichloride (0.238 g, 1 mmol) in CCl_4 (40 mL) and stirred at $-5^\circ C$. After 6 hours, the precipitate was filtered and washed with H_2O . The product recrystallized from chloroform/*n*-heptane. Elemental analysis (%) calcd. for $C_{13}H_{18}N_3O_2P$: C 55.91, H 6.50, N 15.05; found: C 55.87, H 6.49, N 15.03.

1H NMR (500.13 MHz, $CDCl_3$, $25^\circ C$, TMS): 2.26 (m, 4 H), 3.91 (m, 4 H), 4.06 (m, 4 H), 7.46 (t, $^3J(H,H) = 7.6$ Hz, 2 H, Ar-H), 7.55 (t, $^3J(H,H) = 7.3$ Hz, 1 H, Ar-H), 7.62 (d, $^2J(PNH) = 5.4$ Hz, 1 H, NH_{amide}), 7.93 (d, $^3J(H,H) = 7.6$ Hz, 2 H, Ar-H). ^{13}C NMR (125.77 MHz, $CDCl_3$, $25^\circ C$,

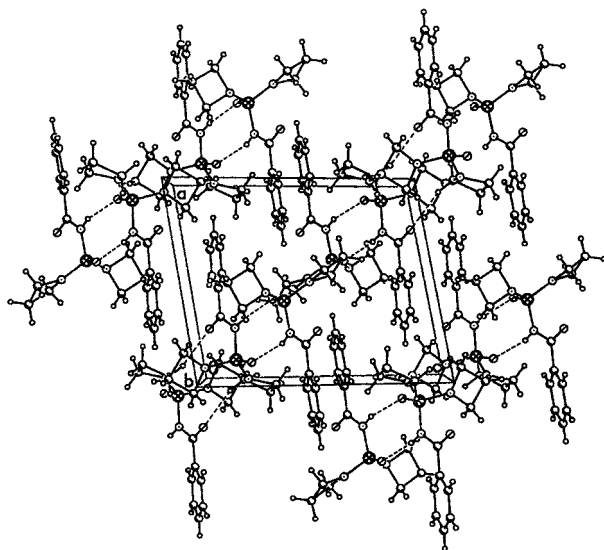


Figure 2 Molecular structure of $C_6H_5C(O)N(H)P(O)(NC_6H_{12})_2$ showing the atom-labeling scheme and 50 % probability level displacement ellipsoids.

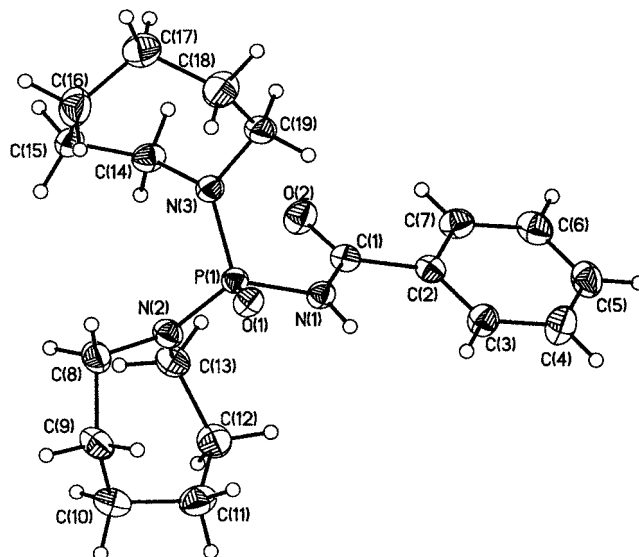


Figure 3 A view of the unit cell packing for compound 1.

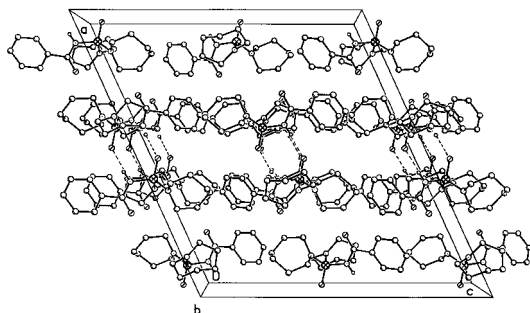


Figure 4 A view of the unit cell packing for compound 2.

