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Synthesis and Spectral Characterization of Some New Carbacylamidophosphate Derivatives. Crystal Structures of $CCl_3C(O)NHP(O)[NH(C_5H_9)]_2$ and $CH_3C_6H_4C(O)NHP(O)[NH(C_5H_9)]_2$

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ABSTRACT

Some new carbacylamidophosphate derivatives with the general formula $RC(O)NHP(O)[NH(C_5H_9)]_2$: (R=$CCl_3$), 1a**; (R=$CHCl_2$),** 2a**; (R=$CH_2Cl$),** 3a**; (R=$CF_3$),** 4a**; (R=$C_6H_5$), 1b; (R=*p*-Cl-$C_6H_4$),** 2b**; (R=*p*-Br-$C_6H_4$),** 3b**; (R=*p*-Me-$C_6H_4$),** 4b**; were synthesized and characterized by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy and elemental analysis. The crystalline solids of** 1a **and** 4b **were studied by single crystal X-ray diffraction analysis. The dimeric aggregate and the centrosymmetric dimer formed *via* intermolecular N-H....O=P and N-H....O=C hydrogen bonds in** 1a **and** 4b**, respectively. In all the synthesized molecules, similar spectral patterns were obtained in the ^{13}C NMR spectra for carbon atoms of cyclic amines with $^2J_{PNC} = 0$ and $^3J_{PNC}$ ranging from 4 to 6 Hz.**

KEYWORDS

Carbacylamidophosphates, hydrogen bonds, IR spectroscopy, NMR spectroscopy.

1. Introduction

The synthesis of numerous compounds with P-N bonds was responsible for the development of organophosphorus chemistry.[1–3] Carbacylamidophosphates, organophosphorus derivatives with a -C(O)NHP(O)- skeleton, are attractive to study due to their applications as O,O-donor ligands for metal complexation.[4,5] These derivatives have promising biological properties[6,7] and serve as urea inhibitors.[8] Our group has studied the formation and conformational structures of some phosphoramidates in solution and in the solid state as well as the energy calculation of the most stable conformers.[9–11] We have also studied the experimental IR spectra of some carbacylamidophosphates and compared them with the calculated harmonic vibrations calculated using Restricted Hartree-Fock (RHF) and Density Functional Theory (DFT – B3LYP) methods and assigned the main absorption bands of the respective IR spectra.[12] The presence of independent molecules in the crystal lattice and the disordered forms of the phosphoramidates with five- and six- membered ring amine groups were previously discussed.[11–15] The effects of various substituents on the structural parameters and on near-range P-C spin-spin coupling constants were considered in various phosphoramidates.[16–18] We have developed this field of study by comparing two- and three-bond distances and P-C coupling constants in compounds containing acyclic and five- and six-membered ring cyclic amine groups.[19,20] In this communication, the syntheses and structures of some novel carbacylamidophosphate derivatives are reported, namely

$CCl_3C(O)NHP(O)[NH(C_5H_9)]_2$, **1a**;
$CHCl_2C(O)NHP(O)[NH(C_5H_9)]_2$, **2a**;
$CH_2ClC(O)NHP(O)[NH(C_5H_9)]_2$, **3a**;
$CF_3C(O)NHP(O)[NH(C_5H_9)]_2$, **4a**;
$C_6H_5C(O)NHP(O)[NH(C_5H_9)]_2$, **1b**;
p-Cl- $C_6H_4C(O)NHP(O)[NH(C_5H_9)]_2$, **2b**;
p-Br-$C_6H_4C(O)NHP(O)[NH(C_5H_9)]_2$, **3b**;
p-Me-$C_6H_4C(O)NHP(O)[NH(C_5H_9)]_2$, **4b** (Scheme 1).

These compounds were characterized by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. We report and discuss the substituent effects of the amidic group using two- and three-bond coupling constants, $^2J_{PC}$ and $^3J_{PC}$, between phosphorus and amine carbons. In addition, the effects of phosphorus substitutions on the IR vibrational frequencies are also presented. The structures of compounds **1a** and **4b** were determined by X-ray crystallography. The structural data of these compounds were compared with those of other similar carbacylamidophosphate compounds.

2. Results and Discussion

The reaction of cyclopentylamine with N-acetyl and N-benzoyl phosphoramidic dichloride derivatives led to the corresponding phosphoric triamides (Scheme 2).

2.1. Spectroscopic Study

The NMR and IR spectral data are summarized in Tables 1 and 2, respectively. The two-bond distances coupling constant, $^2J_{PNH}$, for the amidic hydrogen in compounds **1–4** and **1a–4a** with acetamide derivatives differ from **5–8** and **1b–3b** with benzamide derivatives. In **1** and **4** $^2J_{PNH} = 0$ but in **2** and **3** $^2J_{PNH} =$ 10.5 Hz and 11.6 Hz, respectively. The $^2J_{PNH}$ vanishing may occur due to the increasing acidity of the NH amide hydrogen (δ = 9.94 ppm for **1** and 10.26 ppm for **4**). The electron-withdrawing effect of the chlorine and fluorine atoms in **1** and **4** may be responsible for the increased acidity of the NH amide proton. In **2a** and **3a**, containing dicyclopentylamine-substituted amine groups, a decrease of the $^2J_{PNH}$ coupling constant between the phosphorus atom and the amidic hydrogen atom is observed. This effect may correspond to a decreasing interaction between the phosphorus atom and the amidic hydrogen atom after

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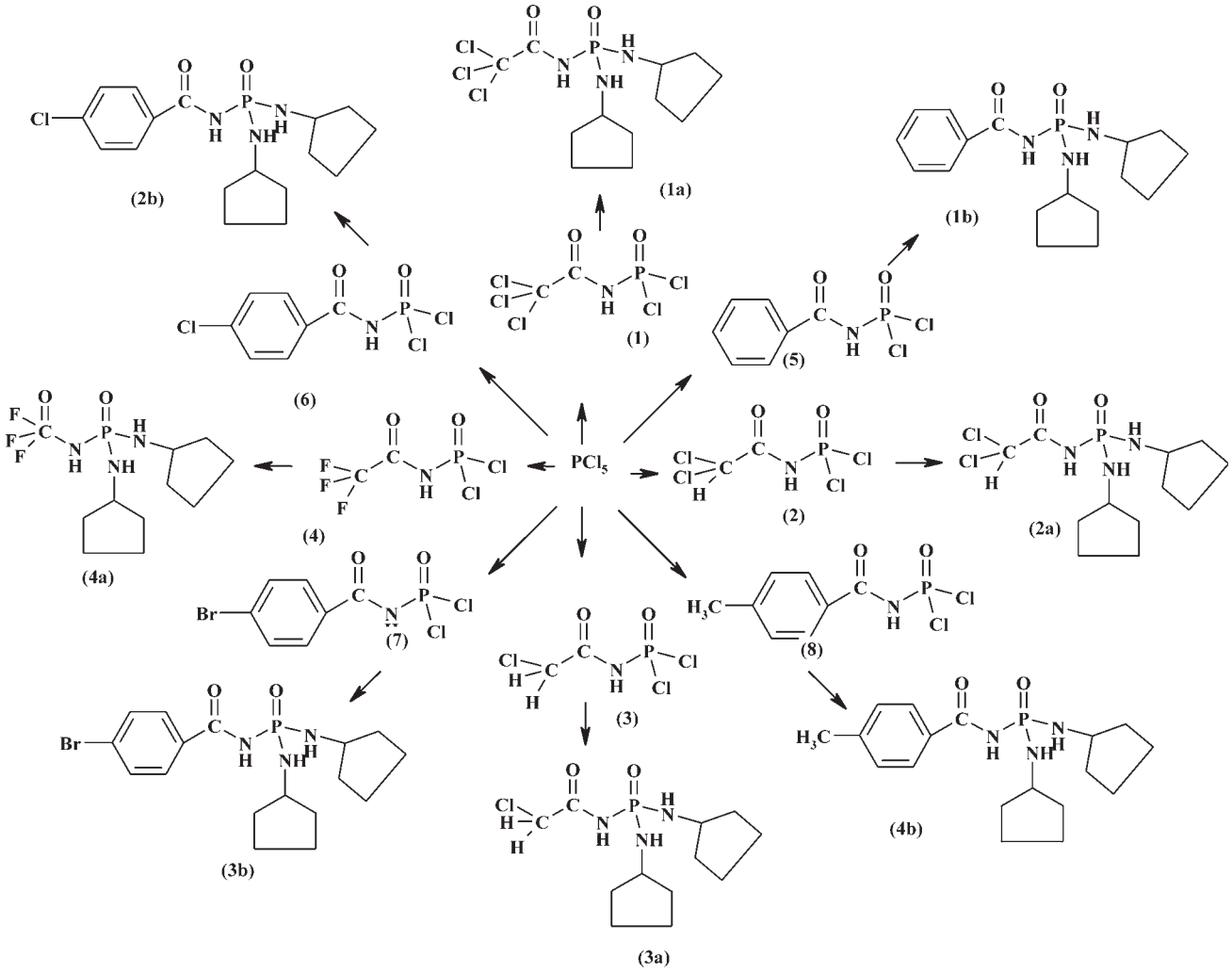
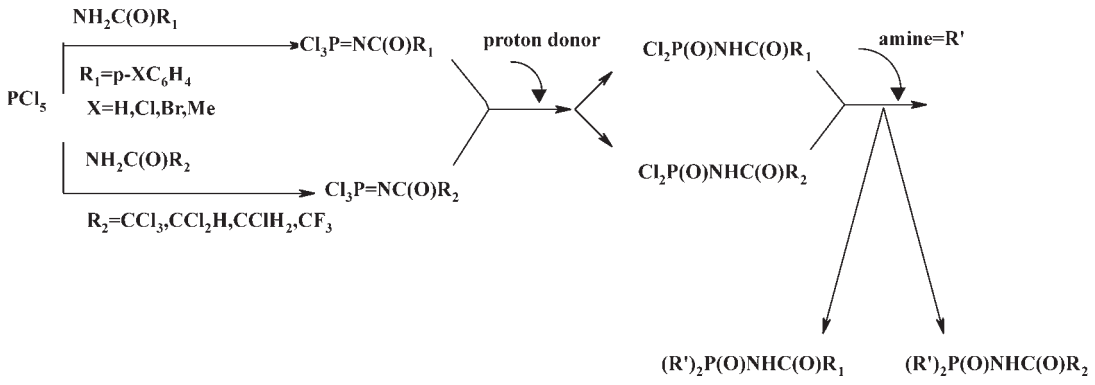


