

$^{2,3}J(\text{P},\text{X})$ [$\text{X} = \text{H}, \text{C}$] coupling constants dependency on the ring size, hybridization and substituents in new diazaphospholes and diazaphosphorinanes, NMR and X-ray crystallography studies

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Abstract

New diazaphospholes and diazaphosphorinanes (**1–12**) were synthesized and characterized by ^1H , ^{13}C , ^{31}P NMR, mass and IR spectroscopy and elemental analysis. The factors which affect the $^{2,3}J(\text{P},\text{X})$ ($\text{X}=\text{H}, \text{C}$) coupling constants in compounds **1–12** were considered. The ring size and the hybridization are parameters which change the $^2J(\text{PNH})$ coupling constant in the sequence benzodiazaphospholes > diazaphospholes > diazaphosphorinanes. Also, attention was paid to exocyclic substituent effects. Asymmetric diazaphospholes **5–8** indicate two different $^2J(\text{P},\text{C})_{\text{aliphatic}}$ values, and the more deshielded carbon atom has a higher coupling constant. The crystal structures of compounds **7** and **10–12** were determined by X-ray crystallography. Hydrogen bonds produce a 2D framework for compound **10**, which is composed of two symmetrically independent molecules. Compounds **7**, **11** and **12** exist as a polymeric chain, 2D framework and centrosymmetric dimer, respectively, which are made by hydrogen bonds.

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Keywords: Diazaphospholes; Diazaphosphorinanes; NMR; X-ray crystallography

1. Introduction

Diazaphospholes and diazaphosphorinanes are considered as important compounds due to their great applications in chemistry and medicine [1,2]. So far, a few structures [3,4] and coupling constant assignments of these compounds have been reported [3]. Stereochemistry, P–C coupling constants in 1,3,2-benzodiazaphospholes [5] and 2-oxo-, 2-thio-diazaphosphorinanes have been presented [6]. Phosphorus–hydrogen coupling constants in some diazaphospholes with three coordinated phosphorus atoms were studied [7]. To further investigate this area, the new diazaphospholes and diazaphosphorinanes **1–12** were syn-

thesized and characterized to find effective parameters for $^{2,3}J(\text{P},\text{X})$ coupling constants ($\text{X} = \text{H}, \text{C}$).

