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Study on H-bond patterns in phosphoric triamides having a P(O)NHC(O) skeleton, a *gauche* orientation of P(O) *vs* C(O) in new compounds

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ABSTRACT

The crystal and packing structures of new phosphoric triamides, in a rare *gauche* orientation of P(O) *versus* C(O), with the formula $(CCl_2HC(O)NH)X_2P(O)$, X = NC_4H_8 (**1**), $N(C_2H_5)_2$ (**2**), $N(CH_3)(C_6H_{11})$ (**3**) and $(CCl_2HC(O)NH)(Y)P(O)$, Y = $NHCH_2C(CH_3)_2CH_2NH$ (**4**) have been investigated. This article also reviews 91 similar structures deposited in the CSD aiming to classify hydrogen bond patterns in this category of phosphorus compounds. The present X-ray structural analysis shows that the H-bond pattern in the studied structures strongly depends on the conformation in the P(O)NHC(O) skeleton and the kind of amide linked to the P atom. The spectroscopic features ($^{31}P\{^1H\}$, ^1H and ^{13}C NMR, IR) of the new compounds have been investigated.

1. Introduction

Hydrogen bonds (HBs) are the most important directional intermolecular interactions which may affect the preference of a molecular conformation and arrangement [1]. Many efforts have been performed to classify HBs based on their strengths [2,3] and morphology [4–6]. Such considerations help to predict crystal structures based on molecular structures. However, this is not yet completely possible, but it leads to classify HB patterns in analogous compounds and to obtain empirical "rules" which are most useful for predicting hydrogen-bond patterns of systems with a limited number of functional groups [7]. In this area, HB patterns have been discussed for nitroanilines [7], diarylureas [7], amides [8], imides [8], diamides [8] and different co-crystals [8]. Now, we wish to organize the existing data related to a biologically important functional group, P(O)NHC(O), belonging to *N*-carbonyl phosphoric triamides (CPAs, $RC(O)NHP(O)[NR^1R^2]_2$) [9]. Some derivatives have been investigated structurally [10–64], the cif files of which have been used for studying and classifying hydrogen bond patterns in CPAs and evaluating the behavior of different parts of the molecule in relation to the hydrogen bonds. This paper attempts to study the collective behavior of HBs in the crystal packing of CPAs. Among the 91 crystal structures found in the Cambridge Structural Database (CSD version 5.31 (November 2009)) and recently published papers (Table 1), there are only 10 structures with a non-*anti* orientation of C=O *versus* P=O. Here, we report 4 new structures with a *gauche* orientation and classify the H-bond patterns affected by the conformation of the P(O)NHC(O) skeleton and the kind of amide substituents linked to the P atom.

2. Experimental

2.1. Spectroscopic measurements

^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to TMS and ^{31}P chemical shifts relative to 85% H_3PO_4 as the external standards. The field strengths for the acquisition of ^1H, ^{13}C and ^{31}P spectra were 500.13, 125.77 and 202.46 MHz, respectively. Infrared (IR) spectra were recorded on a Buck 500 scientific spectrometer using KBr discs.

2.2. X-ray measurements

Single colorless crystals of compounds **1–4** were selected and glued on glass fibers. Diffraction data were collected on an Oxford Diffraction KM4 four-circle goniometer equipped with a Sapphire CCD detector. The crystals to detector distance was 45.0 mm and graphite monochromated Mo Kα (λ = 0.71073 Å) X-radiation was employed in all measurements. The frame widths of 1° in ω, with exp. time between 8 and 60 s were used to acquire each frame for **1**, **2**, **3** and **4**. More than one hemisphere of three-dimensional data was collected in all measurements. The data were reduced using the Oxford Diffraction program CRYSALISPRO [65]. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were corrected for Lorentz,

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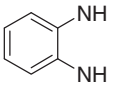
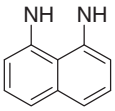
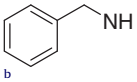
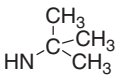
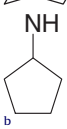
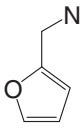
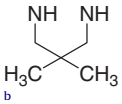
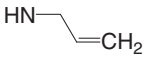
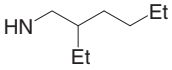
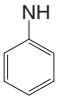
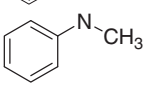
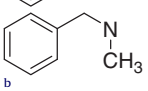
Table 1
[a]H-bond pattern for RC(O)NHP(O)[X]$_2$ compounds (X = Cl; XH = primary or secondary amine, alcohol; [XH]$_2$ = diamine); the point groups of H-bonded dimers are given in parenthesis as C_i for centrosymmetric and C_1 for non-centrosymmetric.

No	R	X/[X]$_2$ for diamine	O–P–N–C	Orientation	Packing	Refcode	Ref
1	4-F-C_6H_4		−177.6(3)	*anti*	1-D ladder	SAYJIM	[38]
2	CCl_3		−62.3(3)	*gauche*	2-D		[10]
3	C_6H_5		173.85(19)	*anti*	1-D chain	TOKXOH	[29]
4	4-F-C_6H_4	[b]	−179.04(11)	*anti*	1-D chain	KEBPOX	[39]
5	$CNCH_2$	[b]	164.06(17)	*anti*	1-D ladder	LOPBOI	[28]
6	CCl_3		177.7(3)	*anti*	1-D chain	PACNIR	[11]
7	3-NO_2-C_6H_4	[b]	177.6(1) 179.0(1) −180.0(1)	*anti*	Hexamer		[50]
8	C_6H_5	[b]	−174.8(2) 176.6(2)	*anti*	Two symmetrically independent 1-D chains	PACNEN	[11]
9	4-F-C_6H_4	[b]	−174.16(11)	*anti*	1-D chain	KEBPIR	[39]
10	NC_5H_4	[b]	[c]	*anti*	[c]		[64]
11	NC_5H_4	[b]	[c]	*anti*	[c]		[64]
12	4-NO_2-C_6H_4		170.69(13)	*anti*	1-D chain		[46]
13	CCl_3		−168.55(19)	*anti*	1-D chain	YIVPAV	[12]
14	4-Cl-C_6H_4	[b]	173.92(19)	*anti*	1-D chain	NOBHUI	[18]
15	4-CH_3-C_6H_4	[b]	166.55(12)	*anti*	1-D chain	YIVPEZ	[12]
16	$CNCH_2$		−163.85(16)	*anti*	1-D ladder	LOPCAV	[28]
17	$CHCl_2$		61.32(2)	*gauche*	1-D chain		[d]
18	4-F-C_6H_4	[b]	−57.2(2)	*gauche*	2-D		[40]
19	CCl_3		−169.9(3) −161.9(3) 161.1(3) 168.8(3)	*anti*	Two symmetrically independent 1-D chains		[13]
20	4-F-C_6H_4	[b]	166.2(1)	*anti*	1-D chain	TOKXEX	[29]
21	C_6H_5		178.5(4)	*anti*	1-D chain	GOKMEZ	[30]
22	CCl_3		174.8(6)	*anti*	[e]Dimer (C_i)	POKZAQ	[14]
23	CCl_3		174.9(4) 175.3(4)	*anti*	Dimer (C_1)		[15]
24	CCl_3		162.01(16)	*anti*	Dimer (C_i)	RAMBEN	[16]
25	$CHCl_2$	[b]	−178.16(17)	*anti*	Dimer (C_i)		[27]
26	C_6H_5	[b]	−165.2(2)	*anti*	Dimer (C_i)	RALZUA	[16]
27	4-F-C_6H_4	[b]	172.10(11)	*anti*	Dimer (C_i)	KEBPUD	[39]
28	4-Cl-C_6H_4	[b]	−171.90(14)	*anti*	Dimer (C_i)		[27]
29	4-Br-C_6H_4	[b]	−171.6(3)	*anti*	Dimer (C_i)	LIVWAP	[53]
30	CF_3	[b]	−176.2(2)	*anti*	Dimer (C_i)	WALRAD	[22]
31	2-F-C_6H_4	[b]	154.62(9)	*anti*	Dimer (C_i)	XIQZAZ	[42]
32	CCl_3		171.7(3) −151.1(4)	*anti*	Two symmetrically independent dimers (C_1)	VEHTAE	[17]
33	$CHCl_2$	[b]	56.2(3)	*gauche*	1-D chain		[d]