Scheme 1
Schematic diagram of synthesized compounds.

formation of the P-N_{amine} bonds. The IR spectral data (Table 2) show that the vibrational frequencies of both the P=O and C=O groups decrease when the chlorine atoms are replaced by amine groups. This may be due to the bond order changes in the phosphoryl and carbonyl groups in order to accommodate the substitutions. Otherwise, the C=O vibrational frequencies of compounds **1–4** and **1a–4a** (with a CH_xCl_yC(O)NHP(O) moiety) appear in the ranges of 1736–1748 cm^{-1} and 1671–1705 cm^{-1}, respectively, but those of compounds **5–8** and **1b–3b** (containing a X-C_6H_4C(O)NHP(O) moiety) are observed at 1680–1682 cm^{-1} and 1621–1631 cm^{-1}, respectively, due to the greater electronegativity of CH_xCl_y- compared with X-C_6H_4- groups. On the other hand, the stretching vibrations of P-N_{amidic} appear at higher frequencies for **1–4** than for **5–8** (1125–1194 cm^{-1} for **1–4** and 1060–1074 cm^{-1} for **5–8**), which can be the result of the above mentioned effect of CH_xCl_y- groups. The CH_xCl_y- chemical shifts in the ^{13}C NMR spectra of **1a–3a** show an upfield shift:

3a (δ = 43.15 ppm) < **2a** (δ = 66.49 ppm) < **1a** (δ = 93.52 ppm).

It is clear that the substitution of chlorine atoms with hydrogen



Scheme 2
Reaction mechanism for preparing compounds **1–8** and **1a–4b**.

Table 1 Selected NMR parameters (chemical shifts and coupling constants) of the synthesized compounds.

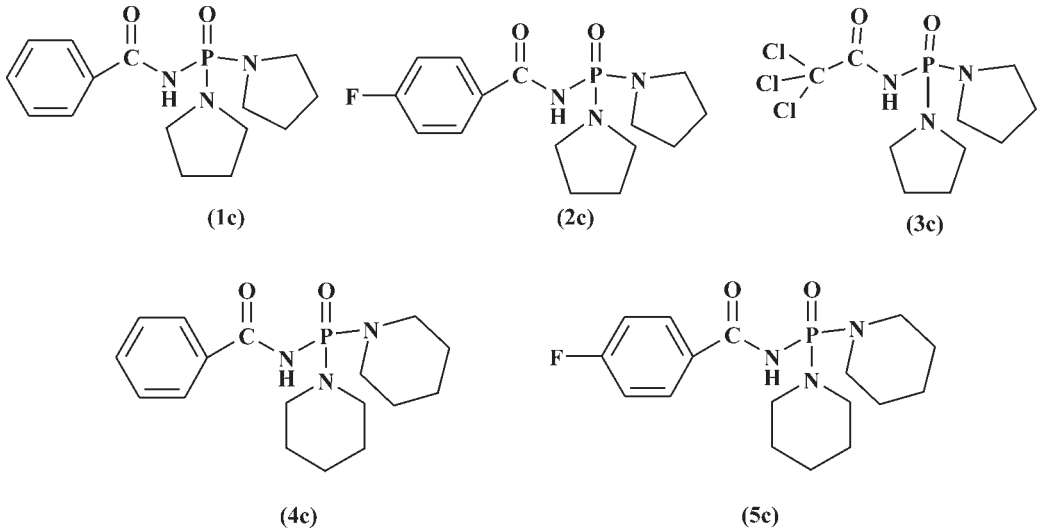
Parameter	1	2	3	4	5	6	7	8	1a	2a	3a	4a	1b	2b	3b	4b
δP/ppm	8.08	8.20	6.62	7.42	9.29	10.52	10.47	10.41	6.15	6.79	6.72	5.49	8.99	8.86	8.96	8.93
δNH [a]/ppm	9.94	9.68	9.16	10.24	9.77	9.91	9.89	9.88	8.44	9.76	8.619	9.53	9.04	9.06	9.99	9.17
δCO/ppm	160.3	163.2	168.7	157.5	166.3	165.4	165.8	166.4	163.6	165.9	168.8	157.7	170.4	169.3	168.8	169.4
δNH[b]/ppm	0	–	–	–	–	–	–	–	3.18	3.05	3.00	3.01	3.18	3.19	3.22	3.21
$^2J_{PNH}$ [a]/Hz	0	10.5	11.6	0	12.0	12.03	12.01	11.9	0	5.6	3.92	0	0	5.1	5.6	5.48
$^3J_{PNC}$/Hz	–	–	–	–	–	–	–	–	6.91	6.79	6.67	6.77	6.16	6.99	6.92	6.96
$^3J_{PNC}$/Hz	–	–	–	–	–	–	–	–	4.65	4.65	4.77	4.61	4.82	4.72	4.84	4.8

[a] Amide; [b] amine.

Table 2 IR vibrational frequencies of the synthesized compounds.