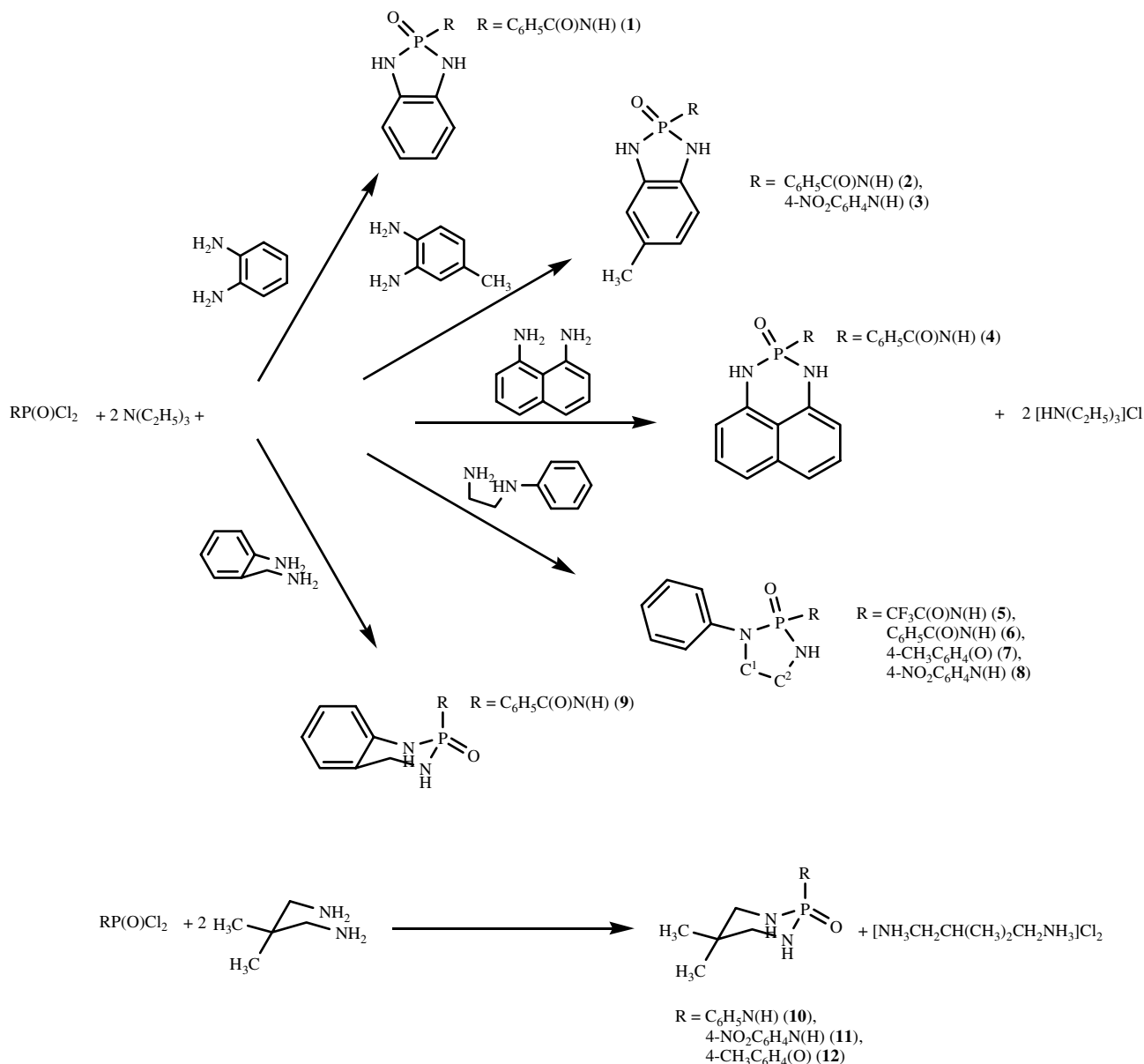
2. Experimental

2.1. Spectroscopic measurements

NMR spectra of compounds **1–12** were obtained from their prepared solutions, which must be fresh. ^1H and ^{13}C NMR spectra were recorded on a Bruker (Avance DRS) 500 spectrometer. ^1H and ^{13}C , and ^{31}P chemical shifts were determined relative to tetramethylsilane (TMS) and 85% H_3PO_4 as external standards, respectively, and HSQC ^1H – ^{15}N spectra to external TMS and CH_3 – NO_2 standards. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. High-resolution Mass spectra were obtained with a Shimadzu model QP-1100EX spectrometer (EI, 20 eV).

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Scheme 1. The preparation of compounds 1–12.

2.2. Syntheses

Syntheses of compounds 1–12 were performed by the reaction of *N*-benzoyl- [8], *N*-trifluoroacetyl- [9], *N*-phenyl- [10] and *N*-4-nitrophenyl- [11] phosphoramidic dichloride and (4-tolyl)-dichlorophosphate [12] with the corresponding amines in the presence of an HCl scavenger (triethylamine or an excess amount of the corresponding diamine).

2.3. X-ray measurements

X-ray data were collected on a Bruker SMART 1000 CCD single crystal diffractometer. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program [13].

The structures were refined with SHELXL-97 [14] by full-matrix least-squares on F^2 .

3. Results and discussion

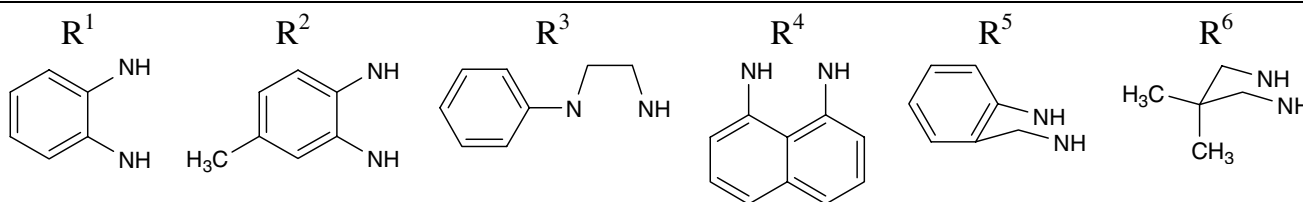
3.1. NMR study

Several new diazaphospholes and diazaphosphorinanes 1–12 (Scheme 1) were synthesized to study effective parameters for $^{2,3}J(P,X)$ coupling constants ($X = H, C$).

The effect of ring size on $^2J(PNH)$: Although the variation of the $^2J(PNH)$ coupling constant in acyclic phosphoramidates has been considered (in the range of 4–12 Hz) [15–17], less attention has been paid to diazaphospholes and diazaphosphorinanes. The 1H NMR spectrum of

Table 1
 ^{31}P chemical shifts (ppm) and $^2J(\text{PNH})$ (Hz) in compounds 1–14

No.	Compound	$^2J(\text{PNH})_{\text{endocyclic}}$	$^2J(\text{PNH})_{\text{exocyclic}}$	δ (^{31}P)
1	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^1$	17.9	8.4	13.2
2	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^2$	17.8, 18.0	6.5	13.7
3	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{N}(\text{H})\text{P}(\text{O})\text{R}^2$	17.1, 17.2	8.1	12.2
4	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^4$	5.0	9.4	-10.6
5	$\text{CF}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^3$	15.3	b	12.8
6	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^3$	14.8	6.7	14.2
7	$4\text{-CH}_3\text{-C}_6\text{H}_4\text{OP}(\text{O})\text{R}^3$	13.9		18.6
8	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{N}(\text{H})\text{P}(\text{O})\text{R}^3$	13.1	6.5	14.9
9	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^5$	4.6, 5.7	4.9	0.2
10	$\text{C}_6\text{H}_5\text{N}(\text{H})\text{P}(\text{O})\text{R}^6$	5.0	b	5.0
11	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{N}(\text{H})\text{P}(\text{O})\text{R}^6$	5.4	10.3	4.0
12	$4\text{-CH}_3\text{-C}_6\text{H}_4\text{OP}(\text{O})\text{R}^6$	5.2		7.6
13 ^a	$\text{C}_6\text{H}_5\text{OP}(\text{O})\text{R}^1$	15.0		
14 ^b	$\text{ClP}(\text{O})\text{R}^2$	11.2 and 11.3		1.2



^{a,b} For compounds 13 and 14 see Refs. [15a] and [15b], respectively.