TMS): 17.79 (d, $^3J(\text{P,C}) = 18.0$ Hz, 2 C, CH_2), 48.44 (s, 4 C, CH_2), 127.79 (s), 128.72 (s), 132.53 (s), 133.28 (d, $^3J(\text{P,C}) = 8.7$ Hz, 1 C, C_{ipso}), 168.02 (s, 1 C, C=O). ^{31}P NMR (202.46 MHz, CDCl_3 , 25 °C, H_3PO_4 external): 6.95 (m). IR (KBr): $\tilde{\nu} = 3430$ (m, NH), 3065 (m), 2945 (s), 1667 (s, C=O), 1449 (s), 1266 (s), 1211 (s), 1172 (s), 1144 (m), 1099 (m), 1051 (m), 1025 (m), 953 (m), 864 (m), 837 (m), 709 (s), 629 (m), 552 (w), 491 (w).

N-Benzoyl-N',N''-bis(hexamethylenyl) phosphoric triamide (2): Hexamethyleneimine (0.396 g, 4 mmol) was added to a solution of N-benzoyl phosphoramidic dichloride (0.238 g, 1 mmol) in chloroform (30 mL) and stirred at -5 °C. After 8 hours, the solvent was removed and the residue that formed was stirred in H_2O . Product was filtered and recrystallized from chloroform/n-hexane. Elemental analysis (%) calcd. for $\text{C}_{19}\text{H}_{30}\text{N}_3\text{O}_2\text{P}$: C 62.79, H 8.32, N 11.56; found: C 62.75, H 8.31, N 11.58.

^1H NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): 1.61 (m, 8 H), 1.70 (m, 8 H), 3.22 (m, 8 H), 7.43 (t, $^3J(\text{H,H}) = 7.6$ Hz, 2 H, Ar-H), 7.52 (t, $^3J(\text{H,H}) = 7.4$ Hz, 1 H, Ar-H), 7.73 (d, $^2J(\text{PNH}) = 3.8$ Hz, 1 H, NH_{amide}), 7.90 (d, $^3J(\text{H,H}) = 7.3$ Hz, 2 H, Ar-H). $^1\text{H}\{^{31}\text{P}\}$ NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): 1.61 (m, 8 H), 1.70 (m, 8 H), 3.22 (m, 8 H), 7.43 (t, $^3J(\text{H,H}) = 7.6$ Hz, 2 H, Ar-H), 7.52 (t, $^3J(\text{H,H}) = 7.4$ Hz, 1 H, Ar-H), 7.73 (s, 1 H, NH_{amide}), 7.90 (d, $^3J(\text{H,H}) = 7.3$ Hz, 2 H, Ar-H). ^{13}C NMR (125.77 MHz, CDCl_3 , 25 °C, TMS): 26.91 (s, 4 C, CH_2), 30.24 (d, $^3J(\text{P,C}) = 4.2$ Hz, 4 C, CH_2), 47.86 (d, $^2J(\text{P,C}) = 4.7$ Hz, 4 C, CH_2), 127.73 (s), 128.69 (s), 132.39 (s), 133.70 (d, $^3J(\text{P,C}) = 8.7$ Hz, 1 C, C_{ipso}), 167.87 (s, 1 C, C=O). ^{31}P NMR (202.46 MHz, CDCl_3 , 25 °C, H_3PO_4 external): 14.70 (m). IR (KBr): $\tilde{\nu} = 3415$ (w, NH), 3060 (m), 2905 (s), 1660 (s, C=O), 1447 (s), 1425 (s), 1257 (m), 1218 (m), 1182 (s), 1096 (m), 1047 (s), 991 (w), 957 (w), 931 (m), 887 (w), 852 (w), 820 (m), 696 (s), 548 (w).

N-Benzoyl-N',N''-diallyl phosphoric triamide (3): To a solution of N-benzoyl phosphoramidic dichloride (0.238 g, 1 mmol) in chloroform (35 mL), allylamine (0.228 g, 1 mmol) was added and stirred at -5 °C. After 5 hours, the solvent was removed and the product was filtered, washed with H_2O and recrystallized from chloroform/n-hexane. $\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_2\text{P}$: C 55.91, H 6.50, N 15.05; found: C 55.94, H 6.49, N 15.04 %.

