Spectrochimica Acta Part A 75 (2010) 1236–1243

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Solid state and solution study of some phosphoramidate derivatives containing the P(O)NHC(O) bifunctional group: Crystal structures of $CCl_2HC(O)NHP(O)(NCH_3(CH_2C_6H_5))_2$, $p\text{-}ClC_6H_4C(O)NHP(O)(NCH_3(CH_2C_6H_5))_2$, $CCl_2HC(O)NHP(O)(N(CH_2C_6H_5)_2)_2$ and $p\text{-}BrC_6H_4C(O)NHP(O)(N(CH_2C_6H_5)_2)_2$

Saeed Dehghanpour[a,*], Richard Welter[b], Aliou Hamady Barry[c], Farzaneh Tabasi[a]

[a] Department of Chemistry, Alzahra University, Vanak, Tehran, Iran
[b] Laboratoire DECMET, UMR CNRS 7513, Universiteĭ Louis Pasteur, Strasbourg, France
[c] Deĭpartement de Chimie, Faculteĭ des Sciences et Techniques, Universiteĭ de Nouakchott, Nouakchott, Mauritania

ARTICLE INFO

Article history:
Received 21 October 2009
Received in revised form
23 November 2009
Accepted 8 December 2009

Keywords:
Phosphoramidate
Synthesis
Structure
Spectroscopic properties

ABSTRACT

Synthetic methods for several novel phosphoramidate compounds containing the P(O)NHC(O) bifunctional group were developed. These compounds with the general formula $R_1C(O)NHP(O)(N(R_2)(CH_2C_6H_5))_2$, where $R_1 = CCl_2H$, $p\text{-}ClC_6H_4$, $p\text{-}BrC_6H_4$, $o\text{-}FC_6H_4$ and R_2 = hydrogen, methyl, benzyl, were characterized by several spectroscopic methods and analytical techniques. The effects of phosphorus substituents on the rotation rate around the $P–N_{amine}$ bond were also investigated. ^1H NMR study of the synthesized compounds demonstrated that the presence of bulky groups attached to the phosphorus center and electron withdrawing groups in the amide moiety lead to large chemical-shift non-equivalence ($\Delta\delta_H$) of diastereotopic methylene protons. The crystal structures of $CCl_2HC(O)NHP(O)(NCH_3(CH_2C_6H_5))_2$, $p\text{-}ClC_6H_4C(O)NHP(O)(NCH_3(CH_2C_6H_5))_2$, $CCl_2HC(O)NHP(O)(N(CH_2C_6H_5)_2)_2$ and $p\text{-}BrC_6H_4C(O)NHP(O)(N(CH_2C_6H_5)_2)_2$ were determined by X-ray crystallography using single crystals. The coordination around the phosphorus center in these compounds is best described as distorted tetrahedral and the P(O) and C(O) groups are anti with respect to each other. In the compound $Br\text{-}C_6H_4C(O)NHP(O)(N(CH_2C_6H_5)_2)_2$ (with two independent molecules in the unit cell), two conformers are connected to each other via two different N–H···O hydrogen bonds forming a non-centrosymmetric dimer. In the crystalline lattice of other compounds, the molecules form centrosymmetric dimers via pairs of same N–H···O hydrogen bonds. The structure of $CCl_2HC(O)NHP(O)(N(CH_2C_6H_5)_2)_2$ reveals an unusual intramolecular interaction between the oxygen of C=O group and amine nitrogen.

1. Introduction

There has been a growing interest in the synthesis and characterization of phosphoramidate compounds due to their potential applications as acetylcholinesterase and urease inhibitors, antioxidants, antirust additives in lubricating oils, pesticides, and anticancer drugs [1–4]. The three or two nitrogen subunits of these compounds provide the opportunity for a large number of structurally diverse analogues and hence a broad spectrum of properties and shapes can be customized [5,6]. Most of these studies refer to four-coordinated compounds of the $P(O)R_3$ type, where R is a substituted amine, phenol or alkyl group. Considerably less attention has been devoted to phosphoramidate compounds containing the P(O)NHC(O) bifunctional group incorporating both phosphoryl-nitrogen and carbonyl-nitrogen bonds [7–13]. These compounds have drawn special attention because of the biological behavior of β-diketophosphonate system [14–17] and bidentate O, O-donor chelating ligands for metal ions, particularly for lanthanides [18–27]. Factors such as steric, electronic, and conformational interactions influence the biochemical activity and type of complexation reactions of these compounds [16–20]. The phosphorus substituents may modify the steric and electronic interactions and tune the physical and chemical properties of phosphoramidate compounds. A thorough knowledge of the spectral and structural properties of the phosphoramidate should be beneficial to a detailed understanding of their effect on the properties of these compounds. Our interest in the chemistry of phosphoramidate derivatives was stimulated to explore how the variations in the phosphorus substituents influence the structural and spectral properties of these compounds.