^a ^{31}P chemical shift was not reported in Ref. [15a].

compound 1 shows a doublet at 8.58 ppm with a high value $^2J(\text{PNH})$ coupling constant (17.9 Hz) for two equivalent NH protons and a doublet at 9.96 ppm with $^2J(\text{PNH}) = 8.4$ Hz for the amidic proton. Also, in diazaphospholes 2 and 3, the two non-equivalent NH protons (of the ring) indicate two high value $^2J(\text{PNH})$ coupling constants, Table 1. Compound 4 shows a drastically reduction ($^2J(\text{PNH}) = 5.0$ Hz) on increasing the ring size (from five to six). ^1H NMR spectra of diazaphospholes 5–8 show $^2J(\text{PNH})$ values in the range 13.1–15.3 Hz, which are reduced in comparison with compounds 1–3. A further reduction was obtained by increasing the ring size in cyclic aliphatic compounds 10–12, Table 1. A major part of the observed changes more likely results from conformational averaging of the orientation of bond vectors in the six-member rings when compared with the more fixed orientation of bond vectors in the five-member rings.

The effect of hybridization on $^2J(\text{PNH})$: In compounds 1–3 the endocyclic nitrogen atoms of the NH groups are bonded to the carbon atoms with sp^2 hybridization in five-membered rings, but in compounds 5–8 they are bonded to sp^3 carbon atoms. $^2J(\text{PNH})$ in compounds 5–8 are lower than those of compounds 1–3. In molecule 9, possessing two various NH groups, one of the two NH protons is bonded to a $\text{C}(\text{sp}^2)$ atom and the other to $\text{C}(\text{sp}^3)$ in a six-membered ring. The ^1H NMR spectrum shows two different coupling constants, $^2J(\text{PNH}) = 5.7$ Hz (sp^2) and $^2J(\text{PNH}) = 4.6$ Hz (sp^3).

The effect of the substituent on $^2J(\text{PNH})$: A comparison of the benzodiazaphospholes 1–3, 13 and 14 indicates a substituent effect (of the exocyclic group) on $^2J(\text{PN}_{\text{endocyclic}}\text{H})$, in the range of 18.0 Hz (for 1 with a

$\text{C}_6\text{H}_5\text{C}(\text{O})\text{NH}$ moiety) to 11.2 Hz (for 14 with a Cl substituent), Table 1. Furthermore, in diazaphospholes 5–8, the highest value of $^2J(\text{PNH})$ is observed for compound 5 with a $\text{CF}_3\text{C}(\text{O})\text{N}(\text{H})$ electronegative moiety.

$^3J(\text{PNCH})$ coupling constants: In the asymmetric diazaphospholes 5–8, four H atoms of the $-\text{CH}_2\text{CH}_2-$ moiety appear at different chemical shifts with various $^3J(\text{PNCH})_{\text{aliphatic}}$ coupling constants. Two benzylic protons of diazaphosphorinane 9 are diastereotopic and have different $^3J(\text{PNCH})$ coupling constants depending on the dihedral angles with the P atom. ^1H NMR spectra of

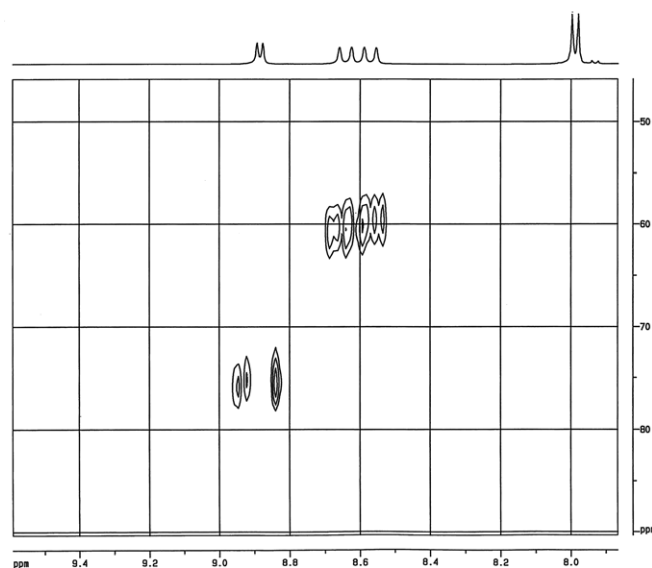


Fig. 1. 2D HSQC ^1H - ^{15}N spectrum for compound 3.