^1H NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): 3.51 (m, 2 H, NH), 3.61 (m, 4 H, 2 CH_2), 5.02 (d, $^3J(\text{H,H}) = 10.4$ Hz, 2 H), 5.20 (d, $^3J(\text{H,H}) = 17.0$ Hz, 2 H), 5.81 (m, 2 H), 7.41 (t, $^3J(\text{H,H}) = 7.6$ Hz, 2 H, Ar-H), 7.52 (t, $^3J(\text{H,H}) = 7.4$ Hz, 1 H, Ar-H), 8.07 (d, $^3J(\text{H,H}) = 7.7$ Hz, 2 H, Ar-H), 9.58 (d, $^2J(\text{PNH}) = 6.1$ Hz, 1 H, NH_{amide}). ^{13}C NMR (125.77 MHz, CDCl_3 , 25 °C, TMS): 43.20 (s, 2 C, CH_2), 115.42 (s), 128.31 (s), 128.50 (s), 132.54 (s), 133.02 (d, $^3J(\text{P,C}) = 8.0$ Hz, 1 C, C_{ipso}), 136.36 (d, $^3J(\text{P,C}) = 6.4$ Hz, 2 C, CH), 169.62 (s, 1 C, C=O). ^{31}P NMR (202.46 MHz, CDCl_3 , 25 °C, H_3PO_4 external): 10.82 (m). IR (KBr): $\tilde{\nu} = 3255$ (s, NH), 3080 (w), 2850 (w), 1640 (s, C=O), 1448 (s), 1419 (s), 1271 (m), 1201 (s), 1165 (m), 1116 (w), 1092 (m), 1029 (w), 986 (w), 917 (m), 883 (m), 788 (w), 704 (m), 530 (w).

N-Benzoyl, N',N',N'',N''-tetrapropyl, phosphoric triamide (4): To a solution of N-benzoyl phosphoramidic dichloride (0.238 g, 1 mmol) in chloroform (35 mL), dipropylamine (0.404 g, 4 mmol) was added and stirred at -5 °C. After 7 hours, the solvent was removed and the precipitate was washed with H_2O and recrystallized from acetone/chloroform. Elemental analysis (%) calcd.

for $\text{C}_{19}\text{H}_{34}\text{N}_3\text{O}_2\text{P}$: C 62.10, H 9.33, N 11.43; found: C 62.07, H 9.32, N 11.44.

^1H NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): 0.82 (t, $^3J(\text{H,H}) = 7.3$ Hz, 12 H, 4 CH_3), 1.55 (m, 8 H, 4 CH_2), 3.05 (m, 8 H, 4 CH_2), 7.38 (t, 2 H, $^3J(\text{H,H}) = 7.6$ Hz), 7.51 (t, 1 H, $^3J(\text{H,H}) = 7.3$ Hz), 8.02 (d, 2 H, $^3J(\text{H,H}) = 7.2$ Hz), 8.60 (b, 1 H, NH_{amide}). ^{13}C NMR (125.77 MHz, CDCl_3 , 25 °C, TMS): 11.47 (s, 4 CH_3), 21.83 (d, $^3J(\text{P,C}) = 2.5$ Hz, 4 C, CH_2), 47.83 (d, $^2J(\text{P,C}) = 4.7$ Hz, 4 C, CH_2), 128.23 (s), 128.47 (s), 132.10 (s), 134.09 (d, $^3J(\text{P,C}) = 8.7$ Hz, 1 C, C_{ipso}), 168.17 (s, 1 C, C=O). ^{31}P NMR (202.46 MHz, CDCl_3 , 25 °C, H_3PO_4 external): 14.79 (m). IR (KBr): $\tilde{\nu} = 3440$ (w), 3310 (w), 3055 (m), 2870 (s), 2725 (w), 1657 (s, C=O), 1493 (w), 1446 (s), 1376 (w), 1260 (m), 1187 (s), 1173 (s), 1040 (w), 1007 (m), 865 (m), 799 (m), 705 (m), 526 (w).