* Corresponding author. Tel.: +98 021 88041344; fax: +98 021 88041344.
E-mail address: Dehganpour_farasha@yahoo.com (S. Dehghanpour).

1386-1425/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2009.12.033

$R_1C(O)NHP(O)(N(R_2)(CH_2C_6H_5))_2$

R_2 \ R_1	CCl_2H	p-Br-C_6H_4	p-Cl-C_6H_4	o-F-C_6H_4
H	1a	2a	3a	4a
CH_3	1b	2b	3b	4b
$CH_2C_6H_5$	1c	2c	3c	4c

Scheme 1.

Herein, some phosphoramidate derivatives were synthesized and characterized by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy and elemental analysis (Scheme 1). In candidate molecules, different behaviors of benzylic proton were studied. Furthermore, two bond distance-coupling constants; $^2J_{PN(CH_2)}$ of **1b**–**4b** were compared to $^2J_{PN(CH_3)}$. The experimental IR spectra of these compounds were studied and the main absorption bands of similar compounds were assigned. Finally, the structures of compounds **1b**, **3b**, **1c** and **2c** were determined by X-ray crystallography. Combined crystallographic and spectroscopic types of evidence were presented for the intramolecular N···O=C interaction between the benzylic nitrogen and the carbonyl group.

2. Experimental

2.1. Materials and physical measurements

Compounds $RC(O)NHP(O)Cl_2$, (R = $CHCl_2$, **1**; p-Br-C_6H_4, **2**; p-Cl-C_6H_4, **3**; o-F-C_6H_4, **4**) were prepared by published methods [12]. Melting points were determined on a Gallenkamp apparatus. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker (Avance DRS 500 MHz spectrometer) (298 K). ^{31}P, ^1H and ^{13}C chemical shifts were determined relative to 85% H_3PO_4 and TMS, respectively, as external standards. IR spectra (KBr) were obtained using a Shimadzu, IR-60-model spectrophotometer. Elemental analyses were performed using a Heraeus CHN-O-RAPID. Other compounds used in the syntheses were obtained from Aldrich Chemical Co. and used without further purification. All solvents were dried and distilled before use.

2.2. Preparations of the compounds

2.2.1. N,N,N′,N′-benzyl-N″-(dichloroacetyl)-phosphoric triamide (*1a*)

A solution of **1** (0.4 g, 1.7 mmol) in acetonitrile (50 mL) was added dropwise to (0.36 g, 1.7 mmol) benzylamine in acetonitrile in N_2 atmosphere at −15 °C. The reaction mixture was stirred for 3 h, accompanied by precipitation of a white solid. The solution was filtered and the crude product was washed with water (3× 100 mL) and n-hexane (2× 100 mL) and dried *in vacuo*. The pure product was obtained after recrystallization from a chloroform/n-heptane mixture (5:1). Yield: 88%, mp 182–184 °C. Anal. Calc. for $C_{16}H_{18}Cl_2N_3O_2P$: C, 49.76; H, 4.70; N, 10.88; found: C, 49.80; H, 4.64; N, 10.93. ^1H NMR ($CDCl_3$): δ = 4.03 (m, 4H, CH_2), 5.93 (m, 2H, NH), 5.97 (d, $^2J_{PH}$ = 4.9 Hz, 1H, CH), 7.26–7.34 (m, 5H, Ar–H), 8.86 (b, 1H, NH). ^{13}C {^1H} NMR ($CDCl_3$): δ = 44.8 (d, $^2J_{PC}$ = 6.7 Hz, CH_2), 66.35 (d, $^2J_{PC}$ = 5.33 Hz, CH), 127.4 (s), 127.5 (s), 127.7 (s), 139.05 (d, J_{PC} = 6.1 Hz), 165.9 (d, $^2J_{PC}$ = 3.6, CO). ^{31}P {^1H} NMR ($CDCl_3$): δ = 8.05 (s). IR (KBr, cm^{-1}): 3396 (m), 3020 (w), 2915 (w), 1714 (s), 1452 (vs), 1208 (s), 1008 (m), 834 (s).