(*continued on next page*)

Table 1 (*continued*)

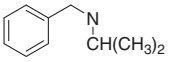
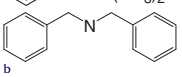
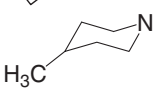
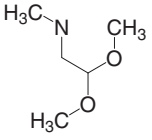
No	R	X/[X]$_2$ for diamine	O–P–N–C	Orientation	Packing	Refcode	Ref
34	3-NO_2-C_6H_4	[b]	171.2(1)	*anti*	Dimer (C_i)		[47]
35	C_6H_5	[b]	168.1(4) −157.2(4)	*anti*	Dimer (C_1)	IYAVEJ	[31]
36	4-F-C_6H_4	[b]	178.21(11)	*anti*	Dimer (C_i)	LEHVOK	[41]
37	CCl_3		−157.80(17)	*anti*	Dimer (C_i)	NOBHES	[18]
38	$CHCl_2$	[b]	171.94(14)	*anti*	Dimer (C_i)	NOBHIW	[18]
39	C_6H_5	[b]	−175.9(14) −176.0(14) 177.5(15) 179.5(14)	*anti*	Two symmetrically independent dimers (C_1)		[32]
40	4-F-C_6H_4	[b]	179.7(3) 178.2(3) −176.9(3) −171.0(5)	*anti*	Two symmetrically independent dimers (C_1)	LEHWEB	[41]
41	4-Cl-C_6H_4	[b]	−162.04(17)	*anti*	Dimer (C_i)	TESJUX	[51]
42	4-Br-C_6H_4	[b]	−161.9(8) 178.4(9)	*anti*	Two symmetrically independent dimers (C_i)	TESJOR	[51]
43	2,4-$Cl_2C_6H_3$	[b]	151.85(11)	*anti*	Dimer (C_i)		[57]
44	4-NO_2-C_6H_4		−53.76(15)	*gauche*	1-D chain		[47]
45	4-F-C_6H_4	[b]	172.89(17)	*anti*	Dimer (C_i)	LEHWAX	[41]
46	4-Cl-C_6H_4	[b]	161.41(13)	*anti*	Dimer (C_i)	NOBHOC	[18]
47	4-Br-C_6H_4	[b]	−166.24(11)	*anti*	Dimer (C_i)	SIRXIB	[23]
48	CF_3	[b]	160.40(12)	*anti*	Dimer (C_i)	SIRXEX	[23]
49	2,4-$Cl_2C_6H_3$	[b]	−160.5(2)	*anti*	Dimer (C_i)		[57]
50	2,4-$Cl_2C_6H_3$	[b]	−161.34(17)	*anti*	Dimer (C_i)		[57]
51	CCl_3	[b]	−171.2(3)	*anti*	Dimer (C_i)	SAGPAR	[19]
52	C_6H_5	[b]	172.6(3)	*anti*	Dimer (C_i)	WIYTUT	[33]
53	NC_4H_8O	[b]	171.9(2) −171.6(2)	*anti*	Dimer (C_1)	GAQDEH	[63]
54	C_6H_5		−154.48(15)	*anti*	Dimer (C_i)	LAYMOO	[34]
55	4-F-C_6H_4	[b]	155.7(3)	*anti*	Dimer (C_i)	LEHVUQ	[41]
56	4-Cl-C_6H_4	[b]	−172.9(1)	*anti*	Dimer (C_i)	HOJPOM	[24]
57	4-Br-C_6H_4	[b]	172.0(3)	*anti*	Dimer (C_i)	HOJPIG	[24]
58	CF_3	[b]	154.47(17)	*anti*	Dimer (C_i)	HOJPUS	[24]
59	2,4-$Cl_2C_6H_3$	[b]	156.30(17)	*anti*	Dimer (C_i)		[57]
60	$CHCl_2$	$N(C_2H_5)_2$	51.4(2)	*gauche*	1-D chain		[d]
61	4-NO_2-C_6H_4	[b]	161.2(2)	*anti*	Dimer (C_i)		[47]
62	2,4-$Cl_2C_6H_3$	[b]	[c]	*anti*	[c]		[58]
63	C_6H_5	[b]	161.8(2)	*anti*	Dimer (C_i)	POKZIY	[14]
64	CCl_3	[b]	−158.5(3)	*anti*	Dimer (C_i)	TUNREZ	[20]
65	$CHCl_2$		46.1(2)	*gauche*	1-D chain		[d]
66	4-NO_2-C_6H_4	[b]	173.62(13)	*anti*	Dimer (C_i)		[48]
67	C_6H_5	[b]	154.11(15)	*anti*	Dimer (C_i)	SEYPES	[35]
68	CF_3	[b]	161.7(1)	*anti*	Dimer (C_i)	GIQTUW	[25]
69	2,4-$Cl_2C_6H_3$	[b]	169.3(3)	*anti*	Dimer (C_i)		[57]
70	4-NO_2-C_6H_4		177.5(2)	*anti*	Dimer (C_i)		[49]
71	$CHCl_2$		−173.68(18)	*anti*	Dimer (C_i)		[27]
72	C_6H_5	[b]	−178.55(12)	*anti*	Dimer (C_i)	VEFLUO	[36]
73	2-F-C_6H_4	[b]	−172.49(9)	*anti*	Dimer (C_i)	TEZWUR	[43]
74	4-Br-C_6H_4	[b]	−179.93(19) −174.75(19)	*anti*	Dimer (C_1)		[27]
75	C_6H_5		−171.69(17) 165.86(17)	*anti*	Dimer (C_1)	LAYMII	[34]
76	C_6H_5		−177.8(12) −171.7(12)	*anti*	Dimer (C_1)	LARTII	[32]
77	C_6H_5		154.44(13)	*anti*	Dimer (C_i)	SEYPAO	[35]

Table 1 (*continued*)