N-Trichloroacetyl-N',N''-bis(trimethylenyl) phosphoric triamide (5):

To a solution of N-trichloroacetyl phosphoramidic dichloride (0.279 g, 1 mmol) in CCl_4 (30 mL), trimethyleneimine (0.228 g, 4 mmol) was added dropwise and stirred at -5 °C. After 4 hours, the solvent was removed and the precipitate was washed with H_2O and recrystallized from acetonitrile/chloroform. Elemental analysis (%) calcd. for $\text{C}_8\text{H}_{13}\text{Cl}_3\text{N}_3\text{O}_2\text{P}$: C 29.98, H 1.27, N 13.11; found: C 29.96, H 1.26, N 13.12.

^1H NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): 2.33 (m, 4 H), 3.93 (m, 4 H), 4.06 (m, 4 H), 7.46 (b, 1 H, NH_{amide}). $^1\text{H}\{^{31}\text{P}\}$ NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): 2.33 (m, 4 H), 3.93 (dd, $^2J(\text{H,H}) = 15.2$ Hz, $^3J(\text{H,H}) = 7.6$ Hz, 4 H), 4.06 (dd, $^2J(\text{H,H}) = 15.2$ Hz, $^3J(\text{H,H}) = 7.5$ Hz, 4 H), 7.46 (b, 1 H, NH_{amide}). ^{13}C NMR (125.77 MHz, CDCl_3 , 25 °C, TMS): 17.86 (d, $^3J(\text{P,C}) = 18.0$ Hz, 2 C, CH_2), 48.59 (d, $^2J(\text{P,C}) = 1.5$ Hz, 4 C, CH_2), 91.94 (d, $^3J(\text{P,C}) = 9.2$ Hz, CCl_3), 162.21 (s, 1 C, C=O). ^{31}P NMR (202.46 MHz, CDCl_3 , 25 °C, H_3PO_4 external): 4.65 (m). IR (KBr): $\tilde{\nu} = 3415$ (w, NH), 3090 (m), 2960 (m), 1710 (s, C=O), 1424 (s), 1231 (s), 1190 (s), 1140 (m), 1104 (m), 1030 (m), 953 (m), 864 (m), 820 (m), 797 (m), 667 (s), 537 (w), 476 (m).

N-Trichloroacetyl-N',N''-diallyl phosphoric triamide (6): allylamine (0.228 g, 4 mmol) was added to a solution of N-trichloroacetyl phosphoramidic dichloride (0.279 g, 1 mmol) in chloroform (35 mL) and stirred at -5 °C. After 6 hours, the solvent was removed and the precipitate was washed with H_2O and recrystallized from acetonitrile/n-heptane. Elemental analysis (%) calcd. for $\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_2\text{P}$: C 55.91, H 6.50, N 15.05; found: C 55.92, H 6.49, N 15.03.

^1H NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): 3.62 (b, 2 H, NH), 3.61 (dd, $^3J(\text{P,H}) = 5.0$ Hz, $^3J(\text{H,H}) = 11.4$ Hz, 2 H, CH_2), 5.08 (d, 9.58 (d, $^3J(\text{H,H}) = 10.3$ Hz, 2 H, CH), 5.22 (d, $^3J(\text{H,H}) = 17.1$ Hz, 2 H, CH), 5.81 (m, 2 H, CH), 8.91 (d, $^2J(\text{PNH}) = 4.8$ Hz, 1 H, NH_{amide}). ^{13}C NMR (125.77 MHz, CDCl_3 , 25 °C, TMS): 43.12 (s, 2 C, CH_2), 92.53 (d, $^3J(\text{P,C}) = 9.6$ Hz, CCl_3), 115.96 (s), 135.83 (d, $^3J(\text{P,C}) = 5.8$ Hz, 2 C, CH), 162.99 (s, 1 C, C=O). ^{31}P NMR (202.46 MHz, CDCl_3 , 25 °C, H_3PO_4 external): 8.28 (m). IR (KBr): $\tilde{\nu} = 3385$ (m, NH), 3265 (w), 3020 (m), 2910 (w), 2655 (w), 1697 (s, C=O), 1418 (s), 1224 (s), 1199 (s), 1137 (w), 1089 (m), 913 (m), 877 (m), 827 (m), 670 (m), 561 (w).

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