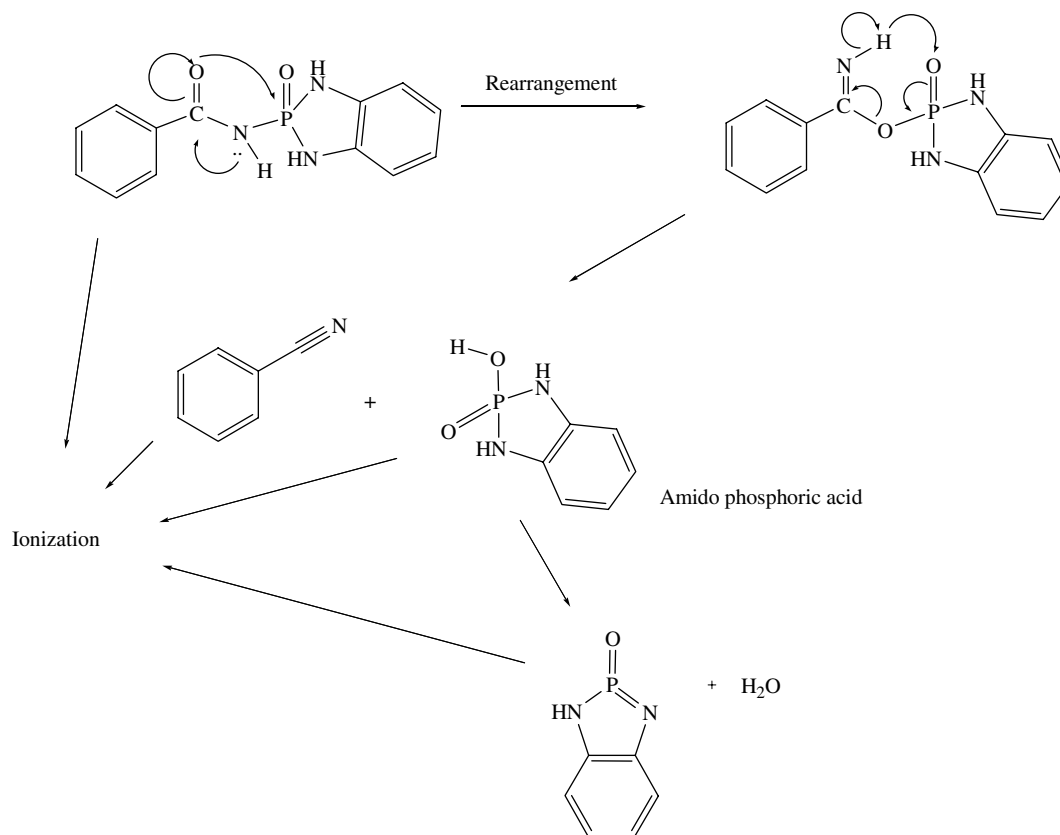
Scheme 2. Fragmentation pathway in the mass spectrum of compound **1**.

Table 2

The intensities of $\text{C}_6\text{H}_5\text{CN}^+$ ($m/z = 103$) and other fragments in mass spectra of compounds **1**, **2**, **4**, **6** and **9** (the numbers in parentheses are intensities of these fragments)

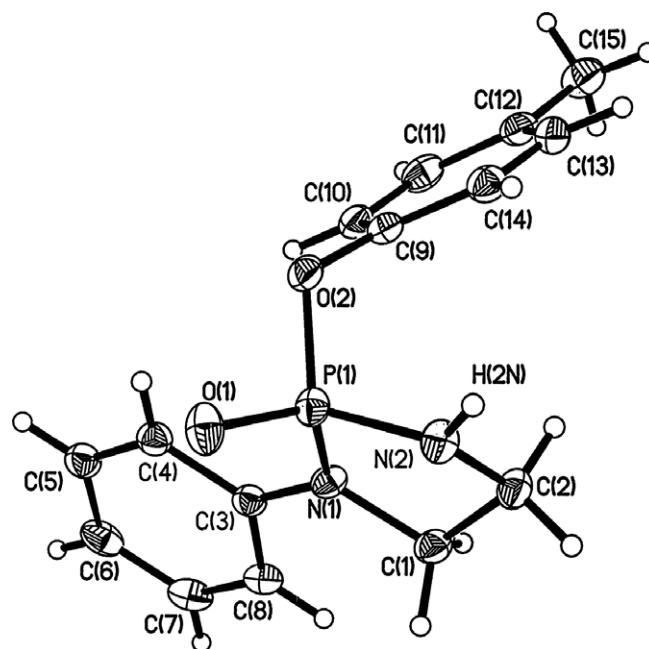
Compound	$\text{C}_6\text{H}_5\text{CN}^+$	Amidophosphoric acid	Amidophosphoric acid- H_2O
1	69	170(100)	152(59)
2	100	184(14)	166(2)
4	100	220(65)	202(45)
6	100	184(9)	166(3)
9	100	198(55)	180(21)

compounds **10–12** show two different signals for H_{axial} and $\text{H}_{\text{equatorial}}$. The torsion angles of $\text{P–N–C–H}_{\text{axial}}$ and $\text{P–N–C–H}_{\text{equatorial}}$ are about $\pm 70^\circ$ and $\pm 170^\circ$, respectively, obtained from X-ray crystallography. Considering the Karplus equation [18], the values 24.8, 25.1 and 26.7 Hz are related to $^3J(\text{PNCH}_{\text{equatorial}})$ values in **10–12**. These values are larger than $^3J(\text{PNCH})$ values for acyclic phosphoramidates [15–17]. For H_{axial} , the coupling with the P atom was not observed.