No	R	X/[X]$_2$ for diamine	O–P–N–C	Orientation	Packing	Refcode	Ref
78	4-Br-C_6H_4		176.7(2)	*anti*	Dimer (C_i)		[54]
79	2,4-$Cl_2C_6H_3$	$N(CH_2CH_2CH_3)_2$	[c]	*anti*	[c]		[58]
80	2,4-$Cl_2C_6H_3$	$N(CH_2CH_2CH_2CH_3)_2$	[c]	*anti*	[c]		[58]
81	CF_3	Cl	−178.2(3)	*anti*	Dimer (C_i)		[26]
82	3-F-C_6H_4		47.9(3)	*gauche*	1-D chain	VAXLUB	[45]
83	4-Cl-C_6H_4	[b]	−56.7(4)	*gauche*	1-D chain	WAJFAO	[52]
84	3-I-C_6H_4	[b]	175.6(9) −174.5(9)	*anti*	Two symmetrically independent dimers (C_i)	DIHRIV	[56]
85	3-(CH_2CHCH_2O)-C_6H_4	[b]	−170.7(3)	*anti*	Dimer (C_i)	DUCXUU	[62]
86	3-Cl-C_6H_4	[b]	52.5(5)	*gauche*	1-D chain	SEGWUW	[55]
87	3-Br-C_6H_4	[b]	53(1)	*gauche*	1-D chain	SEGXAD	[55]
88	4-OCH_3-C_6H_4	[b]	−53.8(5)	*gauche*	1-D chain	DUCYEF	[59]
89	3-OCH_3-C_6H_4	[b]	−50.8(4)	*gauche*	1-D chain	FATLIV	[60]
90	4-OCH_3-C_6H_4N(Et)	[b]	167.0(1)	*anti*	Dimer (C_i)	FOTXIV	[61]
91	C_6H_5	[b]	−174.26	*anti*	Dimer (C_i)	BOVNAB	[37]
92	4-Cl-C_6H_4	$N(CH_3)_2$	162.4(3) 156.5(3)	*anti*	Dimer (C_1)	LOVRET	[44]
93	2-F-C_6H_4	[b]	178.2(3)	*anti*	Dimer (C_i)	LOVRIX	[44]
94	C_6H_5	[b]	−160.8(1)	*anti*	Dimer (C_i)	WIYVAB	[33]
95	CCl_3	[b]	−53.07(8)	*gauche*	1-D chain		[21]

[a] The patterns are based on normal N–H···O HBs; considering the weak N–H···O HBs, the packing in entries 7, 12 and 19 are 1-D chain for 7 and 2-D for 12 and 19.
[b] The amide is the same as the previous entry in the Table.
[c] The cif file is not available.
[d] This work.
[e] Considering the solvated dioxane molecules, the packing is as a centrosymmetric tetramer (containing two H-bonded phosphoramide molecules and two H-bonded solvents).

polarization and background effects. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from the International Tables for X-ray Crystallography [66]. The structures were solved by direct methods [67] and the figures were drawn using MERCURY [68]. Refinements were based on F^2 values and done by full-matrix least-squares [69] with all non-H atoms anisotropic. The positions of all non-H atoms were located by direct methods. The positions of hydrogen atoms were found from the inspection of the difference Fourier maps. The final refinement included atomic positional and displacement parameters for all non-H atoms. At the final stage of the refinement, H atoms were positioned geometrically (N–H = 0.86 and C–H = 0.93–0.97 Å) and refined using a riding model with fixed isotropic displacement parameters. The absolute configuration of **1** was determined (Flack parameter 0.05(10)) [70]. The crystal data and refinement parameters are listed in Tables 2 and 3.

2.3. General procedure for the synthesis of compounds *1–4*

$CCl_2HC(O)NHP(O)Cl_2$ was prepared according to the method used for the analogous compound 4-NO_2-$C_6H_4C(O)NHP(O)Cl_2$, by using $CCl_2HC(O)NH_2$ instead of 4-NO_2-$C_6H_4C(O)NH_2$ [49]. To synthesize compounds **1–4**, a solution of 4 mmol amine for **1**, **2** and **3** or 2 mmol diamine for **4** in dry $CHCl_3$ (5 mL) was added dropwise to a stirred solution of 1 mmol $CCl_2HC(O)NHP(O)Cl_2$ in dry $CHCl_3$ (30 mL) at 0 °C. After 4 h, the solvent was removed in vacuum and the solid was washed with H_2O. Suitable single crystals for X-ray crystallography were obtained at room temperature from a mixture of CH_3OH/CH_3CN (4:1 ratio) for **1** and **2**, $CH_3OH/CH_3CHOHCH_3$ (1:1) for **3** and $CHCl_3/n$-C_7H_{16} (4:1) for **4**.

2.3.1. N-(dichloroacetyl)-N′,N″-bis(pyrrolidinyl)-phosphoric triamide (*1*)

IR (KBr, cm^{-1}): 3080 (NH), 1709 (C═O), 1190. ^1H NMR (DMSO-d_6) δ: 1.74 (m, 8H), 3.05 (m, 4H), 3.11 (m, 4H), 6.51 (b, 1H, CH), 9.46 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) δ: 25.78 (d, ^3J(P,C) = 8.3 Hz, 4C), 45.74 (d, ^2J(P,C) = 4.9 Hz, 4C), 66.73 (d, ^3J(P,C) = 8.9 Hz, 1C, $CHCl_2$), 164.50 (s, 1C, C═O). $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ: 5.88 (s).

2.3.2. N-(dichloroacetyl)-N′,N′,N″,N″-tetra(ethyl)-phosphoric triamide (*2*)

IR (KBr, cm^{-1}): 3100 (NH), 1719 (C═O), 1183, 960 (P–N_{amide}), 730. ^1H NMR (DMSO-d_6) δ: 1.02 (t, ^3J(H,H) = 7.1 Hz, 12H, 4CH_3), 2.97–3.04 (m, 8H, 4CH_2), 6.52 (b, 1H, CH), 9.45 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) δ: 13.72 (d, ^3J(P,C) = 2.3 Hz, 4C), 38.64 (d, ^2J(P,C) = 5.0 Hz, 4C), 66.72 (d, ^3J(P,C) = 11.2 Hz, 1C, $CHCl_2$), 164.21 (s, 1C, C═O). $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ: 11.50 (s).

2.3.3. N-dichloroacetyl-N′,N″-dicyclohexyl-N′,N″-dimethyl phosphoric triamide (*3*)

IR (KBr, cm^{-1}): 3100 (NH), 1725 (C═O), 1482, 1227, 1190, 1005, 899 (P–N_{amide}), 638. ^1H NMR (DMSO-d_6) δ: 1.03 (m, 2H), 1.20 (m, 4H), 1.59 (m, 14H), 2.47 (m, 6H), 3.23 (m, 2H), 6.51 (b, 1H, $CHCl_2$), 9.38 (d, ^2J(P,H) = 7.2 Hz, 1H, NH). ^{13}C NMR (DMSO-d_6) δ: 24.99 (s, 2C, C^4), 25.58 (s, 2C, $C^{2\ or\ 6}$), 27.19 (d, ^3J(P,C) = 4.7 Hz, 2C, $C^{2\ or\ 6}$), 30.20 (s, 2C, $C^{3\ or\ 5}$), 30.22 (s, 2C, $C^{3\ or\ 5}$), 30.26 (d, ^2J(P,C) = 3.4 Hz, 2C, C^7), 54.26 (d, ^2J(P,C) = 4.5 Hz, 2C, C^1), 66.79 (d, ^3J(P,C) = 10.8 Hz, 1C, $CHCl_2$), 164.55 (s, 1C, C(O)) [numbering of carbon atoms are according to the scheme of Table 4). $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ: 12.27 (s).