2.2.2. N,N,N′,N′-benzyl-N″-(4-bromobenzoyl)-phosphoric diamide (*2a*)

This compound was prepared by a procedure similar to that used for **1a** employing (0.4 g, 1.3 mmol) of compound **2**, and (0.27 g, 1.3 mmol) of benzylamine. Yield: 91%, mp 188–191 °C. Anal. Calc. for $C_{21}H_{21}BrN_3O_2P$: C, 55.04; H, 4.62; N, 9.17; found: C, 55.06; H, 4.61; N, 9.18. ^1H NMR ($CDCl_3$): δ = 3.47 (m, 2H, NH), 4.17 (d, $^2J_{PH}$ = 9.6 Hz, 4H, CH_2), 7.15–7.86 (m, 14H, Ar–H), 8.85 (b, 1H, NH). ^{13}C {^1H} NMR ($CDCl_3$): δ = 45.91 (d, $^2J_{PC}$ = 7.2 Hz, CH_2), 126.94 (s), 128.10 (s), 128.46 (s), 128.94 (s), 129.04 (s), 130.43 (s), 131.70 (s), 133.84 (s), 141.49 (d, $^2J_{PC}$ = 4.9), 167.43 (s). ^{31}P {^1H} NMR ($CDCl_3$): δ = 9.21 (s). IR (KBr, cm^{-1}): 3415 (m), 3050 (w), 2910 (w), 1666 (s), 1605 (w), 1521 (w), 1446 (vs), 1193 (s), 1005 (m), 799 (s).

2.2.3. N,N,N′,N′-benzyl-N″-(4-chlorobenzoyl)-phosphoric diamide (*3a*)

This compound was prepared by a procedure similar to that used for **1a** employing (0.4 g, 1.5 mmol) of compound **3**, and (0.37 g, 1.5 mmol) of benzylamine. Yield: 65%, mp 187–190 °C. Anal. Calc. for $C_{21}H_{21}ClN_3O_2P$: C, 60.95; H, 5.11; N, 10.15; found: C, 60.92; H, 5.10; N, 10.14. ^1H NMR ($CDCl_3$): δ = 4.04 (m, 4H, CH_2), 5.15 (m, 2H, NH), 7.11–7.78 (m, 14H, Ar–H), 8.91 (b, 1H, NH). ^{13}C {^1H} NMR ($CDCl_3$): δ = 46.85 (d, $^2J_{PC}$ = 6.1 Hz, CH_2), 127.01 (s), 127.99 (s), 128.55 (s), 128.92 (s), 129.06 (s), 130.22 (s), 130.74 (s), 133.99 (d, $^2J_{PC}$ = 5.4), 142.49, 142.66, 169.54 (d, $^2J_{PC}$ = 3.6, CO). ^{31}P {^1H} NMR ($CDCl_3$): δ = 9.01 (s). IR (KBr, cm^{-1}): 3402 (m), 3041 (w), 2920 (w), 1652 (s), 1621 (w), 1531 (m), 1445 (vs), 1188 (s), 1008 (m), 785 (s).

2.2.4. N,N,N′,N′-benzyl-N″-(2-fluorobenzoyl)-phosphoric diamide (*4a*)

This compound was prepared by a procedure similar to that used for **1a** employing (0.4 g, 1.6 mmol) of compound **4**, and (0.34 g, 1.6 mmol) of benzylamine. Yield: 60%, mp 185–198 °C. Anal. Calc. for $C_{21}H_{21}FN_3O_2P$: C, 63.47; H, 5.33; N, 10.57; found: C, 63.46; H, 5.30; N, 10.48. ^1H NMR ($CDCl_3$): δ = 4.17 (b, 4H, CH_2), 5.05 (b, 2H, NH), 7.19 (m, 14H, Ar–H), 8.94 (b, 1H, NH). ^{13}C {^1H} NMR ($CDCl_3$): δ = 44.21 (d, $^2J_{PC}$ = 6.1 Hz, CH_2), 126.98 (s), 127.70 (s), 128.49 (s), 129.29 (s), 130.56 (s), 133.43 (s), 141.49 (d, $^2J_{PC}$ = 5.9), 141.56 (s), 166.13 (s). ^{31}P {^1H} NMR ($CDCl_3$): δ = 8.18 (s). IR (KBr, cm^{-1}): 3411 (m), 3039 (w), 2901 (w), 1669 (s), 1614 (w), 1509 (w), 1449 (vs), 1184 (s), 1011 (m), 801 (s).