Ring size influence on $^2J(\text{P}, \text{C})_{\text{aromatic}}$: Similar to the $^2J(\text{PNH})$ value, high values for $^2J(\text{P}, \text{C})_{\text{aromatic}}$ were observed for diazaphospholes **1–3** (about 14.0 Hz) which are larger than the values of acyclic phosphoramidates [19].

Deshielded carbon atoms and $^2J(\text{P}, \text{C})$: In compounds **5–8**, two different signals (and two different $^2J(\text{P}, \text{C})$ values)

appear for the aliphatic carbon atoms (C^1 and C^2 , Scheme 1) and the deshielded C^1 atoms show high values for $^2J(\text{P}, \text{C})$ due to the effect of the phenyl ring.

Fig. 2. Molecular structure and atom-labelling scheme for compound **7**, $(4\text{-CH}_3\text{-C}_6\text{H}_4\text{O})\text{P}(\text{O})[\text{NHCH}_2\text{CH}_2\text{N}(\text{C}_6\text{H}_5)]$ (50% probability ellipsoids).

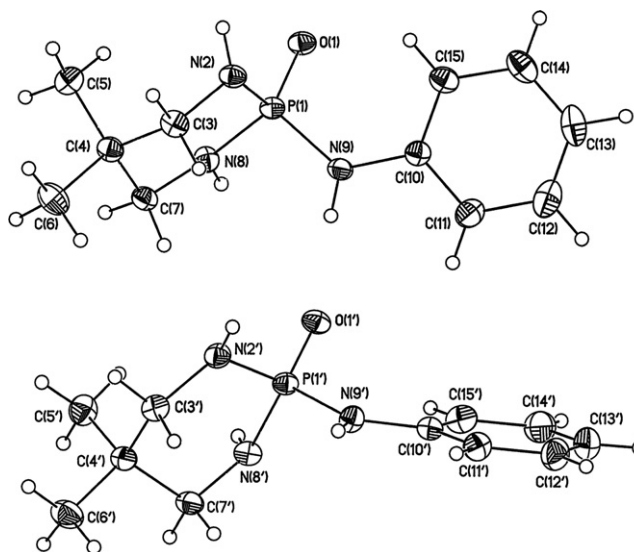


Fig. 3. Molecular structure and atom-labelling scheme for compound **10**, $C_6H_5N(H)P(O)[NHCH_2C(CH_3)_2CH_2NH]$ (50% probability ellipsoids).

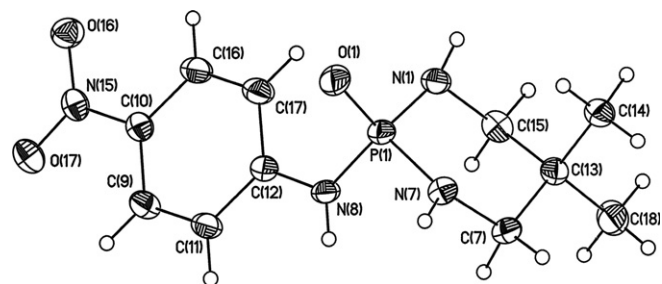


Fig. 4. Molecular structure and atom-labelling scheme for compound **11**, $4-NO_2-C_6H_4N(H)P(O)[NHCH_2C(CH_3)_2CH_2NH]$ (50% probability ellipsoids).

Substituent effect on $^2J(P,C)$: In compounds **5–8**, both $^2J(P,C^1)$ and $^2J(PNH)$ coupling constants vary with different substituents in the following order: $CF_3C(O)N(H) > C_6H_5C(O)N(H) > 4-CH_3C_6H_4-O > 4-NO_2-C_6H_4NH$. Similarly, the highest value of $^2J(P,C^2)$ was revealed for compound **5** with the $CF_3C(O)N(H)$ substituent. $^2J(P,C^2)$ values were observed in the sequence $CF_3C(O)N(H) > C_6H_5C(O)N(H) > 4-NO_2-C_6H_4NH > 4-CH_3C_6H_4-O$.