2.3.4. 5,5-Dimethyl-2-[N-(dichloroacetyl)]-2-oxo-1,3,2-diazaphosphorinane (*4*)

IR (KBr, cm^{-1}): 3329 (NH), 3179, 3091, 1777, 1690 (C═O), 1578, 1481, 1398, 1340, 1296, 1208 (P═O), 1087, 838 (P–N_{amide}). ^1H NMR (DMSO-d_6) δ: 0.76 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.58 (ddd, ^3J(H,H) = 5.8 Hz, ^2J(H,H) = 11.7 Hz, ^3J(P,H) = 26.2 Hz, 2H, CH), 2.96 (d, ^2J(H,H) = 12.0 Hz, 2H, CH), 4.83 (s, 2H, NH_{amide}), 6.42 (s, 1H, $CHCl_2$), 9.40 (s, 1H, $NH_{C(O)NHP(O)}$). ^{13}C NMR (DMSO-d_6) δ: 22.81 (s, 1C, CH_3), 24.68 (s, 1C, CH_3), 30.01 (d, ^3J(P,C) = 4.8 Hz, 1C, CMe_2), 52.89 (d, ^2J(P,C) = 2.1 Hz, 2C, CH_2), 66.83 (d, ^3J(P,C) = 9.4 Hz, 1C, $CHCl_2$), 164.87 (s, 1C, C═O). $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ: 0.30 (s).

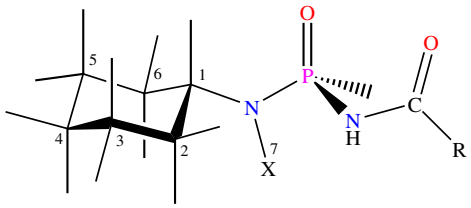
Table 2
Crystal data and structure refinement for **1** and **2**.

	Compound **1**	Compound **2**
Empirical formula	$C_{10}H_{18}Cl_2N_3O_2P$	$C_{10}H_{22}Cl_2N_3O_2P$
Formula weight	314.14	318.18
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	$P2_1/c$
a (Å)	8.817(6)	9.919(1)
b (Å)	18.349(10)	18.454(3)
c (Å)	9.070(7)	9.044(2)
β (°)		103.06(2)
V (Å^3)	1467.4(17)	1612.6(4)
Z	4	4
D_{calc} (g/cm^3)	1.422	1.311
Absorption coefficient (mm^{-1})	0.550	0.501
F(0 0 0)	656	672
Crystal size (mm^3)	0.29 × 0.18 × 0.08	0.35 × 0.10 × 0.05
Crystal color/habit	colorless/prism	colorless/prism
θ Range for data collection (°)	3.91–24.99	3.53–25.0
Index ranges	$-10 \leqslant h \leqslant 8$ $-21 \leqslant k \leqslant 10$ $-8 \leqslant l \leqslant 10$	$-11 \leqslant h \leqslant 10$ $-13 \leqslant k \leqslant 21$ $-10 \leqslant l \leqslant 10$
Reflections collected	3535	6389
Independent reflections	[R_{int} = 0.0189]	[R_{int} = 0.0249]
Completeness to θ = 25.00°	99.6%	99.80%
Absorption correction	multi-scan	multi-scan
Maximum and minimum transmission	1.00000 and 0.95485	1.00000 and 0.771
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	2162/1/163	2830/0/167
Goodness-of-fit on F^2	1.026	1.039
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0405, wR_2 = 0.0972 (for 1855)	R_1 = 0.0448, wR_2 = 0.1141 (for 2188)
R indices (all data)	R_1 = 0.0489, wR_2 = 0.1005	R_1 = 0.0619, wR_2 = 0.1204
Largest difference in peak and hole (e Å^{-3})	0.322 and −0.302	0.469 and −0.428

Table 3
Crystal data and structure refinement for **3** and **4**.

	Compound **3**	Compound **4**
Empirical formula	$C_{16}H_{30}Cl_2N_3O_2P$	$C_7H_{14}Cl_2N_3O_2P$
Formula weight	398.30	274.08
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.459(3)	12.454(1)
b (Å)	20.616(6)	9.3099(5)
c (Å)	9.542(3)	11.4867(9)
β (°)	98.088(3)	114.67(1)
V (Å^3)	2037.0(11)	1210.27(18)
Z	4	4
D_{calc} (g/cm^3)	1.299	1.504
Absorption coefficient (mm^{-1})	0.411	0.654
F(0 0 0)	848	568
Crystal size (mm^3)	0.29 × 0.20 × 0.08	0.17 × 0.07 × 0.05
Crystal color/habit	colorless/prism	colorless/prism
θ Range for data collection (°)	3.6–25.0	3.6–25.0
Index ranges	$-12 \leqslant h \leqslant 9$ $-24 \leqslant k \leqslant 23$ $-11 \leqslant l \leqslant 10$	$-14 \leqslant h \leqslant 10$ $-11 \leqslant k \leqslant 9$ $-13 \leqslant l \leqslant 13$
Reflections collected	7700	4457
Independent reflections	[R_{int} = 0.0205]	[R_{int} = 0.0149]
Completeness to θ = 25.00°	99.70%	99.80%
Absorption correction	multi-scan	multi-scan
Maximum and minimum transmission	1.00000 and 0.97201	1.00000 and 0.98063
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3584/0/219	2121/0/138
Goodness-of-fit on F^2	1.04	1.06
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0423, wR_2 = 0.1091 (for 2648)	R_1 = 0.0403, wR_2 = 0.1051 (for 1716)
R indices (all data)	R_1 = 0.0616, wR_2 = 0.1138	R_1 = 0.0521, wR_2 = 0.1093
Largest difference in peak and hole (e Å^{-3})	0.254 and −0.275	0.607 and −0.416

Table 4
Assignment of ^{13}C NMR signals for compound **3** by comparing the data of 4 analogous compounds with the formula P(O)[NHC(O)R][N(X)(C_6H_{11})]$_2$ [X = CH_3, R = CCl_2H (**3**) and C_6H_4(4- NO_2) (**A**); X = H, R = CCl_2H (**B**) and C_6H_4(4-NO_2) (**C**)]; "*n*" is the label of the carbon atom in the scheme, the other N(X)(C_6H_{11}) moiety is not drawing for clarity.



Compound **3**	Compound A	*n*	Compound B	Compound C	*n*
24.99	25.13	4	24.50	24.71	3 or 5
25.58	25.72 (^3J(P,C) = 3.1 Hz)	2 or 6	25.05	24.78	3 or 5
27.19 (^3J(P,C) = 4.7 Hz)	27.57 (^3J(P,C) = 4.7 Hz)	2 or 6	30.31	25.14	4
30.20	30.29	3 or 5	34.87 (^3J(P,C) = 4.4 Hz)	34.99 (^3J(P,C) = 3.9 Hz)	2 or 6
30.22	30.30	3 or 5	35.24 (^3J(P,C) = 5.5 Hz)	35.26 (^3J(P,C) = 6.0 Hz)	2 or 6
30.26 (^2J(P,C) = 3.4 Hz)	30.43 (^2J(P,C) = 3.4 Hz)	7	–	–	–
54.26 (^2J(P,C) = 4.5 Hz)	54.31 (^2J(P,C) = 4.4 Hz)	1	49.30	49.32	1