2.2.5. N,N′-benzyl-N,N′-metyl-N″-(dichloroacetyl)-phosphoric triamide (*1b*)

A solution of **1** (0.4 g, 1.7 mmol) in chloroform was added to a solution of methylbenzylamine (0.4 g, 1.7 mmol) in dry chloroform (100 mL) at 0 °C. The reaction mixture was stirred for 10 h. The volatile material was removed using a rotary evaporator and the residue obtained was washed with water (3× 100 mL) and dried at reduced pressure. The pure product was obtained after recrystallization from an ethanol/n-hexane mixture (3:1). Yield: 90%, mp 201–203 °C. Anal. Calc. for $C_{18}H_{22}Cl_2N_3O_2P$: C, 52.19; H, 5.35; N, 10.14; found: C, 52.12; H, 5.37; N, 10.21. ^1H NMR ($CDCl_3$): δ = 2.68 (d, $^3J_{P-H}$ = 10.5 Hz, 6H, CH_3), 4.12 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{PH}$ = 10.2 Hz, 2H, CH_2), 4.26 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{PH}$ = 10.2 Hz, 2H, CH_2), 6.30 (s, 1H, CH), 7.27–7.41 (m, 10H, 2Ar–H), 9.99 (b, 1H, NH). ^{13}C {^1H} NMR ($CDCl_3$): δ = 33.55 (d, $^2J_{PC}$ = 5.3 Hz, CH_3), 52.95 (d, $^2J_{PC}$ = 6.9 Hz, CH_2), 66.7 (d, J_{PC} = 12.5 Hz), 127.5 (s), 128.1 (s), 128.6 (s), 137.2 (d, J_{PC} = 7.1 Hz), 165.5 (d, $^2J_{PC}$ = 4.1, CO). ^{31}P {^1H} NMR($CDCl_3$): δ = 15.59 (s). IR (KBr, cm^{-1}): 3411 (m), 3030 (w), 2932 (w), 1711 (s), 1444 (vs), 1185 (s), 1017 (m), 855 (s).

*2.2.6. N,N′-dibenzyl-N,N′-dimetyl-N″-(4-bromobenzoyl)-phosphoric diamide (**2b**)*

This compound was prepared by a procedure similar to that used for **1b** employing (0.4 g, 1.3 mmol) of compound **2**, and (0.3 g, 1.3 mmol) of benzylmethylamine. Yield: 82%, mp 210–212 °C. Anal. Calc. for $C_{35}H_{33}BrN_3O_2P$: C, 65.83; H, 5.21; N, 6.58; found: C, 65.80; H, 5.21; N, 6.55. ^{1}H NMR ($CDCl_3$): δ = 2.52 (d, $^3J_{PH}$ = 9.3 Hz, 6H, CH_3), 4.11 (dd, $^2J_{HH}$ = 15.3 Hz, $^3J_{PH}$ = 10.6 Hz, 2H, CH_2), 4.18 (dd, $^2J_{HH}$ = 15.3 Hz, $^3J_{PH}$ = 10.6 Hz, 2H, CH_2), 7.17–7.81 (m, 24H, Ar–H), 9.18 (s, 1H, NH). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 33.85 (d, $^2J_{PC}$ = 4.1 Hz, CH_3), 55.96 (d, $^2J_{PC}$ = 6.8 Hz, CH_2), 127.3 (s), 128.5 (s), 129.8 (s), 131.7 (s), 132.4 (s), 132.6 (s), 136.8 (d, J_{PC} = 5.8 Hz), 137.9 (s), 167.6 (d, $^2J_{PC}$ = 2.5, CO). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 16.71 (s). IR (KBr, cm^{-1}): 3392 (m), 3018 (w), 2927 (w), 1662 (s), 1617 (w), 1489 (w), 1441 (vs), 1177 (s), 1015 (m), 794 (s).

*2.2.7. N,N′-dibenzyl-N,N′-dimetyl-N″-(4-chlorobenzoyl)-phosphoric diamide (**3b**)*

This compound was prepared by a procedure similar to that used for **1b** employing (0.4 g, 1.5 mmol) of compound **3**, and (0.4 g, 1.5 mmol) of benzylmethylamine. Yield: 86%, mp 207–210 °C. Anal. Calc. for $C_{23}H_{25}ClN_3O_2P$: C, 62.51; H, 5.70; N, 9.51; found: C, 62.54; H, 5.72; N, 9.47. ^{1}H NMR ($CDCl_3$): δ = 2.69 (d, 6H, J_{PH} = 10.3 Hz, 2CH_3), 4.18 (dd, $^2J_{HH}$ = 15.2 Hz, $^3J_{PH}$ = 10.1 Hz, 2H, CH_2), 4.27 (dd, $^2J_{HH}$ = 15.2 Hz, $^3J_{PH}$ = 10.1 Hz, 2H, CH_2), 7.22–8.00 (m, 14H, 3Ar–H), 9.11 (b, 1H, NH). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 33.85 (d, $^2J_{PC}$ = 6.1 Hz, CH_3), 53.05 (d, $^2J_{PC}$ = 6.8 Hz), 127.3 (s), 128.1 (s), 128.7 (s), 129.8 (d, J_{PC} = 3.2 Hz), 131.8 (s), 138.9 (s), 137.8 (s), 138.8 (s), 167.7 (s, CO). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 16.39 (s). IR (KBr, cm^{-1}): 3414 (m), 3071 (w), 2909 (w), 1669 (s), 1611 (w), 1541 (m), 1449 (vs), 1173 (s), 1022 (m), 802 (s).