Table 3
Crystallographic data for compounds **7** and **10–12**

	7	10	11	12
Empirical formula	$C_{15}H_{17}N_2O_2P$	$C_{11}H_{18}N_3OP$	$C_{11}H_{17}N_4O_3P$	$C_{12}H_{19}N_2O_2P$
Formula weight	288.28	239.25	284.26	254.26
Temperature (K)	120(2)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	orthorhombic, $Pna2(1)$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	15.348(4)	10.853(3)	14.084(3)	11.8400(11)
<i>b</i> (Å)	13.981(3)	9.139(3)	9.6692(18)	8.9365(8)
<i>c</i> (Å)	6.6695(16)	25.091(7)	9.8710(19)	12.7536(12)
α (°)	90.0	90.0	90.0	90.0
β (°)	90.0	98.274(6)	92.759(4)	104.122(2)
γ (°)	90.0	90.0	90.0	90.0
<i>V</i> (Å ³)	1431.1(6)	2462.8(11)	1342.6(4)	1308.7(2)
<i>Z</i> , calculated density (Mg m ⁻³)	4, 1.338	8, 1.291	4, 1.406	4, 1.291
Absorption coefficient (mm ⁻¹)	0.195	0.208	0.215	0.203
<i>F</i> (000)	608	1024	600	544
Crystal size (mm ³)	0.50 × 0.35 × 0.25	0.35 × 0.29 × 0.21	0.32 × 0.29 × 0.21	0.4 × 0.3 × 0.08
θ Range for data collection (°)	1.97–27.50	1.90–30.01	2.56–30.06	2.81–30.05
Limiting indices	$-19 \leq h \leq 19$, $-18 \leq k \leq 18$, $-8 \leq l \leq 8$	$-15 \leq h \leq 15$, $-12 \leq k \leq 11$, $-35 \leq l \leq 34$	$-19 \leq h \leq 19$, $-13 \leq k \leq 12$, $-13 \leq l \leq 13$	$-14 \leq h \leq 16$, $-12 \leq k \leq 11$, $-17 \leq l \leq 17$
Reflections collected/unique [<i>R</i> _{int}]	9981/2943 [0.0299]	22982/7118 [0.0485]	15405/3901 [0.0332]	9946/3746 [0.0270]
Completeness to θ (%)	(27.50°) 93.7	(30.01°) 99.1	(30.06°) 99.0	(30.05°) 97.9
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2943/1/181	7118/0/317	3901/0/174	3746/0/154
Goodness-of-fit on <i>F</i> ²	1.035	1.040	1.009	1.002
Final <i>R</i> indices	$R_1 = 0.0388$, $wR_2 = 0.0821$	$R_1 = 0.0559$, $wR_2 = 0.1278$	$R_1 = 0.0546$, $wR_2 = 0.1237$	$R_1 = 0.0482$, $wR_2 = 0.1141$
<i>R</i> indices (all data)	$R_1 = 0.0495$, $wR_2 = 0.0858$	$R_1 = 0.0700$, $wR_2 = 0.1342$	$R_1 = 0.0697$, $wR_2 = 0.1301$	$R_1 = 0.0536$, $wR_2 = 0.1175$
Absolute structure parameter	0.09(9)			
Maximum and minimum transmission	0.928 and 0.741	0.862203 and 0.600168	0.801651 and 0.679937	0.984 and 0.923
Largest difference in peak and hole (e Å ⁻³)	0.359 and -0.189	0.659 and -0.405	0.512 and -0.376	0.384 and -0.337

Table 4
Selected bond lengths (Å) and angles (°) for compounds **7** and **10–12**

7	10		11		12		
P(1)–O(1)	1.4724(17)	P(1)–O(1)	1.4883(13)	P(1)–O(1)	1.4730(14)	P(1)–O(1)	1.4737(10)
P(1)–O(2)	1.6140(15)	P(1)–N(2)	1.6512(15)	P(1)–N(1)	1.6386(17)	P(1)–N(1)	1.6191(12)
P(1)–N(1)	1.6718(16)	P(1)–N(9)	1.6522(16)	P(1)–N(7)	1.6325(16)	P(1)–O(2)	1.6226(10)
P(1)–N(2)	1.6142(19)	P(1')–O(1')	1.4862(13)	P(1)–N(8)	1.6708(15)	P(1)–N(2)	1.6275(13)
O(2)–C(9)	1.399(3)	P(1')–N(9')	1.6537(16)	O(16)–N(15)	1.245(2)	O(2)–C(6)	1.4103(17)
N(1)–P(1)–N(2)	95.82(9)	O(1)–P(1)–N(2)	109.69(8)	O(1)–P(1)–N(1)	112.06(8)	O(1)–P(1)–N(1)	115.28(6)
O(1)–P(1)–O(2)	105.25(9)	O(1)–P(1)–N(9)	111.37(8)	O(1)–P(1)–N(7)	114.60(9)	O(1)–P(1)–O(2)	111.65(6)
O(1)–P(1)–N(1)	118.69(9)	N(2)–P(1)–N(9)	110.11(8)	O(1)–P(1)–N(8)	113.35(8)	N(1)–P(1)–O(2)	104.39(6)
O(2)–P(1)–N(1)	106.89(8)	O(1')–P(1')–N(2')	114.93(8)	N(1)–P(1)–N(7)	105.41(8)	O(1)–P(1)–N(2)	114.92(6)
P(1)–O(2)–C(9)	121.92(12)	O(1')–P(1')–N(8')	109.74(8)	N(1)–P(1)–N(8)	105.16(8)	N(1)–P(1)–N(2)	106.41(6)
P(1)–N(1)–C(3)	125.65(14)	N(8')–P(1')–N(2')	105.62(8)	N(7)–P(1)–N(8)	105.45(8)	O(2)–P(1)–N(2)	102.95(6)
P(1)–N(1)–C(1)	111.23(13)	O(1')–P(1')–N(9')	111.52(8)	P(1)–N(8)–C(12)	126.54(12)	C(6)–O(2)–P(1)	118.56(8)
P(1)–N(2)–C(2)	111.80(14)	N(2')–P(1')–N(9')	104.51(8)	P(1)–N(7)–C(7)	119.74(13)	C(1)–N(1)–P(1)	117.89(9)

$^{2,3}J(P,C)_{\text{aliphatic}}$: In compounds **10–12**, $^3J(P,C)_{\text{aliphatic}} > ^2J(P,C)_{\text{aliphatic}}$. Also, $^2J(P,C)_{\text{aliphatic}}$ in compound **7** is greater than that of compound **12**, due to the ring size effect.