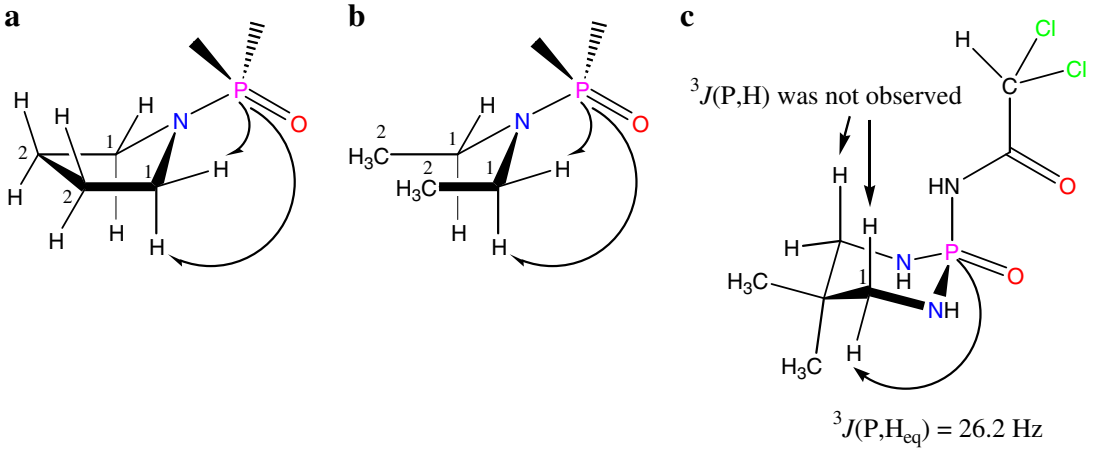
3. Results and discussion

3.1. Spectroscopic characterization

In compounds **1**–**4**, the ^{31}P NMR chemical shifts are revealed to be in the range 0.30 (compound **4**) to 12.27 ppm (compound **3**). The proton of the C(O)NHP(O) skeleton appears as a doublet signal only in **3** (^2J(P,H) = 7.2 Hz), whereas this splitting is not observed in the other compounds. The multiplet signals in the ^1H NMR spectra of **1** and **2**, resulting from the simultaneous ^3J(P,H), ^3J(H,H) and ^2J(H,H) coupling constants, at 1.74 and 2.97–3.04 ppm are respectively related to the H atoms bonded to C^1 in the NC_4H_8 and $N(C_2H_5)_2$ groups (Scheme 1a and b). The related signals of H_{axial} and $H_{equatorial}$ in **4** (Scheme 1c) are distinguished by their different splitting patterns. Considering the Karplus equation [71] and the different torsion angles for P–N–C–H_{axial} and P–N–C–$H_{equatorial}$ (about ±70° and ±170° [10]), the signal at 2.58 ppm is assigned to $H_{equatorial}$ with $^3J(PNCH_{equatorial})$ = 26.2 Hz, which is more than the ^3J(PNCH) values for acyclic phosphoramidates [16]. The P–H_{axial} coupling was not observed in this compound. Each carbon atom of the NC_4H_8, $N(C_2H_5)_2$ and $NHCH_2C(CH_3)_2CH_2NH$ moieties, with two or three bond separations from the corresponding P atom, appear as a doublet signal due to the P–C coupling. The $N(CH_3)(C_6H_{11})$ moiety in **3** shows seven magnetically different carbon atoms, the assignment of which was done by comparing their shifts to the ^{13}C NMR spectra of the analogous CPAs [18,72], Table 4. As the aliphatic moieties of phosphoramidate compounds do not usually show ^nJ(P,C) for $n > 3$, the doublet signals at 27.19, 30.26 and 54.26 ppm are assigned to $C^{2\ or\ 6}$ ($n = 3$), C^7 and C^1 ($n = 2$), Scheme of Table 4. The five-membered amide ring in **1** and the acyclic amide in **2**, which have equal numbers of C atoms, show relatively equal ^2J(P,C) coupling constants (4.9 Hz in **1** and 5.0 Hz in **2**); whereas the ^3J(P,C) value is 8.3 Hz in **1** and 2.3 Hz in **2**. So $^3J(P,C) > {}^2J(P,C)$ in **1** and while there is a *vice versa* relation in **2**. Compound **4**, with a six-membered heterocyclic moiety containing a P atom, shows $^3J(P,C) = 4.8\ Hz > {}^2J(P,C) = 2.1$ Hz. The C atoms of the CCl_2H unit in compounds **1**–**4** exhibit splitting by the corresponding P atoms, the ^3J(P,C) values of which are in the range 8.9–11.2 Hz.

3.2. X-ray crystallography

The molecular structures of compounds **1**–**4** are shown in Figs. 1–4. The P atoms have a distorted tetrahedral configuration



Scheme 1. The hydrogen atoms bonded to C^1 in compounds **1** (a) and **2** (b) are coupled to the related P atom. Only H_{eq} in **4** (c) shows a ^3J(P,H) coupling constant.

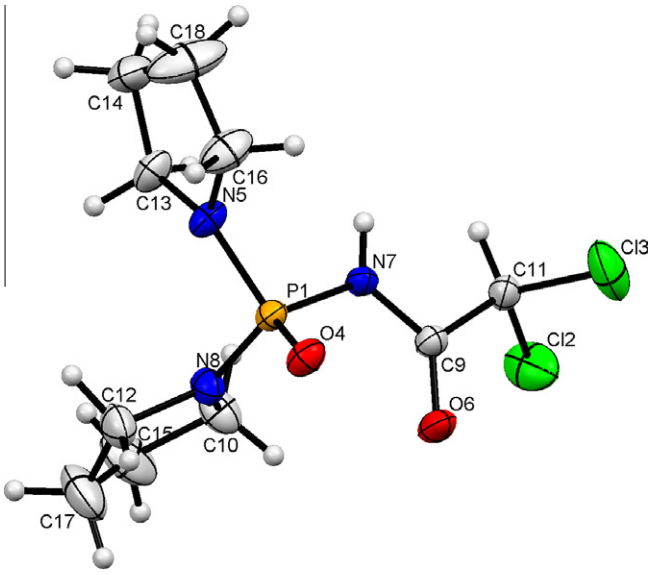


Fig. 1. Molecular structure and atom labeling scheme for compound **1** with displacement ellipsoids at the 30% probability level.

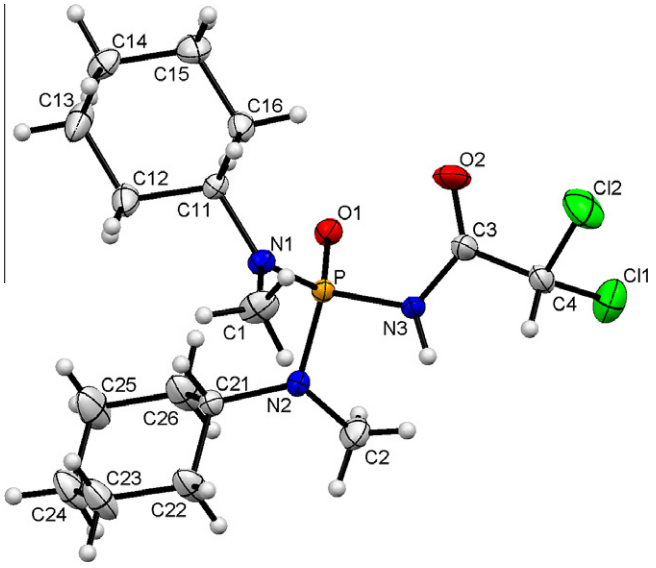


Fig. 3. Molecular structure and atom labeling scheme for compound **3** with displacement ellipsoids at the 30% probability level.