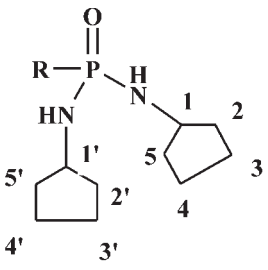
$\bar{\nu}$/cm^{-1}	1	2	3	4	5	6	7	8	1a	2a	3a	4a	1b	2b	3b	4b
ν(P=O)	1274	1260	1280	1211	1221	1226	1232	1230	1243	1215	1180	1224	1204	1218	1217	1218
ν(C=O)	1736	1710	1721	1748	1682	1683	1684	1680	1671	1680	1699	1705	1637	1621	1635	1631
ν(P-N) [a]	1181	1194	1125	1180	1060	1064	1074	1065	848	832	904	948	925	911	907	910
ν(P-N) [b]	–	–	–	–	–	–	–	–	1103	1108	1106	1104	1106	1053	1102	1052
ν(C-N)	1426	1421	1451	1466	1405	1413	1416	1414	1418	1447	1471	1451	1106	1053	1102	1052

[a] Amide; [b] amine.



Scheme 3
Chemical structures of compounds **1c** to **5c.**

atoms in **1a–3a** is responsible for a decrease of the electronegativity of the CH_xCl_y-group and leads to greater shielding of the carbon atom. Also the coupling constants between the phosphorus atom and the carbonyl carbon atoms in **1–4**, observed in the ^{13}C NMR spectra, are 2.8 Hz, 3.6 Hz, 3.6 Hz and 3.5 Hz, respectively.[23] The corresponding coupling constants for **1a–4a** are 2.65 Hz, 2.01 Hz, 2.18 Hz and 2.85 Hz, respectively. The ^{13}C NMR spectra of all synthesized compounds (**1a**, **2a**, **3a**, **4a**, **1b**, **2b**, **3b** and **4b**) show five signals for the carbon atoms of the two cyclic amines. The data given in Table 1 reveal that only one singlet signal is observed for the C-1 and C-1′ carbon atoms with $^2J_{PNC} = 0$ (^{13}C NMR spectra). Otherwise, two different doublet signals for the 2,2′ and 5,5′ carbon atoms are shown in the ^{13}C NMR spectra which are split by the phosphorus atom with $^3J_{PNC} = 4–6$ Hz (Table 1). Finally, the 3, 3′ and 4, 4′ carbon atoms show two different singlet signals (Scheme 4 and ^{13}C NMR spectra). This splitting pattern is confirmed by the crystal structures of **1a** (Fig. 1) and **4b** (Fig. 2), which exhibit different positions for the two cyclic amines with respect to each other. The three-bond coupling constants between the phosphorus and haloalkyl carbon atoms in **1–4** are 13.1 Hz, 12.02 Hz, 10.5 Hz and 16.4 Hz, respectively,[23] but $^3J_{PC} = 8.67$ Hz for **1a**, 10.69 Hz for **2a**, 8.3 Hz for **3a** and 12.07 Hz for **4a**. It is stated that, in the case of the compounds **4** and **4a**, two different couplings, observed as a doublet of quartets, which arise from coupling of the fluorine



Scheme 4
The carbon types for five-membered amine rings according to the ^{13}C NMR spectra for synthesized compounds.

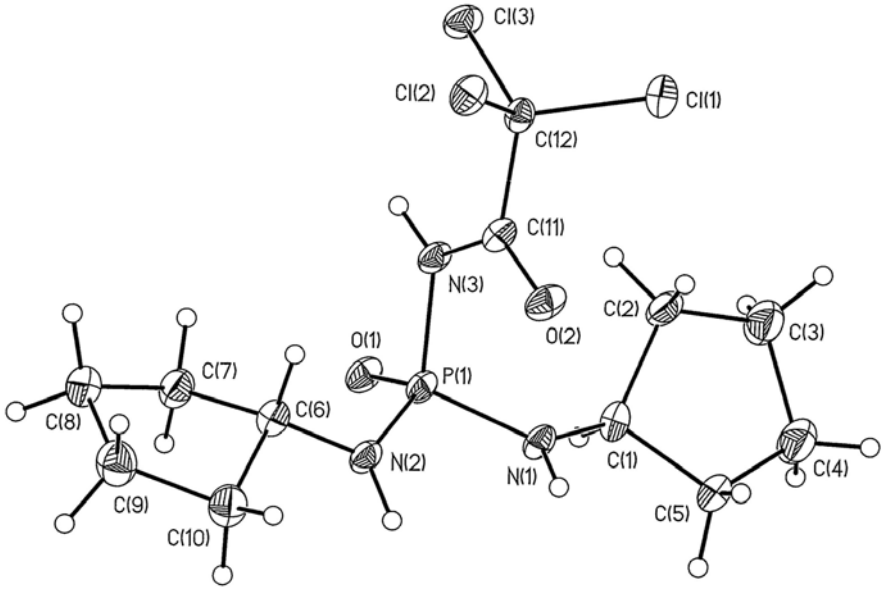


Figure 1 Molecular structure for **1a** with atomic numbering (50% probability ellipsoids).

and phosphorus atoms, were observed in the ^{13}C NMR spectra of the CF_3 group ($^1J_{CF}$ = 288.5 Hz for **4** and 301.42 Hz for **4a**). A similar effect was observed for the carbonyl carbon atom of **4** with $^2J_{CF}$ = 45.85 Hz and 38.85 Hz for **4a**, which leads to another doublet of quartets in the ^{13}C NMR spectra in the C(O) chemical shift region.

No coupling between the carbonyl carbon atom and the phosphorus atom can be observed in compounds **5–8** and **1b–3b**. This observation is in accordance with previous reports for similar compounds.[25]

2.2. X-ray Structural Study

The crystal data and some details of the X-ray analysis for **1a** and **4b** are given in Table 3. Also, selected bond lengths and bond angles are presented in Tables 4 and 5. The molecular structures with the atom labelling for **1a** and **4b** are shown in Figs 1 and 4,