*2.2.8. N,N′-dibenzyl-N,N′-dimetyl-N″-(2-fluoro benzoyl)-phosphoric diamide (**4b**)*

This compound was prepared by a procedure similar to that used for **1b** employing (0.4 g, 1.6 mmol) of compound **4**, and (0.38 g, 1.6 mmol) of benzylmethylamine (0.38 g, 1.6 mmol). Yield: 81%, mp 215–219 °C. Anal. Calc. for $C_{23}H_{25}FN_3O_2P$: C, 64.93; H, 5.92; N, 9.88; found: C, 64.95; H, 5.90; N, 9.88. ^{1}H NMR ($CDCl_3$): δ = 2.71 (d, 6H, J_{PH} = 10.41, 2CH_3), 4.36 (dd, $^2J_{HH}$ = 15.7 Hz, $^3J_{PH}$ = 10.2 Hz, 2H, CH_2), 4.46 (dd, $^2J_{HH}$ = 15.7 Hz, $^3J_{PH}$ = 10.2 Hz, 2H, CH_2), 7.12–8.03 (m, 14H, 3Ar–H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 33.71 (d, $^2J_{PC}$ = 4.83 Hz, CH_3), 53.05 (d, $^2J_{PC}$ = 5.43 Hz, CH_2), 120.85 (s), 121.00 (s), 124.95 (s), 127.29 (s), 128.52 (s), 131.93 (s), 134.52 (s), 137.70 (d, J_{PC} = 5.4 Hz), 162.37 (d, $^2J_{PC}$ = 2.2 Hz, CO). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 15.43 (s). IR (KBr, cm^{-1}): 3401 (m), 3005 (w), 2928 (w), 1661 (s), 1624 (w), 1522 (w), 1440 (vs), 1169 (s), 1029 (m), 811 (s).

*2.2.9. N,N,N′,N′-dibenzyl-N″-(dichloroacetyl)-phosphoric triamide (**1c**)*

A solution of (0.4 g, 1.7 mmol) **1** in chloroform (50 mL) was added dropwise to a solution of dibenzylamine (0.7 g, 1.7 mmol) in dry chloroform (100 mL). The colorless solution obtained was cooled to −10 °C and maintained at that temperature for 30 min. The −10 °C bath was then removed and the solution was refluxed for 48 h. Volatiles were removed using a rotary evaporator and the remaining crude solid was washed with water (3× 100 mL) and dried *in vacuo*. The pure product was obtained after recrystallization from a chloroform/n-heptane mixture (5:1). Yield: 65%, mp 236–239 °C. Anal. Calc. for $C_{30}H_{30}Cl_2N_3O_2P$: C, 63.61; H, 5.34; N, 7.42; found: C, 63.60; H, 5.34; N, 7.46. ^{1}H NMR ($CDCl_3$): δ = 4.42 (dd, $^2J_{HH}$ = 15.62 Hz, $^3J_{PH}$ = 7.8 Hz, 2H, CH_2), 4.47 (dd, $^2J_{HH}$ = 15.62 Hz, $^3J_{PH}$ = 10.2 Hz, 2H, CH_2), 6.13 (s, 1H, CH), 7.21–7.33 (m, 20H, 4Ar–H), 9.32 (b, 1H, NH). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 48.9 (d, $^2J_{PC}$ = 6.3 Hz, CH_2), 66.6 (s), 127.5 (s), 128.5 (s), 128.7 (s), 136.2 (d, J_{PC} = 6.1 Hz), 164.8 (s). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 15.59 (s). IR (KBr, cm^{-1}): 3409 (m), 3024 (w), 2919 (w), 1719 (s), 1440 (vs), 1172 (s), 1019 (m), 821 (s).