with bond angles in the range 103.44(16)–115.41(16)° around the P atom of **1**, 104.33(10)–113.72(10)° for **2**, 99.79(9)–118.17(9)° for **3** and 103.57(11)–116.07(12)° for **4**. The P–N_{amide} distances of 1.623(3) and 1.626(3) Å for **1**, 1.631(2) and 1.636(2) Å for **2**, 1.626(2) and 1.640(2) Å for **3** and 1.618(3) and 1.627(2) Å for **4** are significantly shorter than the related P–$N_{C(O)NHP(O)}$ bond distance. Selected bond lengths and angles for **1**–**4** are presented in Table 5, and the hydrogen bonds geometries are summarized in Table 6. The phosphoryl and carbonyl groups adopt a *gauche* position with respect to each other in **1**–**4**. However, an *anti* orientation has been observed for most of the reported CPAs. Considering this work, the non-*anti* orientation has been found only for 14 structures of the reported 95 CPAs (entries 2, 17, 18, 33, 44, 60, 65, 82, 83, 86–89 and 95 in Table 1). The |O=P–N–C| dihedral angles are in the range of 180.0(1)–151.1(4)° and 62.3(3)–46.1(2)° for *anti* and *gauche* orientations respectively, Table 1. An interesting point in this work is the *gauche* orientation in **1**–**3**; whereas the previously reported CPAs containing similar NC_4H_8, $N(C_2H_5)_2$ and $N(CH_3)(C_6H_{11})$ amide moieties appeared with *anti* orientations, Table 1. So, the substituent amide attached to the phosphoryl group exerts a minor effect on the conformational properties, and the conformational inversion may be attributed to the packing effect. All the reported diazaphosphorinanes (entries 2 and 18, Table 1) having a C(O)NHP(O) skeleton, similar to **4** (entry 17), have a non-*anti* orientation.

3.3. Pattern of H-bonds in CPAs

Usually, the environment of each nitrogen atom bonded to phosphorus in a CPA compound is almost planar; so these atoms do not form any HBs as an acceptor, showing their low Lewis-base character. Therefore, two different problems may be considered when a primary or a secondary amine is used in the preparation of CPAs as follows: (a) compounds with two H-acceptors and one H-donor site and (b) compounds with two H-acceptors and three H-donors. The known motifs in the crystal packing of CPAs are shown in Scheme 2.

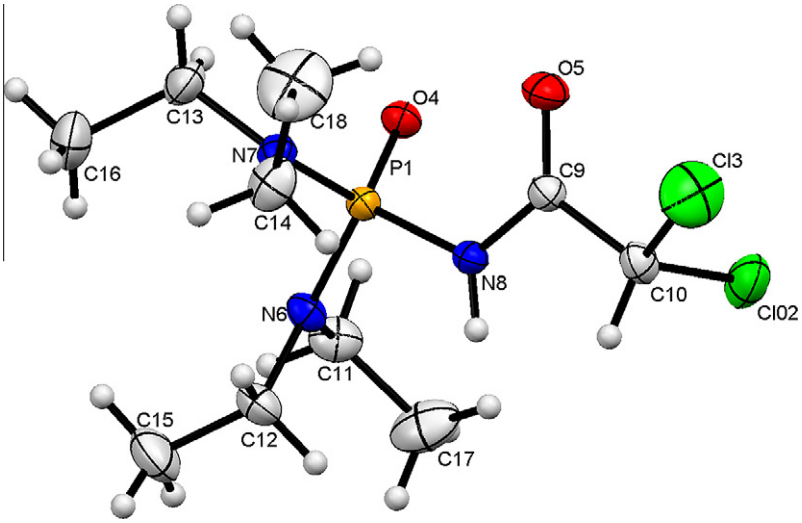


Fig. 2. Molecular structure and atom labeling scheme for compound **2** with displacement ellipsoids at the 30% probability level.

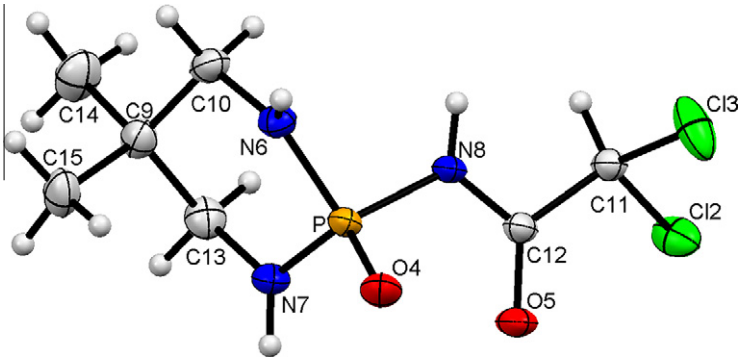


Fig. 4. Molecular structure and atom labeling scheme for compound **4** with displacement ellipsoids at the 30% probability level.

Table 5
Selected bond distances (Å) and angles (°) for compounds **1**–**4**.