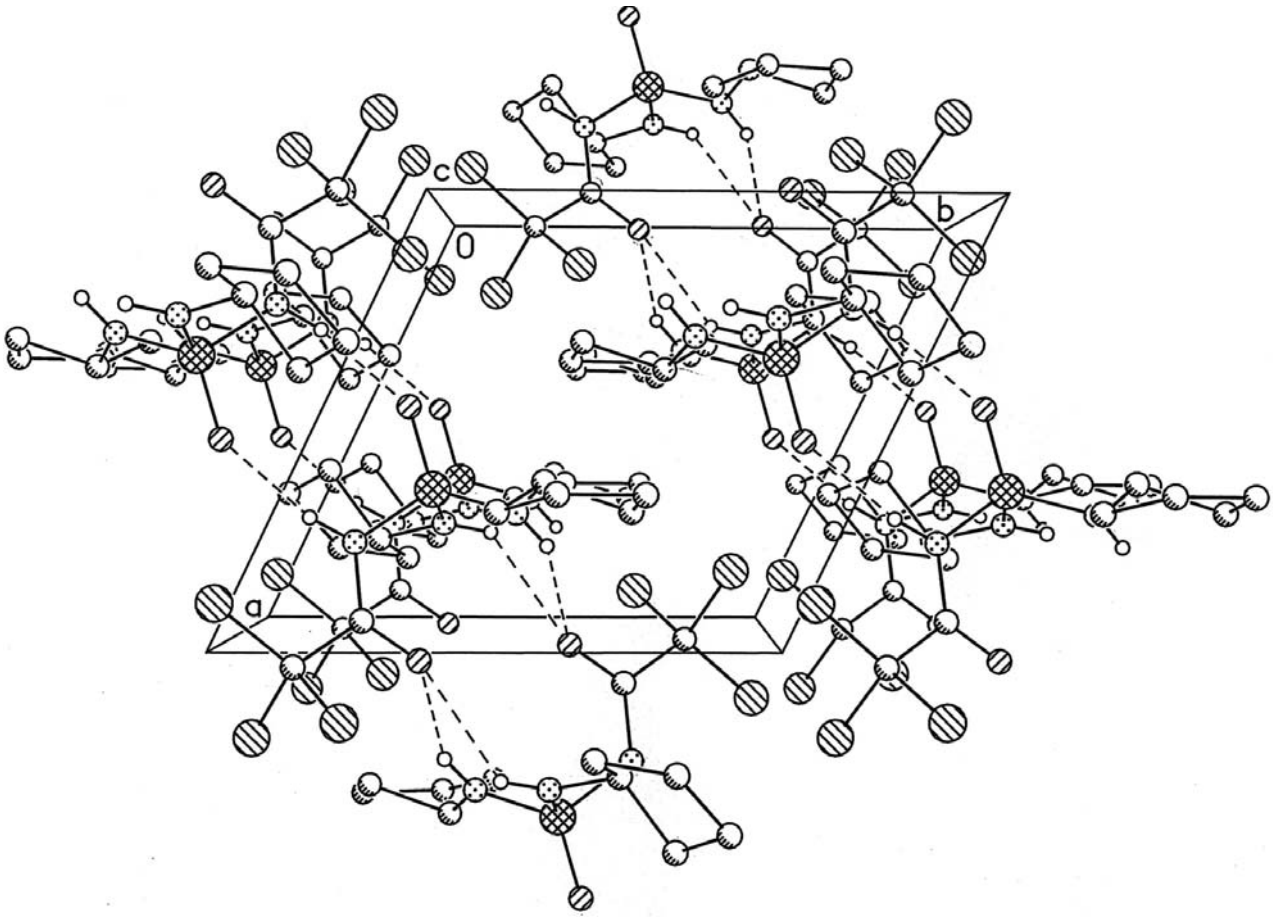


Figure 2 Unit cell for **1a**, showing the hydrogen bonds.

Table 3 Crystal data and structure refinement parameters of **1a** and **4b**.

Structure parameter		**1a**		**4b**	
Empirical formula		$C_{12}H_{21}Cl_3N_3O_2P$		$C_{18}H_{28}N_3O_2P$	
Temperature/K		120(2)		120(2)	
Formula mass/g mol^{-1}		697.17		349.40	
Wavelength/Å		0.71073		0.71073	
Crystal system		Triclinic		Monoclinic	
Space group		P_{-1}		P 21/n	
a/Å	α/°	8.677(3)	92.824(7)	11.8702(6)	90
b/Å	β/°	9.801(3)	94.934(7)	9.8791(5)	96.6500(10)
c/Å	γ/°	10.673(3)	115.089(6)	16.1556(8)	90
V/Å^3		815.3(4)		1881.77(16)	
Z		2		4	
D/Mg m^{-3}		1.534		1.233	
Absorption coefficient/mm^{-1}		0.667		0.161	
F (0 0 0)		392		752	
Crystal size/mm		0.3 ×0.2 ×0.2		0.3 ×0.23 ×0.2	
Refinement method		Full-matrix least squares on F^2		Full-matrix least squres on F^2	
Reflections collected /unique		8945/4282[R(int)=0.0213]		16239/4995[R(int)=0.0375]	
Data/restraints/parameters		4282/0/190		4995/62/217	
Goodness-of-fit on F^2		1.037		1.007	
Final R_1 and wR_2 [I> 2σ (I)]		0.0483, 0.1044		0.0473, 0.1124	
R_1 and wR_2 indices (all data)		0.0586, 0.1069		0.0676, 0.1213	
Largest diff. peak and hole/e Å^{-3}		0.722 and –0.673		0.397 and –0.343	
Θ range for data collection/°		1.92–29.07		2.02–29.00	
Index ranges		–11 ≤ h ≤ 11, –13 ≤ k ≤ 13, –14 ≤ l ≤ 14		–16 ≤ h ≤ 14, –13 ≤ k ≤ 12, –21 ≤ l ≤ 22	

respectively. In addition, the selected parameters of some synthesized carbacylamidophosphates (**1c–5c**) for the comparative analysis are listed in Table 8. As shown in Figs 2 and 3 for **1a**, the dimeric aggregate formed *via* three types of hydrogen bonding and these molecules are held together in the crystal by N-H…O bonds, for which the bond lengths and bond angles are listed in Table 6. Hydrogen bonds are formed by the phosphorylic oxygen atoms and the hydrogen atoms of the amide nitrogen and two types of hydrogen bonds are formed by the carbonyl oxygen atoms and the hydrogen atoms of the amine nitrogens (Fig. 3). Similarly, four types of hydrogen bonds can be observed in Fig. 6 for **4b,** for which the hydrogen bond details are collected in Table 7. There exist two types of hydrogen bonds N(2)-H(2A)…O(2) in the structure of **4b,** which correspond to crystallographically different types of O(2) atoms. The one with d(H…A) = 2.54 Å is the weaker hydrogen bond, in comparison with other N(2)-H(2A)…O(2) hydrogen bonds.

According to the substituents around the phosphorus atom, the phosphorus atom in **1a** and **4b** has a slightly disordered tetrahedral configuration, since the average of the six bond angles around the P atom are 109.42 ° and 109.47 ° for **1a** and **4b**, respectively. It is of interest to note the low values of the O(1)-P(1)-N(3) and N(1)-P(1)-N(2) angles for **1a**, and the O(1)-P(1)-N(1) and N(3)-P(1)-N(2) angles for **4b,** which are 103.98 (10) °, 102.40 °,

Table 4 Selected interatomic distances, angles between interatomic vectors and torsion angles for **1a** with standard uncertainties in parentheses.

Bond distances/Å					
P(1)-O(1)	1.4711(18)	N(3)-C(11)	1.338(3)	C(12)-Cl(1)	1.779(2)
P(1)-N(1)	1.627(2)	N(1)-C(1)	1.466(3)	C(12)-Cl(2)	1.766(3)
P(1)-N(2)	1.6279(2)	N(2)-C(6)	1.469(3)	C(12)-Cl(3)	1.756(2)
P(1)-N(3)	1.729(2)	N(3)-C(11)	1.338(3)	C(1)-O(2)	1.221(3)
Bond angles/°					
O(1)-P(1)-N(1)	115.10(11)			N(1)-C(1)-C(5)	110.4(2)
O(1)-P(1)-N(2)	118.42(11)			N(2)-C(6)-C(10)	111.9(2)
O(1)-P(1)-N(3)	103.98(10)			C(6)-N(2)-P(1)	123.20(16)
N(1)-P(1)-N(2)	102.40(11)			C(1)-N(1)-P(1)	124.00(16)
N(1)-P(1)-N(3)	109.60(11)			C(11)-N(3)-P(1)	120.67(17)
N(2)-P(1)-N(3)	107.04(11)			N(3)-C(11)-C(12)	119.0(2)
Torsion angles/°					
O(1)-P(1)-N(1)-C(1)	38.5(2)				
O(1)-P(1)-N(2)-C(6)	–72.3(2)				
O(1)-P(1)-N(3)-C(11)	–168.55(19)				

Table 5 Selected interatomic distances, angles between interatomic vectors and torsion angles for **4b** with standard uncertainties in parentheses.

Bond distances/Å						
P(1)-O(1)	1.4755(12)	P(1)-N(3)	1.6311(14)	C(5)-C(8) 1.511(2)	C(1)-C(2)	1.490(2)
P(1)-N(1)	1.7007(13)	P(1)-N(2)	1.6322(14)	O(2)-C(1) 1.2323(19)	N(1)-C(1)	1.3636(19)
Bond angles/°						
O(1)-P(1)-N(1)	105.25(7)	N(2)-C(9)-C(13)	111.89(15)	C(14)-N(3)-P(1)	124.39(11)	
O(1)-P(1)-N(2)	113.46(7)	N(1)-C(1)-C(2)	119.24(14)	N(3)-C(14)-C(15)	107.47(15)	
O(1)-P(1)-N(3)	116.86(7)	C(1)-N(1)-P(1)	122.11(11)	C(9)-N(2)-P(1)	123.31(12)	
N(2)-P(1)-N(1)	109.87(7)	O(2)-C(1)-N(1)	119.88(14)	N(2)-C(9)-C(10)	116.72(15)	
N(3)-P(1)-N(1)	109.43(7)	N(3)-P(1)-N(2)	101.95(7)	N(3)-C(14)-C(15)	107.47(15)	
Torsion angles/°						
O(1)-P(1)-N(1)-C(1)	166.55(12)					
O(1)-P(1)-N(2)-C(9)	–34.70(15)					
O(1)-P(1)-N(3)-C(14)	78.86(15)					

105.25 (7) ° and 101.95 (7) °, respectively. This distortion can be the result of the influence of the hydrogen bonds (Figs 3 and 6).