*2.2.10. N,N,N′,N′-dibenzyl-N″-(4-bromobenzoyl)-phosphoric diamide (**2c**)*

This compound was prepared by a procedure similar to that used for **1c** employing (0.4 g, 1.3 mmol) of compound **2**, and (0.5 g, 1.3 mmol) of dibenzylamine. Yield: 67%, mp 242–245 °C. Anal. Calc. for $C_{35}H_{33}BrN_3O_2P$: C, 65.83; H, 5.21; N, 6.58; found: C, 65.80; H, 5.21; N, 6.55. ^{1}H NMR ($CDCl_3$): δ = 4.06 (dd, $^2J_{HH}$ = 15.5 Hz, $^3J_{PH}$ = 10.2 Hz, 2H, CH_2), 4.28 (dd, $^2J_{HH}$ = 15.5 Hz, $^3J_{PH}$ = 10.2 Hz, 2H, CH_2), 7.17–7.81 (m, 24H, 5Ar–H), 9.18 (s, 1H, NH). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 49.05 (d, $^2J_{PC}$ = 6.3 Hz), 127.3 (s), 128.4 (s), 128.7 (s), 129.8 (s), 131.7 (s), 132.4 (s), 132.6 (s), 136.8 (d, J_{PC} = 5.9), 136.9, 167.6 (d, $^2J_{PC}$ = 2.3, CO). ^{31}P {^{1}H} NMR($CDCl_3$): δ = 16.71 (s). IR (KBr, cm^{-1}): 3398 (m), 3011 (w), 2905 (w), 1665 (s), 1610 (w), 1510 (w), 1444 (vs), 1175 (s), 1023 (m), 804 (s).

*2.2.11. N,N,N′,N′-dibenzyl-N″-(4-chloro benzoyl)-phosphoric diamide (**3c**)*

This compound was prepared by a procedure similar to that used for **1c** employing (0.4 g, 1.5 mmol) of compound **3**, and (0.7 g, 1.5 mmol) of dibenzylamine. Yield: 93%, mp 245–247 °C. Anal. Calc. for $C_{35}H_{33}ClN_3O_2P$: C, 70.76; H, 5.60; N, 7.07; found: C, 70.77; H, 5.60; N, 7.04. ^{1}H NMR ($CDCl_3$): δ = 4.32 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{PH}$ = 10.3 Hz, 2H, CH_2), 4.53 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{PH}$ = 10.3 Hz, 2H, CH_2), 7.18–7.84 (m, 24H, m, 5Ar–H), 8.89 (b, 1H, NH). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 49.15 (d, $^2J_{PC}$ = 6.6 Hz), 127.3 (s), 128.4 (s), 128.7 (s), 129.6 (s), 131.4 (s), 132.6 (s) 136.9 (s), 138.8 (d, J_{PC} = 3.9 Hz), 167.5 (s). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 16.60 (s). IR (KBr, cm^{-1}): 3405 (m), 3101 (w), 2933 (w), 1666 (s), 1637 (w), 1545 (m), 1441 (vs), 1169 (s), 1028 (m), 812 (s).

*2.2.12. N,N,N′,N′-dibenzyl-N″-(2-fluoro benzoyl)-phosphoric diamide (**4c**)*

This compound was prepared by a procedure similar to that used for **1c** employing (0.4 g, 1.6 mmol) of compound **4**, and (0.38 g, 1.6 mmol) of dibenzylamine. Yield: 94%, mp 239–243 °C. Anal. Calc. for $C_{35}H_{33}FN_3O_2P$: C, 72.78; H, 5.76; N, 7.27; found: C, 72.76; H, 5.76; N, 7.22. ^{1}H NMR ($CDCl_3$): δ = 4.34 (dd, $^2J_{HH}$ = 15.1 Hz, $^3J_{PH}$ = 10.5 Hz, 2H, CH_2), 4.49 (dd, $^2J_{HH}$ = 15.1 Hz, $^3J_{PH}$ = 10.5 Hz, 2H, CH_2), 7.11–7.88 (m, 24H, 5Ar–H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 49.02 (d, $^2J_{PC}$ = 7.1 Hz), 127.28 (s), 128.40 (s), 128.79 (s), 129.94 (s) 132.11 (s), 136.65 (s), 136.70 (d, J_{PC} = 6.3 Hz), 166.12 (s). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 15.50 (s). IR (KBr, cm^{-1}): 3409 (m), 3055 (w), 2930 (w), 1669 (s), 1611 (w), 1492 (w), 1440 (vs), 1167 (s), 1042 (m), 799 (s).

2.3. X-ray crystallography analyses

Single crystals of **1b**, **3b**, **1c** and **2c** were obtained from a solution of chloroform and hexane (4:1 ratio) at room temperature. Data collection and refinement parameters are listed in Table 1. Single crystals were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo K_α λ = 0.71073 Å). The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined using reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software [28]. The absorptions were not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Table 1
Structures determination summary of **1b**, **3b**, **1c** and **2c**.