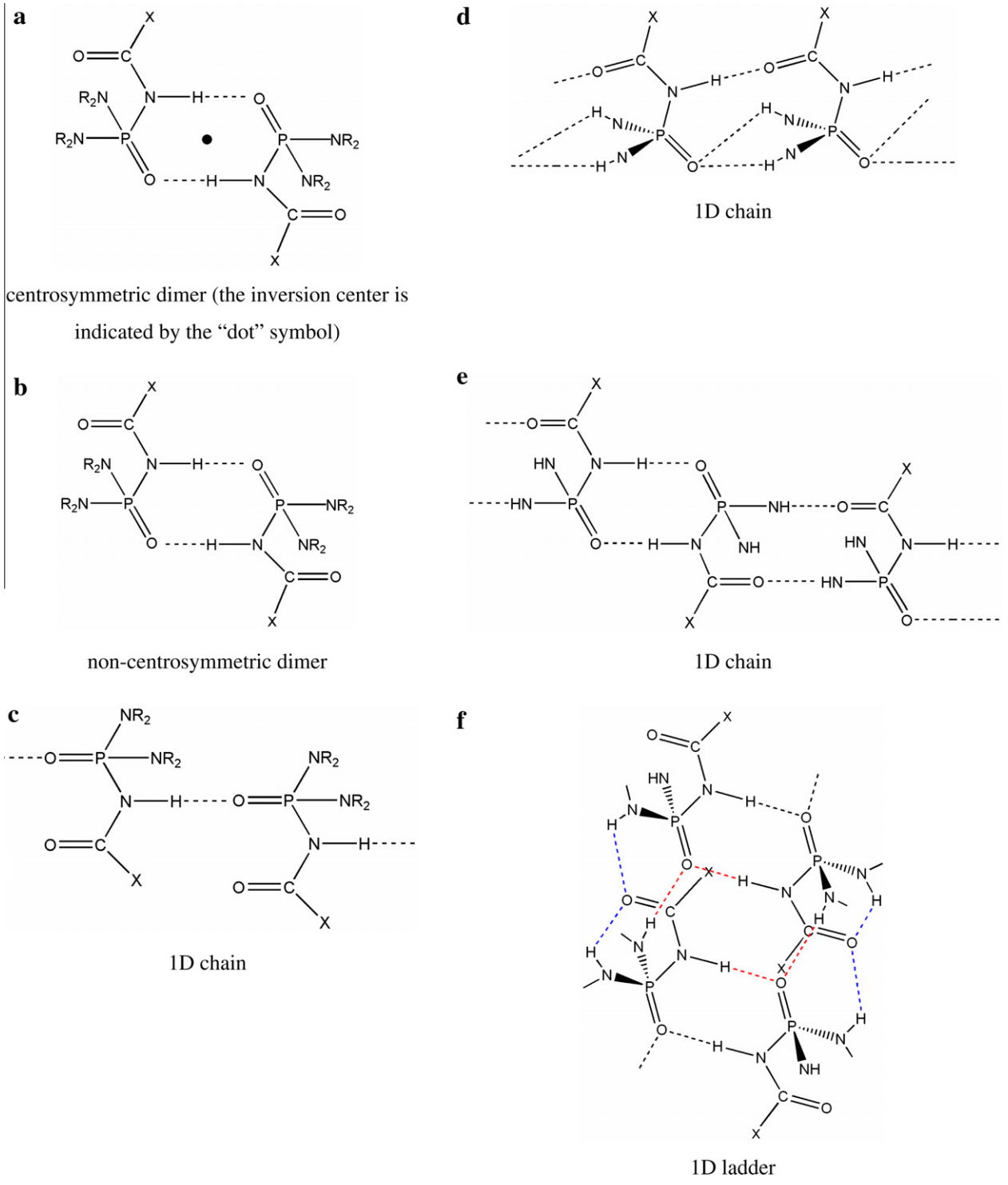
	1	**2**	**3**	**4**
Length				
P=O	1.474(3)	1.4760(18)	1.4742(17)	1.470(2)
P–$N_{C(O)NHP(O)}$	1.695(3)	1.690(2)	1.6926(18)	1.714(2)
P–$N_{(1)amide}$	1.623(3)	1.631(2)	1.6261(17)	1.618(2)
P–$N_{(2)amide}$	1.626(3)	1.636(2)	1.6397(19)	1.627(2)
C=O	1.220(4)	1.211(3)	1.199(3)	1.220(3)
C–$N_{C(O)NHP(O)}$	1.345(5)	1.356(3)	1.357(3)	1.346(3)
Angles				
O=P–$N_{(1)amide}$	115.41(16)	113.72(10)	112.02(9)	114.41(12)
O=P–$N_{(2)amide}$	111.57(16)	110.72(10)	118.17(9)	116.07(12)
O=P–$N_{C(O)NHP(O)}$	112.49(14)	112.73(10)	112.16(9)	110.13(12)
N_{amide}–P–N_{amide}	107.35(16)	109.83(11)	106.11(9)	103.58(12)
$N_{(1)amide}$–P–$N_{C(O)NHP(O)}$	103.44(16)	104.33(10)	107.48(10)	108.23(12)
$N_{(2)amide}$–P–$N_{C(O)NHP(O)}$	105.82(15)	105.00(10)	99.79(9)	103.57(11)
P–$N_{C(O)NHP(O)}$–C	123.6(2)	123.26(17)	123.35(15)	122.69(17)
N–C=O	125.0(3)	124.8(2)	125.1(2)	124.4(2)
Torsion angles				
O=P–$N_{C(O)NHP(O)}$–C	56.2(3)	51.4(2)	46.1(2)	61.3(2)
P–$N_{C(O)NHP(O)}$–C=O	0.9(5)	2.6(3)	0.3(4)	2.0(4)
C–$N_{C(O)NHP(O)}$–P–$N_{(1)amide}$	−69.0(3)	−72.5(2)	−77.4(2)	−64.4(2)
C–$N_{C(O)NHP(O)}$–P–$N_{(2)amide}$	178.2(3)	171.99(18)	172.1(2)	−173.9(2)

(a) Two H-acceptors–one H-donor: If a NHRR′ secondary amine is used for the preparation of CPAs, only the C(O)NHP(O) moiety with two H acceptors and one H donor site is involved in the HB pattern *via* NHP(O) (Scheme 2: "a", "b" and "c") without any cooperation of the C(O) group. This selectivity is attributed to the lower donicity of the carbonyl group compared to the phosphoryl group, which has been supported by X-ray crystallography [73], chemical calculations [74], spectroscopic studies [73] and a lower interaction with metal cations [75]. Moreover, two NRR′ moieties do not cooperate in HB. The *syn* position of P(O) *versus* NH leads to the formation of an H-bonded dimer *via* intermolecular PO···HN HBs as centrosymmetric (C_i symmetry, Scheme 2a) or non-centrosymmetric (C_1 symmetry, Scheme 2b). The C_1 symmetry is obtained when two symmetrically independent molecules are H-bonded, and in some cases when the inversion center is lost from disorder in a non-rigid moiety such as NC_4H_8 in the previously reported CPAs [17,31,47]. In the cases of the reported alkoxide or halide substituents being replaced by an amide group, pairs of intermolecular N–H···O(P) hydrogen bonds form centrosymmetric dimers (entries 78 and 81 in Table 1). If the P(O) adopts an *anti* orientation *versus* NH (and *gauche versus* C=O), another H-bond pattern is obtained as an extended 1-D chain *via* intermolecular PO···HN hydrogen bond, which is observed for **1**–**3** (Scheme 2c).

(b) Two H-acceptors–three H-donors: Fig. 5 shows the different motifs in this category of CPAs. Two H-acceptors and three H-donors sites exist in RC(O)NHP(O)[NHR′]$_2$ molecules. The more acidic NH of the C(O)NHP(O) moiety usually contributes with P(O) in intermolecular hydrogen bonding, whereas the H atom of the NHR′ unit is involved with C(O) in a HB interaction (Scheme 2 e). However, the existence of a PO···HNR′ interaction has been observed for three CPAs as tri-centered PO[···$H_{C(O)NHP(O)}$N][···HNR′] (Scheme 2f, Fig. 5a [28] and Fig. 5e [13]) and PO[···HNR′][···HNR′] hydrogen bonding (Scheme 2d) [29], where the oxygen atom of the phosphoryl acts as a double H-acceptor. In most cases of the two H-acceptors–three H-donors scenario, the HBs lead to a 1-D chain. Different 1-D ladder with tetramer motifs are shown in Fig. 5a and b, and a view of a linear arrangement with two different kinds of motifs is given in Fig. 5e. Therefore, only two H-donors ($HN_{C(O)NHP(O)}$ and one of the HNR′) participate with two O atoms in the intermolecular HBs, the other HNR′ may act as three manners: (a) in an intramolecular HB with C(O), (b) in a weaker HB with P(O) as the above mentioned tri-centered HB and (c) without cooperation

Table 6
Hydrogen bonds for compounds **1**–**4** [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
Compound **1**				
N7–H7···O4 [$x-1/2, -y+1/2, z$]	0.86	1.96	2.811(4)	170.5
Compound **2**				
N8–H8···O4 [$x, -y+1/2, z-1/2$]	0.86	2.02	2.869(3)	169.1
Compound **3**				
N3–H3···O1 [$x, -y+1/2, z+1/2$]	0.86	2.02	2.833(3)	157.8
Compound **4**				
N6–H6···O5 [$-x+2, y-1/2, -z+3/2$]	0.86	2.48	3.004(3)	119.8
N7–H7···Cl2 [$-x+2, -y+1, -z+2$]	0.86	2.58	3.410(3)	163.2
N8–H8···O4 [$-x+2, y-1/2, -z+3/2$]	0.86	1.99	2.850(3)	175.0



Scheme 2. Observed HB patterns in the crystal network of CPAs: "R" represents a substituent group. The non-interacting moieties in the cases "d", "e" and "f" are not shown for clarity.

in any HB. One example reported a CPA molecule with a diazaphosphole (entry 1, Table 1) moiety with an *anti* conformation of P(O) *versus* C(O) which forms a 1-D H-bonded ladder arrangement.