By comparing the two cyclic amines it can be observed that the deviation of the C(3) and C(4) satoms in **1a** from the C(1)-C(2)-C(5) plane and the C(8) and C(9) atoms from the C(6)-C(7)-C(10) plane are equal to –0.972 Å, –0.965 Å, –1.004 Å and –0.991 Å, respectively. Also, the deviation of the C(11) and C(12) atoms in **4b** from the C(10)-C(9)-C(13) plane and the C(16) and C(17) atoms from the C(14)-C(15)-C(18) plane are 0.739 Å, 0.944 Å, 0.909 Å and 0.930 Å, respectively. This reveals that each of the two cyclopentylamines has a pocket configuration but they differ slightly in their orientations. It is demonstrated by comparing the dihedral angles of P(1)-N(1)-C(1)-C(2), P(1)-N(2)-C(6)-C(7), P(1)-N(1)-C(1)-C(5) and P(1)-N(2)-C(6)-C(10) for **1a** and P(1)-N(2)-C(9)-C(10), P(1)-N(2)-C(9)-C(13), P(1)-N(3)-C(14)-C(15) and P(1)-N(3)-C(14)-C(18) for **4b,** which are 68.8 (3) °, 56.6 (3) °, –175.47 (18) °, 172.13 (18) °, –78.68 (19) °, 162.91 (13) °, –172.46 (12) ° and –61.5 (2) °, respectively.

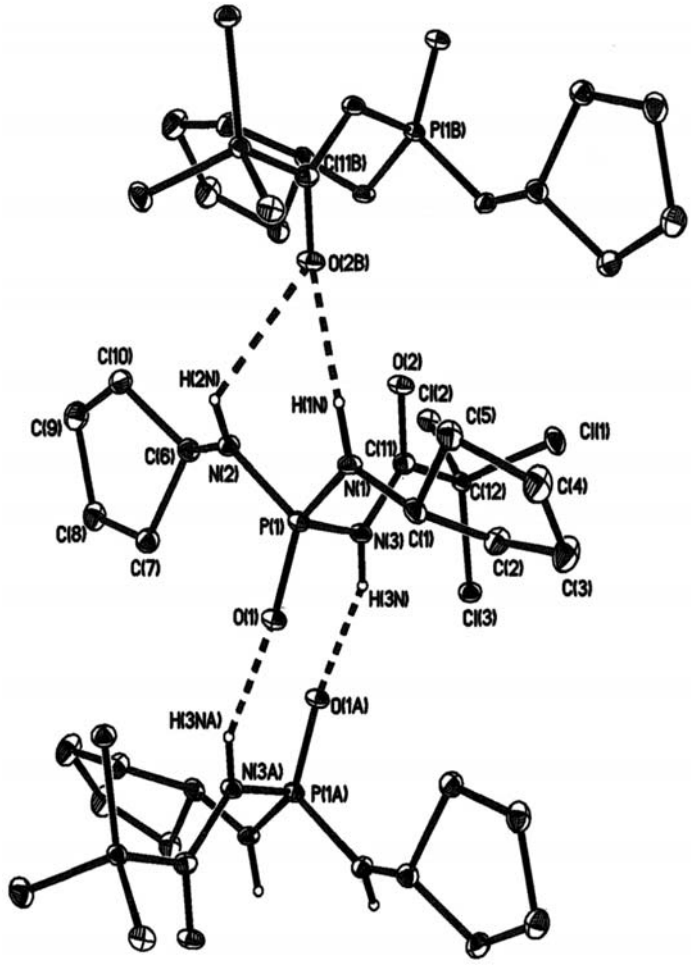


Figure 3 The hydrogen bonding in compound **1a** with ellipsoid probability of 50% (hydrogen atoms omitted for clearer view).

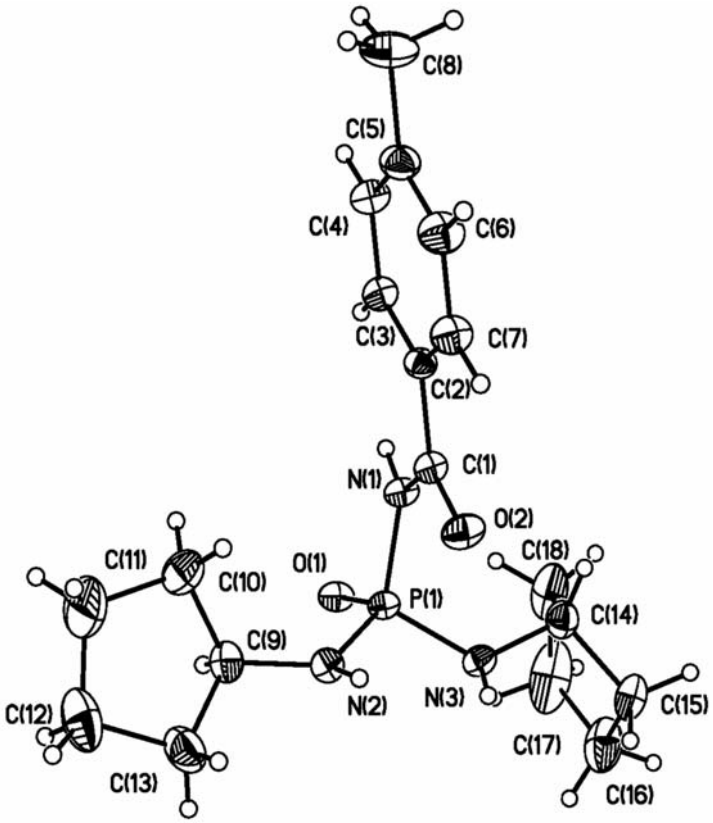


Figure 4 Molecular structure for **4b** with atomic numbering (50% probability ellipsoids).

The data collected in Tables 4 and 5 indicate that the bond lengths between the phosphorus and the amine nitrogen atoms in **1a** and **4b** are shorter than those expected for a P-N single bond (1.77 Å) and longer than for a P=N double bond (1.57 Å).[1] The P-N aminic bond lengths, P(1)-N(1) and P(1)-N(2) for **1a** have the same value, 1.627 (2) Å. However, P(1)-N(2) and P(1)-N(3) for **4b** are equal to 1.6311 (14) Å and 1.6322 (14) Å, respectively. These values are in good agreement with the P-N aminic bond lengths in other synthesized phosphoramidates presented in Table 8 (Scheme 3). In both structures the environment of the amine nitrogen atoms is nearly planar. The planarity can be confirmed by the sum of the three N atom bond angles (ΣN). In compound **1a** the sums of these angles are 360 ° and 359.6 ° for ΣN(1) and ΣN(2). Also, in **4b** they are 346.69 ° and 353.91 ° for ΣN(3) and ΣN(2), respectively. The ΣN(3) for **4b** indicates that the N(3) atom is approximately midway between tetrahedral and planar geometry. The results given for trigonal planar bond angles in these compounds are in accordance with the short P-N bond lengths (Tables 4 and 5). The P-N amidic bond length is about 0.1 Å longer than the P-N aminic ones, which is consistent with the IR vibrational frequencies listed in Table 2. In addition, the planarity around the amidic nitrogen atoms in **1a** and **4b** is influenced by the distances around this atom, such as P(1)-N(3) for **1a** and P(1)-N(1) for **4b,** which are rather shorter than the normal P-N bond length.

The P=O bond lengths in the -C(O)NHP(O)- core for **1a** and **4b** are typical for carbacylamidophosphates, which are 1.471 (18) Å and 1.475 (12) Å, respectively.[27] These values are in good agreement with the P=O bond lengths in **1c–5c** (Scheme 3).