	1b	3b	1c	2c
Formula	$C_{18}H_{22}Cl_2N_3O_2P$	$C_{23}H_{25}Cl\,N_3O_2P$	$C_{30}H_{30}Cl_2N_3O_2P$	$C_{35}H_{33}BrN_3O_2P$
Formula weight	414.26	441.88	566.44	638.52
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	9.832(2)	9.04400(10)	11.3580(3)	16.56200(10)
b (Å)	10.842(2)	13.0320(2)	16.4560(4)	19.4860(2)
c (Å)	11.139(3)	19.4430(3)	15.3540(4)	19.2600(2)
α (°)	69.856(13)	90.00	90.00	90.00
β (°)	66.929(10)	94.7380(8)	93.2520(12)	99.3530(6)
γ (°)	72.696(11)	90.00	90.00	90.00
V (A^3)	1007.3(4)	2283.75(6)	2865.15(13)	6133.09(10)
Z	2	4	4	8
Density (g cm^{-3})	1.366	1.285	1.313	1.383
μ (mm^{-1})	0.42	0.261	0.315	1.429
F (000)	432	928	1184	2640
Crystal size	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.15 × 12 × 0.10	0.10 × 0.10 × 0.10
Theta range for data collection	0.994–30.01	1.88–30.08	1.82–30.01	
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 14$, $-15 \le l \le 15$	$-12 \le h \le 12$, $-18 \le k \le 16$, $-27 \le l \le 27$	$-15 \le h \le 10$, $-23 \le k \le 20$, $-21 \le l \le 21$	$-23 \le h \le 23$, $-27 \le k \le 25$, $-26 \le l \le 27$
Reflections collected	5860	6688	8323	17912
Independent reflections	3702 [*R* (int) = 0.05]	4318 [*R* (int) = 0.074]	4152 [*R* (int) = 0.067]	11814 [*R* (int) = 0.074]
Data/restraints/parameters	3702/0/235	4318/0/271	4152/0/343	11814/0/757
Goodness-of-fit on F^2	1.038	1.043	0.956	1.007
Final *R* indices [*I* > 2sigma(*I*)]	R_1 = 0.0489, wR_2 = 0.1193	R_1 = 0.0570, wR_2 = 0.1489	R_1 = 0.0588, wR_2 = 0.1437	R_1 = 0.0577, wR_2 = 0.1189
R indices (all data)	R_1 = 0.1373, wR_2 = 0.0890	R_1 = 0.0931, wR_2 = 0.1699	R_1 = 0.1370, wR_2 = 0.1785	R_1 = 0.1002, wR_2 = 0.1355
Maximum and average shift/error	0.000, 0.000	0.000, 0.000	0.001, 0.000	0.002, 0.000
Largest diff. peak and hole (e $Å^{-3}$)	−0.40, 0.35	−0.619, 0.204	−0.558, 0.331	−1.026, 1.067

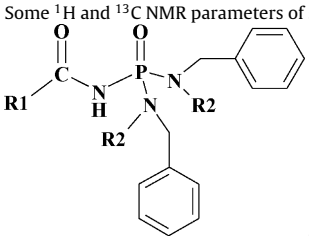
3. Results and discussion

As indicated in Scheme 2, a series of phosphoramidates were synthesized with various amide and amine moieties based on PCl_5 as a common starting material. The synthesis of these compounds is accomplished via elimination of HCl. In an attempt to avoid an acidic system, an excess of amine was added to the reaction mixtures.

3.1. Spectral study

Structural assignment of the synthesized compounds (**1a**–**4a**, **1b**–**4b** and **1c**–**4c**) can be carried out using ^1H, ^{31}P and ^{13}C NMR spectroscopy. A summary of the NMR data of these compounds is given in Table 2. The different behaviors exhibited by benzylic protons for some synthesized compounds are presented in Fig. 1.

Table 2
Some ^1H and ^{13}C NMR parameters of synthesized compounds.