^{31}P NMR study: In diazaphospholes with a five-membered ring heterocycle, the P atoms are more deshielded than those of diazaphosphorinanes with a six-membered ring (Table 1). By considering the high value coupling constants in diazaphospholes, it seems that the deshielded phosphorus atoms in diazaphospholes have a significant interaction with the H atoms.

$2D$ HSQC 1H – ^{15}N : The 2D HSQC 1H – ^{15}N spectrum for **3** (Fig. 1) indicates the endocyclic N atoms are observed at 59.4 and 60.1 ppm, and NO₂ and NH nitrogen atoms in the 4-NO₂C₆H₄NH moiety are at 75.0 and 75.2 ppm. The spectra of compounds **10–12** showed that the aliphatic N atoms appear upfield (at about 20 ppm) and the aromatic N atoms of C₆H₅NH and 4-NO₂C₆H₄NH groups (in **10**, **11**) are downfield (at 61.4 and 75.4 ppm, respectively).

4. Mass spectroscopy investigation

Mass spectra of compounds with the general formula C₆H₅C(O)N(H)P(O)R (**1**, **2**, **4**, **6** and **9**) show a fragment ion at $m/z = 103$, which in compounds **2**, **4**, **6** and **9** are base peaks, and is assigned to PhCN⁺. In earlier work, Lapidot and Samuel reported on the pyrolysis of *N*-benzoyl phosphoramidates that led to PhCN and the related amidophosphoric acids [20]. Mass spectra of these compounds also show the presence of related amidophosphoric acid cations, with high intensity. In compound **1**, the cation $\overline{P(O)(OH)(2-NH-C_6H_4-NH)^+}$ is the base peak. It is assumed that the fragmentation pathway contains P–N cleavage and P–O formation and then the rearranged molecule is cleaved in a pseudo McLafferty mechanism to PhCN and the related amidophosphoric acid cations, see Scheme 2 for compound **1**. The m/z values and the intensities of the amidophosphoric acid fragments of these compounds are given in Table 2. In the next step, a water molecule is removed from the amidophosphoric acid.

4.1. X-ray crystallography

Single crystals of **7** were obtained from a mixture of methanol/acetonitrile and those of **10–12** from a mixture of methanol/*n*-heptane, at room temperature. The structures of these compounds are shown in Figs. 2–5, respectively. Crystallographic data and structure refinement parameters are listed in Table 3 and selected bond lengths and angles are presented in Table 4. The hydrogen bonding data are given in Table 5.

The nitrogen atom environments in the structure of **7** are nearly planar. The sum of the surrounding angles around N(1) and N(2) are slightly lower than sp² angles, 358.38° and 356.31°, respectively. P–N bonds in this molecule are smaller than a P–N single bond (1.77 Å) [21]; also, P–N_{aliphatic} (1.614 Å) is stronger than P–N_{aromatic} (1.672 Å). The angle P(1)–O(2)–C(9) is 121.92(12)° (sp² angle). Compound **10** exists as two independent molecules (**10** and **10'**) in the crystal lattice. The endocyclic nitrogen atoms in compounds **10–12** are distorted from planarity. The deviations from planarity in these structures are larger than that of diazaphosphole **7** and previously reported phosporamidates [19,22]. The sum of the angles around the endocyclic N atoms in compounds **10–12** (that are in the range of 352.76°–338.59°) are lower than those of diazaphosphole **7**. The exocyclic nitrogen atoms of aniline and nitroaniline groups are relatively planar. P–N bonds in these molecules are in the range 1.6708(15)–1.6192(12) Å (smaller than a P–N single bond). The P=O bond lengths in these molecules are slightly longer than the PO double bond length (1.45 Å) [21]. This bond is in an equatorial position. The equatorial preference for the P=O bond was previously observed by Bentruide [23] and was attributed to the overlap of the endocyclic nitrogen p-orbital with the P–N(exocyclic) anti-bonding orbital.

Hydrogen bonds: Compound **7** forms an infinite zigzag chain via an intermolecular –P=O...H–N– hydrogen bond. In diazaphosphorinane **10**, each independent molecule is connected to its symmetrically similar molecule via two equal –P=O...H–N– hydrogen bonds and produces a centrosymmetric dimer in the crystal lattice, P(1)–