Also the C-N amidic bond lengths for **1a** and **4b** are 1.338 (3) Å and 1.3636 (19) Å, which are shorter than a C-N single bond (1.47 Å).[1] Both crystal structures of **1a** and **4b** show that the P(O) and

Table 6 Hydrogen bond geometries D-H....A for compound **1a.**

D-H	d(D-H)/Å	d(H....A)/Å	d(D....A)/Å	<DHA/°A	A
N(1)-H(1)N	0.880	2.140	2.958 (3)	154.39	O2[–x+2,–y+1,–z]
N(2)-H(2)N	0.880	2.521	3.077 (3)	121.81	O2[–x+2,–y+1,–z]
N(3)-H(3)N	0.880	2.012	2.836 (3)	155.25	O1[–x+1,–y,–z]

Table 7 Hydrogen bond geometries D-H....A for compound **4b.**

D-H	d(D-H)/Å	d(H....A)/Å	d(D....A)/Å	<DHA/°	A
N(1)-H(1A)	0.92	1.91	2.81 (2)	168	O1[–x+1,–y,–z]
N(2)-H(2A)	0.89	2.40	3.13 (2)	139	O2[–x+1,–y+1,–z]
N(2)-H(2A)	0.89	2.54	2.99 (2)	112	O2
N(3)-H(3A)	0.89	2.02	2.90 (2)	172	O2[–x+1,–y+1,–z]

Table 8 Selected interatomic distances for **1c–5c** with standard uncertainties in brackets.

Compound	P=O/Å	C=O/Å	P-N_{amide}/Å	P-N_{amine}/Å	C-N_{amide}/Å	Ref.
1c	1.487(3)	1.217(5)	1.679(4)	1.618(4)	1.365(14)	13
2c	1.486 (10)	1.221(16)	1.69(11)	1.624(3)	1.376(15)	26
3c	1.479(3)	1.211(5)	1.697(4)	1.619(3)	1.345(5)	12
4c	1.465(12)	1.235(17)	1.672(13)	1.614(13)	1.368(18)	11
5c	1.480(2)	1.223(4)	1.683(3)	1.625(3)	1.378(4)	26
1a	1.471 (18)	1.221(3)	1.729(2)	1.627(2)	1.338(3)	a
4b	1.475(12)	1.232(19)	1.700(13)	1.632(14)	1.363(19)	a

a = this work.

C(O) oxygen atoms, O(1) and O(2), are in *anti* positions to each other, which is in accordance with other carbacylamidophosphates with a similar -C(O)NHP(O)- core unit.[27]

Finally, in all eight novel synthesized carbacylamidophosphates (**1a** to **4b**), similar ^{13}C NMR spectral patterns were obtained for the cyclopentyl carbon atoms with $^{2}J_{PNC}$ = 0 and $^{3}J_{PNC}$ = 4 to 6 Hz. The study of the crystal structures of **1a** and **4b** show that the intermolecular N-H….O=P and N-H….O=C hydrogen bonds lead to formation of a dimeric aggregate and a centrosymmetric dimer in one unit cell of **1a** and **4b**, respectively.

3. Experimental

All reactions for the synthesis of the compounds were carried out under argon atmosphere. All of the compounds and solvents for the syntheses were obtained from Merck and Aldrich and used without further purification. All solvents were dried and distilled before used. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRS 500 MHz spectrometer. ^{1}H, ^{13}C and ^{31}P chemical shifts were determined relative to TMS and 85% H_3PO_4, respectively, as external standards. IR spectra were obtained using KBr pellets on a Shimadzu model IR-60 spectrometer. Elemental analyses were performed using a Heraeus CHN-O RAPID instrument.

3.1 Chemical Synthesis

Compound **1**, $CCl_3C(O)NHP(O)Cl_2$, was prepared according to the method published by Kirsanov[21] from the reaction of phosphorus pentachloride (1 eq) and 2,2,2-trichloroacetamide

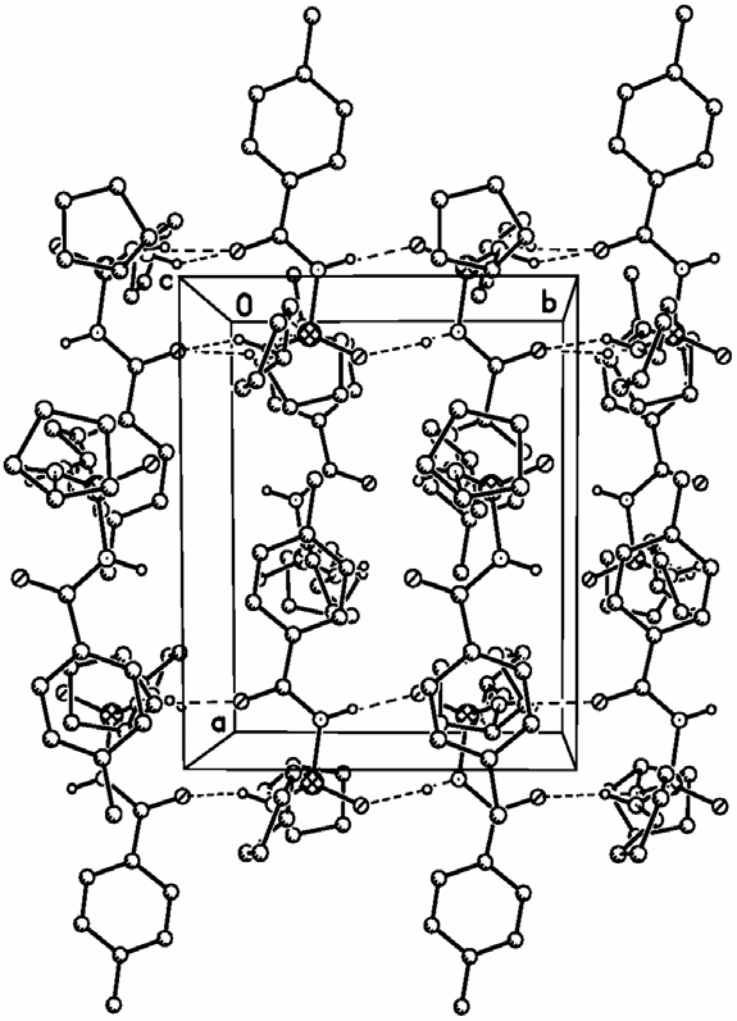


Figure 5 Unit cell for **4b**, showing the hydrogen bonds.

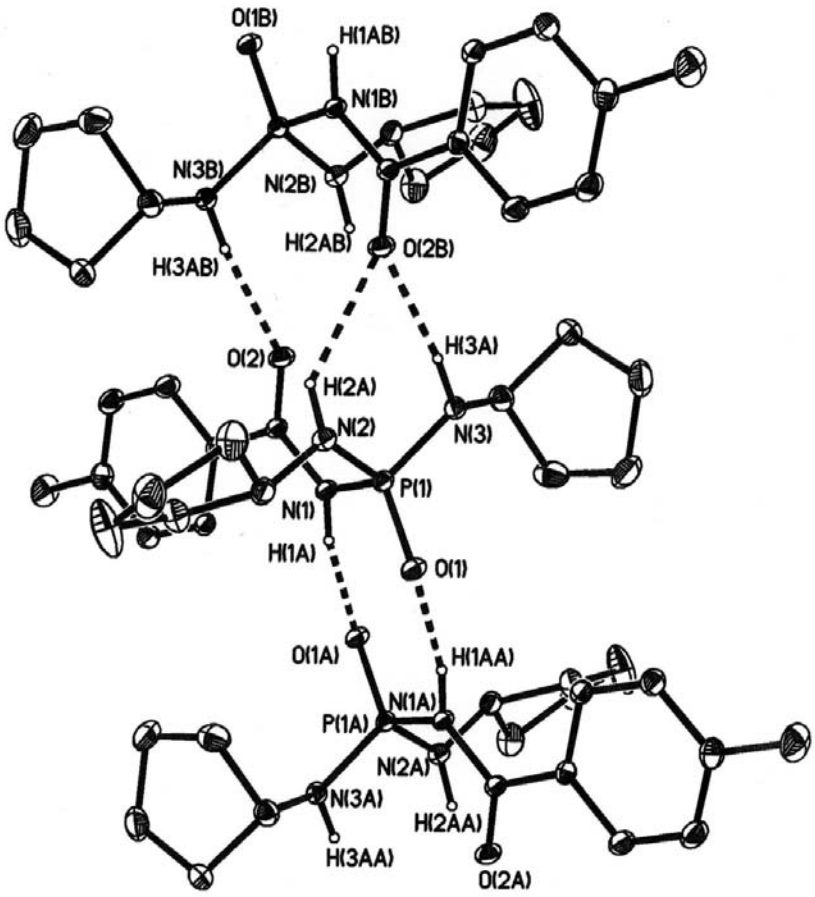


Figure 6 The hydrogen bonding in compound **4b** with ellipsoid probability of 50%.