Diazaphosphorinanes (entries 2, 17 and 18, Table 1) merely show a *gauche* orientation, in spite of all the reported CPAs in the category which are noted as "two H-acceptors–three H-donors". A layer arrangement has been observed with a cyclic tetramer [40] and a cyclic hexamer motif [10], whereas compound **4** exists as a 1-D chain (along the *b*-axis) through the synergistic effect between PO···HN (O4···N8 = 2.850(3) Å) and CO···HN (O5···N6 = 3.004(3) Å) HBs. Moreover, the O···O and Cl···Cl electrostatic interactions are responsible for the connection of 1-D hydrogen bonded chains into a 2-D arrangement, Fig. 6. In this situation, a weak N–H···Cl hydrogen bond also exists (N7···Cl2 = 3.410(3) Å). The O···O and Cl···Cl distances of 2.970(3) and 3.341(1) Å are slightly less than the corresponding sum of the van der Waals radii (3.04 and 3.5 Å [76]).

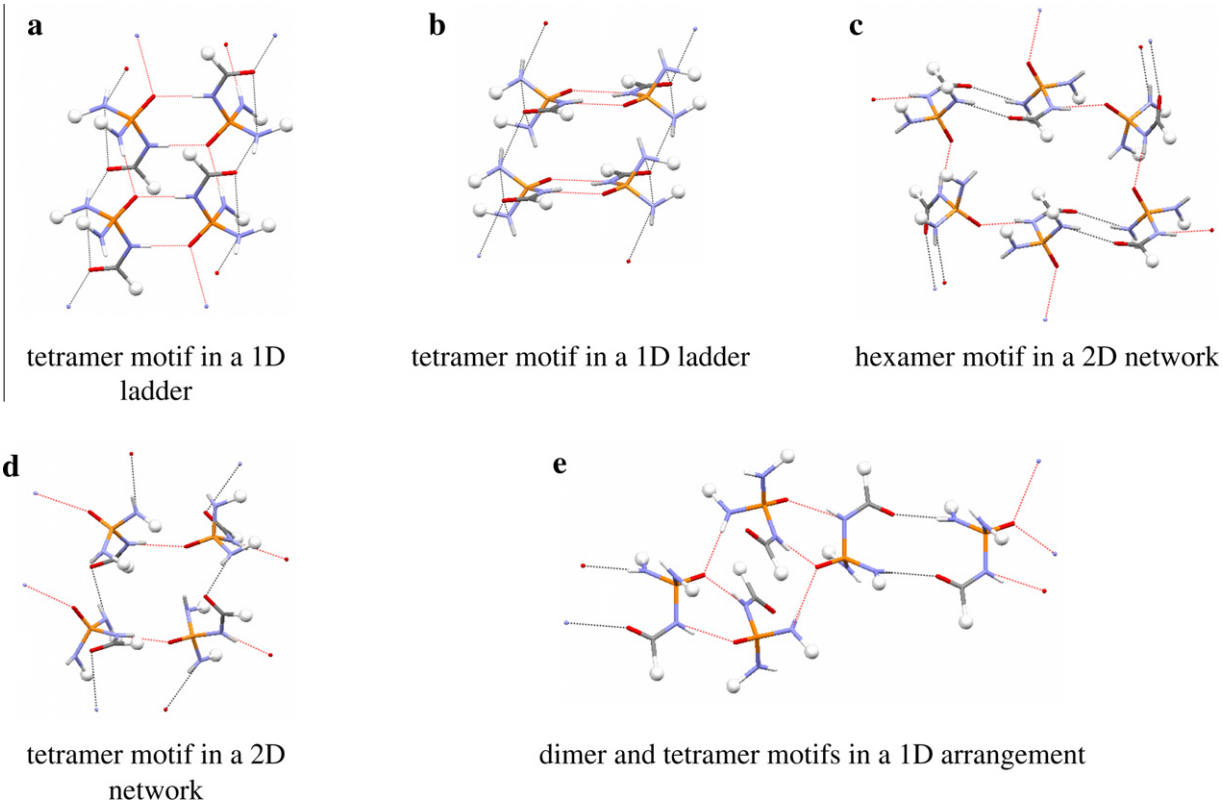


Fig. 5. Different motifs in the two H-acceptors–three H-donors problem.

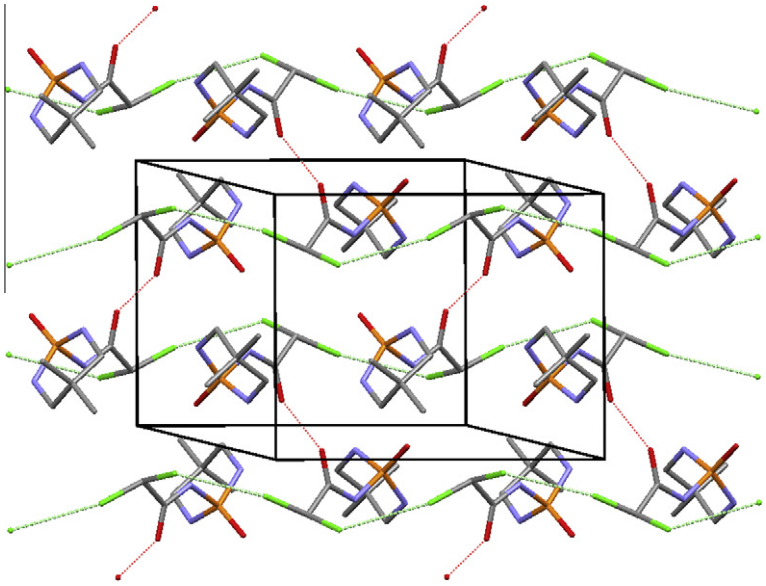


Fig. 6. Packing diagram of **4**; hydrogen atoms are omitted for clarity, the two dimensional structure (along the *bc* plane) is formed due to an O···O interaction (2.97 Å, red line) and a Cl···Cl interaction (3.34 Å, green line).

4. Conclusion

The preferable orientation of P(O) *versus* C(O) in CPAs is *anti* and among the 95 structures found, 14 structures (4 structures in the present work) show a non-*anti* orientation. Usually, the environment of the N atoms in CPAs is almost planar and they do not form any HBs as an acceptor; so on considering the participating atoms in HB interactions, two different classes are known, as follows:

(a) The two H-acceptors–one H-donor problem in molecules of the formula $RC(O)NHP(O)[NR'R'']_2$: there are two kinds of packing: 1-D chain for a *gauche* orientation and dimeric aggregates with C_i and C_1 symmetries for *anti*. The NH proton interacts with the oxygen atom of PO, whereas CO does not cooperate in HB.

(b) Two H-acceptors–three H-donors: only an *anti* situation has been found in acyclic molecules, $RC(O)NHP(O)[NHR']_2$, and one reported diazaphosphole with different kinds of linear H-bonded arrangements; a *gauche* orientation exists in three reported diazaphosphorinanes, RC(O)NHP(O)X (X = NHYNH, Y = $C_{10}H_6$, $CH_2C(CH_3)_2CH_2$) with 1-D and 2-D HB arrangements.

As a non-*anti* orientation may be required for the application of CPAs as chelating ligands, we wish to understand the factors affecting the preference of a non-*anti* orientation in the C(O)NHP(O) skeleton and are continuing work in this area.

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Appendix A. Supplementary data

CCDC 791342, 791344, 791343 and 791345 contains the supplementary crystallographic data for (**1**), (**2**), (**3**) and (**4**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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