Table 5
Hydrogen bonds D–H...A for compounds **7** and **10–12**

Compound	D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	∠DHA	<i>d</i> (D...A)
7	N2–H2N...O1 [− <i>x</i> , − <i>y</i> + 1, <i>z</i> − 1/2]	0.936	1.916	170.42	2.843
10	N8–H8N'... O1' [− <i>x</i> , − <i>y</i> + 1, − <i>z</i>]	0.811	2.139	170.98	2.943
	N2–H2N...O1 [− <i>x</i> + 1, − <i>y</i> , − <i>z</i>]	0.888	2.078	167.51	2.950
	N8–H8N...N8' [− <i>x</i> , − <i>y</i> + 1, − <i>z</i>]	0.840	2.441	156.90	3.231
	N9'–H9N'...O1 [<i>x</i> , <i>y</i> + 1, <i>z</i>]	0.881	1.960	175.93	2.839
	N9–H9N...O1'	0.829	2.020	174.80	2.846
	N2'–H2N'...N2 [− <i>x</i> + 1, − <i>y</i> + 1, − <i>z</i>]	0.828	2.479	159.81	3.269
11	N8–H8N...O1 [− <i>x</i> , − <i>y</i> + 1/2, − <i>z</i> + 1/2]	0.806(2)	2.033(4)	165.57(1)	2.820(4)
	N1–H1N...O16 [− <i>x</i> + 1, − <i>y</i> , − <i>z</i> + 1]	0.854(2)	2.316(4)	161.97(1)	2.139(4)
	N7–H7N...O16 [− <i>x</i> + 1, − <i>y</i> + 1/2, − <i>z</i> + 3/2]	0.876(2)	2.279(4)	145.14(1)	3.039(4)
12	N1–H1N...O1 [− <i>x</i> + 1, − <i>y</i> + 2, − <i>z</i>]	0.86	1.99	176	2.841(2)
	N2–H2N...O2 [− <i>x</i> + 1, − <i>y</i> + 1, − <i>z</i>]	0.78	2.46	156	3.183(2)

O(1)...H(2N)–N(2) and P(1')–O(1')...H(8N')–N(8') hydrogen bonds in **10** and **10'**. These dimeric aggregates are connected to each other to form a 2D polymer. Each

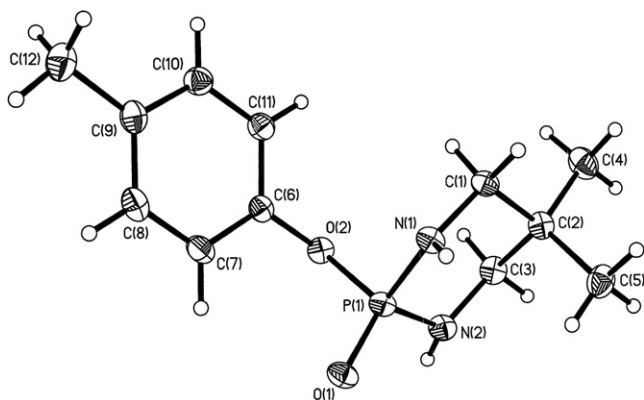


Fig. 5. Molecular structure and atom-labelling scheme for compound **12**, 4-CH₃-C₆H₄OP(O)(NHCH₂C(CH₃)₂CH₂NH) (50% probability ellipsoids).

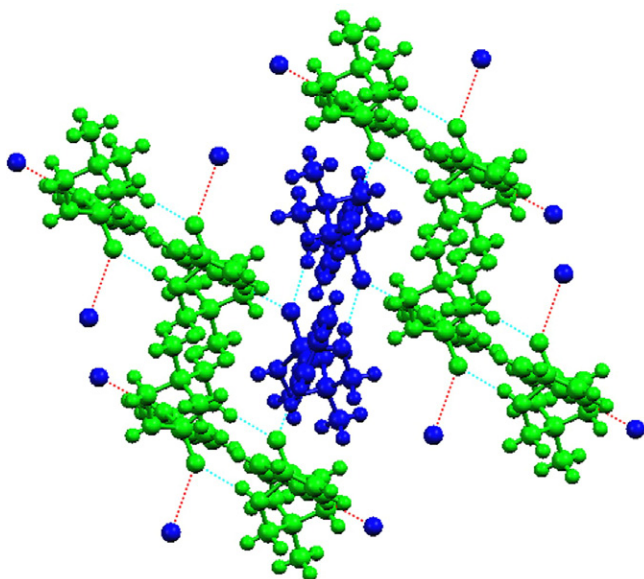


Fig. 6. Each dimer of **10'** is placed between four dimers of **10**.

dimer of **10** is connected to two dimers of **10'** by two equal P(1)–O(1)...H(9N')–N(9') H-bonds and then connected to the two other dimers of **10'** by two other equal P(1')–O(1')...H(9N)–N(9) H-bonds. Therefore, one dimer of **10** is placed between four dimers of **10'** and vice versa, Fig. 6. Furthermore two weak P(1')–N(8')...H(8N)–N(8) and P(1)–N(2)...H(2N')–N(2') H-bonds are produced in the packing. Compound **11** exists as a two dimensional polymer in the crystal lattice via –P=O...H–N– and –N–O...H–N– hydrogen bonds. Compound **12** forms centrosymmetric dimers via two equal P(1)–O(1)...H(1N)–N(1) hydrogen bonds and these dimers are connected via a weak H-bonds, P(1)–O(2)...H(2N)–N(2).

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Appendix A. Supplementary material

CCDC 247599, 247080, 247082 and 247081 contain the supplementary crystallographic data for **7** (C₁₅H₁₇N₂O₂P₁), **10** (C₁₁H₁₈N₃OP), **11** (C₁₁H₁₇N₄O₃P) and **12** (C₁₂H₁₉N₂O₂P). 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. Spectroscopic data of compounds **1–12** can be obtained as supplementary material. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.09.092.

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