(1 eq) in CCl_4. The reaction mixture was refluxed for 2 h. After the solution was allowed to return to room temperature, formic acid (1 eq) was added dropwise while stirring. The solution was stirred for 30 min at –20 °C. A white precipitate formed and it was separated and dried *in vacuo.*

$C_6H_5C(O)NHP(O)Cl_2$, **5**, was prepared in the same way as for compound **1** by using benzamide instead of 2,2,2-trichloroacetamide.[22]

Compounds **2**,**3**,**4**,**6**,**7** and **8** were prepared according to published procedures.[23–25]

1a–4a were synthesized from the reaction of R-C(O)NHP(O)Cl_2 [(R=CCl_3), **1**; (R=$CHCl_2$), **2**; (R=CH_2Cl), **3**; (R=CF_3), **4**] with cyclopentylamine in 1:4 molar ratio. The amine was added dropwise to the reaction mixture in chloroform (30 ml) and stirred at –1 °C. After 2–5 h, the products were filtered off and then washed with H_2O and recrystallized from ethanol.

Physical and spectroscopic data of the compounds **1a–4a** are presented below:

N-2,2,2 -trichloroacetyl, N′,N″-bis (cyclopentyl) phosphoric triamide **1a**

IR (KBr), ν = 3325 (s,N-H), 3075 (m,N-H), 2925 (s,C-$H_{aliphatic}$), 1671 (s,C=O), 1418 (vs,C-N), 1243 (vs,P=O), 1103 (m,P-N_{amine}) and 848 (m,P-N_{amide}) cm^{-1}. ^{1}H NMR (500.14 MHz, $CDCl_3$): δ = 1.30–1.94 (m,16H,CH_2), 3.18 (s,2H,NH_{amine}), 3.60–3.67 (m,2H,CH), 8.44 (s,1H,NH_{amide}) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 24.07 (s,CH_2), 24.25 (s, CH_2), 35.75 (d,CH_2, $^3J_{PNC}$ = 4.65 Hz), 36.01 (d, CH_2, $^3J_{PNC}$ = 6.91 Hz), 53.83 (s,2CH), 93.52 (d, CCl_3, $^3J_{PNCC}$ = 8.67 Hz), 163.5 (s, CO) ppm. ^{31}P {^{1}H} NMR (202.45 MHz, $CDCl_3$): δ = 6.15 (s) ppm. Found: C, 38.21; H, 5.42; N, 11.24. Calc. for $C_{12}H_{21}Cl_3N_3O_2P$: C, 38.24; H, 5.57; N, 11.15, %.

N-2,2 dichloroacetyl, N′,N″-bis (cyclopentyl) phosphoric triamide **2a**

IR (KBr), ν = 3260 (vs,N-H), 2960 (m,C-$H_{aliphatic}$), 1680 (s,C=O), 1447 (s,C-N), 1215 (s,P=O), 1108 (w,P-N_{amine}), 832 (w,P-N_{amide}) cm^{-1}. ^{1}H NMR (500.14 MHz , $CDCl_3$): δ = 1.42–1.95 (m,16H,CH_2), 3.05 (s,2H,NH_{amine}), 3.60–3.66 (m,2H,CH), 6.17 (s,1H,$CHCl_2$), 9.76 (d,1H,NH_{amide}, $^2J_{PNH}$ = 5.6 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 23.12 (s,CH_2), 24.28 (s, CH_2), 34.81 (d,CH_2, $^3J_{PNC}$ = 4.65 Hz), 35.08 (d, CH_2, $^3J_{PNC}$ = 6.79 Hz), 52.95 (s,2CH), 66.49 (d, $CHCl_2$, $^3J_{PNCC}$ = 10.69 Hz), 165.9 (d, CO, $^2J_{PNC}$ = 2.01 Hz) ppm. ^{31}P {^{1}H} NMR (202.45 MHz, $CDCl_3$): δ = 6.79(s) ppm. Found: C, 46.80; H, 7.39; N, 13.72. Calc. for $C_{12}H_{23}ClN_3O_2P$: C, 46.82; H, 7.47; N, 13.65, %.

N-2 chloroacetyl, N′,N″-bis (cyclopentyl) phosphoric triamide **3a**

IR (KBr), ν = 3300 (s,N-H), 2945 (m,C-$H_{aliphatic}$), 1699 (s,C=O), 1471 (s,C-N), 1180 (s,P=O), 1106 (w,P-N_{amine}), 904 (w,P-N_{amide}) cm^{-1}. ^{1}H NMR (500.14 MHz, $CDCl_3$): δ = 1.34–1.95 (m,16H,CH_2), 3.00 (s,2H,NH_{amine}), 3.60–3.66 (m,2H,CH), 4.07 (s,2H,CH_2Cl), 8.61 (d,1H,NH_{amide}, $^2J_{PNH}$ = 3.92 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 23.13 (s,CH_2), 23.29 (s, CH_2), 34.84 (d,CH_2, $^3J_{PNC}$ = 4.77 Hz), 35.13 (d,CH_2,$^3J_{PNC}$ = 6.67 Hz), 43.15 (d,CH_2Cl, $^3J_{PNCC}$ = 8.3 Hz), 52.91 (s,2CH), 168.7 (d, CO, $^2J_{PNC}$ = 2.18 Hz) ppm. ^{31}P {^{1}H} NMR (202.45 MHz, $CDCl_3$): δ = 6.72(s) ppm. Found: C, 42.05; H, 6.40; N, 12.31. Calc. for $C_{12}H_{22}Cl_2N_3O_2P$: C, 42.10; H, 6.43; N, 12.28, %.

N-2,2,2 trifluororoacetyl, N′,N″-bis (cyclopentyl) phosphoric triamide **4a**

IR (KBr), ν = 3366 (vs,N-H), 3266 (vs,N-H), 2065 (w,C-$H_{aliphatic}$), 1705 (s,C=O), 1451 (m,C-N), 1224 (s,P=O), 1104 (s,P-N_{amine}), 948

(m,P-N_{amide}) cm^{-1}. ^1H NMR (500.14 MHz , $CDCl_3$): δ = 1.32–1.97 (m,16H,CH_2), 3.00–3.015 (m,2H,NH_{amine}), 3.62–3.64 (m,2H,CH), 9.53 (d,1H,NH_{amide}, $^2J_{PNH}$ = 5.21 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 23.07 (s,CH_2), 23.24 (s,CH_2), 34.66 (d,CH_2, $^3J_{PNC}$ = 4.61 Hz), 35.05 (d,CH_2,$^3J_{PNC}$ = 6.87 Hz), 52.93 (s,2CH), 115.2 (qd,CF_3,$^1J_{CF}$ = 301.4 Hz, $^3J_{PC}$ = 12.07 Hz), 159.07 (qd,CO,$^1J_{CF}$ = 38.8 Hz, $^2J_{PC}$ = 2.8 Hz) ppm. ^{31}P {^1H} NMR (202.45 MHz, $CDCl_3$): δ= 5.49 (s) ppm. Found: C, 44.00; H, 6.36; N, 12.90. Calc. for $C_{12}H_{21}F_3N_3O_2P$: C, 44.03; H, 6.42; N, 12.84, %.

1b–4b were synthesized from the reaction of (*p*-XC_6H_4)C(O)NHP(O)Cl_2,[(X=H), **5**; (X=Cl), **6**; (X=Br), **7**; (X=Me), **8**; with cyclopentylamine in 1:4 molar ratio by adding the respective amine dropwise (using a syringe) to the reaction mixture in acetonitrile (35 mL). The mixtures were stirred for 4–8 h. The temperature was not allowed to rise above –5 °C. After stirring the products were filtered off and then washed with H_2O. The compounds were recrystallized from 2-propanol.

Physical and spectroscopic data of the compounds **1b–4b** are presented below:

N-benzoyl, N′,N″-bis (cyclopentyl) phosphoric triamide **1b**

IR (KBr), ν = 3285 (s,N-H), 2925 (vs,N-H), 2630 (w,C-$H_{aliphatic}$), 1637 (s,C=O), 1417 (vs,C-N), 1204 (s,P=O), 1106 (w,P-N_{amine}), 925 (w,P-N_{amide}) cm^{-1}. ^1H NMR (500.14 MHz , $CDCl_3$): δ = 1.37–1.94 (m,16H,CH_2), 3.18 (s,2H,NH_{amine}), 3.64–3.69 (m,2H,CH), 7.43–8.03 (m,5H,Ar), 9.04 (s,1H,NH_{amide}) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 24.09 (s,CH_2), 24.23 (s,CH_2), 35.7 (d,CH_2, $^3J_{PNC}$ = 4.82 Hz), 36.01 (d,CH_2,$^3J_{PNC}$ = 6.16 Hz), 53.86 (s,2CH), 129.07 (s,Ar), 129.57 (s,Ar), 133.55 (s,Ar), 134.08 (d,Ar, J_{PC} = 8.1 Hz), 170.27 (s,CO) ppm. ^{31}P {^1H} NMR (202.45 MHz, $CDCl_3$): δ = 8.99(s) ppm. Found: C, 60.73; H, 7.69; N, 12.62. Calc. for $C_{17}H_{26}Cl_2N_3O_2P$: C, 60.89; H, 7.76; N, 12.53, %.

N-(p-*chloro)benzoyl, N′,N″-bis(cyclopentyl) phosphoric triamide* **2b**

IR (KBr), ν = 3290 (w,N-H), 3130 (m,N-H), 2945 (m,C-$H_{aliphatic}$), 1621 (s,C=O), 1430 (vs,C-N), 1218 (s,P=O), 1053 (w,P-N_{amine}), 911 (m,P-N_{amide}) cm^{-1}. ^1H NMR (500.14 MHz , $CDCl_3$): δ = 1.33–1.93 (m,16H,CH_2), 3.19 (s,2H,NH_{amine}), 3.64–3.68 (m,2H,CH), 7.24–7.92 (m,4H,Ar), 9.06 (d,1H,NH_{amide}, $^2J_{PNH}$ = 5.1 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 23.13 (s,CH_2), 23.29 (s, CH_2), 34.74 (d,CH_2, $^3J_{PNC}$ = 4.72 Hz), 35.15 (d,CH_2,$^3J_{PNC}$ = 6.99 Hz), 52.89 (s,2CH), 128.17 (s,Ar), 129.23 (s,Ar), 130.59 (d,Ar,J_{PC} = 7.79 Hz), 143.06 (s,Ar), 169.32 (s,CO) ppm. ^{31}P {^1H} NMR (202.45 MHz, $CDCl_3$): δ = 8.86(s) ppm. Found: C, 55.15; H, 6.68; N, 11.41. Calc. for $C_{17}H_{25}ClN_3O_2P$: C, 55.20; H, 6.76; N, 11.36, %.

N-(p-*bromo)benzoyl, N′,N″-bis(cyclopentyl) phosphoric triamide* **3b**

IR (KBr), ν = 3295 (w,N-H), 3095 (m,N-H), 2950 (m,C-$H_{aliphatic}$), 1635 (s,C=O), 1430 (vs,C-N), 1217 (s,P=O), 1102 (w,P-N_{amine}), 907 (m,P-N_{amide}) cm^{-1}. ^1H NMR (500.14 MHz, $CDCl_3$): δ = 1.33–1.92 (m,16H,CH_2), 3.23–3.25 (m,2H,NH_{amine}), 3.59–3.64 (m,2H,CH), 7.56–8.03 (m,4H,Ar), 9.99 (d,1H,NH_{amide}, $^2J_{PNH}$ = 5.6 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 23.10 (s,CH_2), 23.25 (s, CH_2), 34.72 (d,CH_2, $^3J_{PNC}$ = 4.84 Hz), 35.11 (d,CH_2,$^3J_{PNC}$ = 6.92 Hz), 52.91 (s,2CH), 127.3 (s,Ar), 130.12 (s,Ar), 131.65 (s,Ar), 132.21 (d,Ar,J_{PC} = 8.3 Hz), 168.77 (s,CO) ppm. ^{31}P {^1H} NMR (202.45 MHz, $CDCl_3$): δ= 8.96(s) ppm. Found: C, 50.43; H, 6.12; N, 10.43. Calc. for $C_{17}H_{25}BrN_3O_2P$: C, 50.49; H, 6.18; N, 10.39, %.

N-(p-*methyl)benzoyl, N′,N″-bis(cyclopentyl) phosphoric triamide* **4b**

IR (KBr), ν = 3295 (w,N-H), 3230 (m,N-H), 2950 (m,C-$H_{aliphatic}$), 1631 (s,C=O), 1430 (vs,C-N), 1218 (s,P=O), 1052 (w,P-N_{amine}), 910 (m,P-N_{amide}) cm^{-1}. ^1H NMR (500.14 MHz, $CDCl_3$): δ = 1.32–1.93 (m,16H,CH_2), 3.21–3.26 (m,2H,NH_{amine}), 3.64–3.66 (m,2H,CH), 7.22–7.95 (m,4H,Ar), 9.17 (d,1H,NH_{amide}, $^2J_{PNH}$ = 5.48 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 21.55 (s,CH_3), 23.14 (s, CH_2), 23.29 (s,CH), 34.74 (d,CH_2, $^3J_{PNC}$ = 4.8 Hz), 35.15 (d,CH_2,$^3J_{PNC}$ = 6.96 Hz), 52.89 (s,2CH), 128.22 (s,Ar), 129.21 (s,Ar), 130.60 (d,Ar,J_{PC} = 7.9 Hz), 143.04 (s,Ar), 169.37 (s,CO) ppm. ^{31}P {^1H} NMR (202.45 MHz, $CDCl_3$): δ = 8.93(s) ppm. Found: C, 61.83; H, 7.98; N, 12.08. Calc. for $C_{18}H_{28}N_3O_2P$: C, 61.89; H, 8.02; N, 12.03, %.

3.2. Crystal Structure Determination

Colourless crystals of compounds **1a** and **4b** were obtained by slow evaporation of n-heptane/chloroform (1:7) as a rod-shaped and air-stable crystal. The crystallographic data and refinement parameters are listed in Table 3. X-ray data of compounds **1a** and **4b** were collected on a Bruker SMART 1000 CCD.[28] A single crystal with dimensions 0.3 × 0.2 × 0.2 mm for **1a** and 0.3 × 0.23 × 0.2 mm for **4b** were selected for data collection at 120 (2) K, using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The structures were solved by a direct method, using the SHELX-97 program package[29] by full-matrix least-squares on F^2.

The non-hydrogen atoms were refined anisotropically and all located from subsequent difference Fourier maps and refined to final *R* values of 0.0483 and 0.0473 for **1a** and **4b**, respectively. The positions of the hydrogen atoms were obtained from the difference Fourier map and absorption corrections were performed using the SADABS program.[30] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary material with reference nos. CCDC 240147 for **1a** and CCDC 292755 for **4b**. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1E2, UK (Fax: +441223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Supplementary Material

The NMR spectra of all compounds (**1a**–**4b**) are presented in the online supplement.

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