	R_1	R_2	δCH_2	$^3J_{PNCH}$	$^2J_{HH}$	δCH_3	$^2J_{P-CH_3}$	δCH_2	$^2J_{P-CH_2}$	δCO
1a	CCl_2H	H	4.03	–	–	–	–	44.8	6.7	165.9
2a	p-Br-C_6H_4	H	4.17	9.6	–	–	–	45.9	7.2	167.4
3a	p-Cl-C_6H_4	H	4.04	–	–	–	–	46.8	6.1	169.5
4a	o-F-C_6H_4	H	4.17	–	–	–	–	44.2	6.1	166.1
1b	CCl_2H	CH_3	4.09–4.28	10.2	15.4	33.6	5.3	52.9	6.9	165.5
2b	p-Br-C_6H_4	CH_3	4.08–4.21	10.5	15.3	33.9	4.1	53.1	6.8	167.5
3b	p-Cl-C_6H_4	CH_3	4.16–4.29	10.1	15.2	33.9	6.1	53.1	6.9	167.7
4b	o-F-C_6H_4	CH_3	4.34–4.48	10.2	15.7	33.7	4.8	53.1	5.4	162.3
1c	CCl_2H	$CH_2C_6H_5$	4.13–4.49	7.8, 10.2	15.6	–	–	48.9	6.3	164.8
2c	p-Br-C_6H_4	$CH_2C_6H_5$	4.04–4.31	10.2	15.5	–	–	49.1	6.3	167.6
3c	p-Cl-C_6H_4	$CH_2C_6H_5$	4.30–4.55	10.3	15.4	–	–	49.2	6.6	167.5
4c	o-F-C_6H_4	$CH_2C_6H_5$	4.32–4.51	10.5	15.1	–	–	49.1	7.1	166.1

The diastereotopic benzylic protons in synthesized compounds exhibit splitting by the phosphorus atom, $^3J_{PNCH}$, followed by $^2J_{HH}$ (geminal) splitting. However, as shown in Fig. 1, these protons appear as doublets, multiplets, and two doublets of doublets.

The benzylic protons in **1b**–**4b** and **1c**–**4c** show two doublets of doublets with a large chemical-shift non-equivalence ($\Delta\delta_H$ = 0.13–0.36) and N-acetyl derivatives (CCl_2H–C(O)NHP(O)$(R_2)_2$) with same amine groups have the greatest values of chemical-shift non-equivalence. The ^{1}H NMR spectra of **1a**, **3a** and **4a** with benzylamine substituents reveal a multiplet for the benzylic protons. This means that the two separate signals are coalesced with each other due to the intermediate rotation rate around the P–N bond. However, compound **2a** shows only a doublet produced by a $^3J_{PNCH}$ coupling constant. When the rotational energy barrier around the P–N bond is low, benzylic protons appear with equal chemical shifts on the NMR scale. It can be suggested that this behavior of benzylic protons in the synthesized compounds depends on the degree of steric effect of phosphorus substituents (presence of bulky groups in the phosphorus center) and electronic effect of amide moiety (with influence on the P–N_{amine} bond lengths). The P–N_{amine} bond lengths for **1b** and **1c** containing electron withdrawing groups in amide moiety (chlorine atoms) are slightly shorter than those in N-benzoyl derivatives (**3b** and **2c**) (vide infra). It is of interest to note that the ^{1}H NMR spectrum of **1c** recorded in chloroform shows a remarkably large chemical-shift non-equivalence ($\Delta\delta_H$ = 0.36) of the benzylic protons (Fig. 1). In addition to steric and electronic effects, this result may be a consequence of the retention of the intramolecular C=O···N interaction upon the transfer of **1c** from the solid state to the solution (vide infra).

In compound **1c**, the $^3J_{PNCH}$ values obtained for the individual protons of the benzylic CH_2 group are different, indicating different angular relationship within the fragments P–N–C–HA and P–N–C–HB, which can be retained in solution because of the highly restricted rotation about the P–N bonds. Each of the diastereotopic benzylic protons gives rise to doublets of doublets with a $^2J_{HH}$ (geminal) constant of 15.6 Hz, while $^3J_{PNCH}$ values of 7.8 Hz and 10.2 Hz are obtained.

The phosphorus–hydrogen coupling constants, $^2J_{PNH}$ for the amide nitrogen in the intermediate compounds (**1**–**4**) are about 11 Hz [12]. However, replacement of chlorine substituents by the amine groups decreases the $^2J_{PNH}$ values for the amide nitrogen. In the ^{1}HNMR spectra of the synthesized compounds, $^2J_{PNH}$ values for amidic proton are not observed. These observations indicate p_π–d_π interaction between the phosphorus atom and amine groups.

^{13}C NMR spectra show that methylene and methyl carbon atoms in compounds **1b**–**4b** appear in the 52.95–53.05 range and 33.55–33.85 ppm, respectively (Table 2). The presence of phenyl groups linked to CH_2 may cause deshielding of the CH_2 carbon atoms relative to the CH_3 carbon atoms. The deshielding of methylene groups leads to a greater interaction with the corresponding phosphorus atoms and thereby $^2J_{PC(CH_2)}$ is greater than $^2J_{PC(CH_3)}$.

^{31}P NMR spectra of selected compounds indicate multiplets produced by the couplings with H atoms of amine, methyl and methylene protons. However, ^{31}P signal in **2a** is split only by equivalence methylene hydrogen atoms.

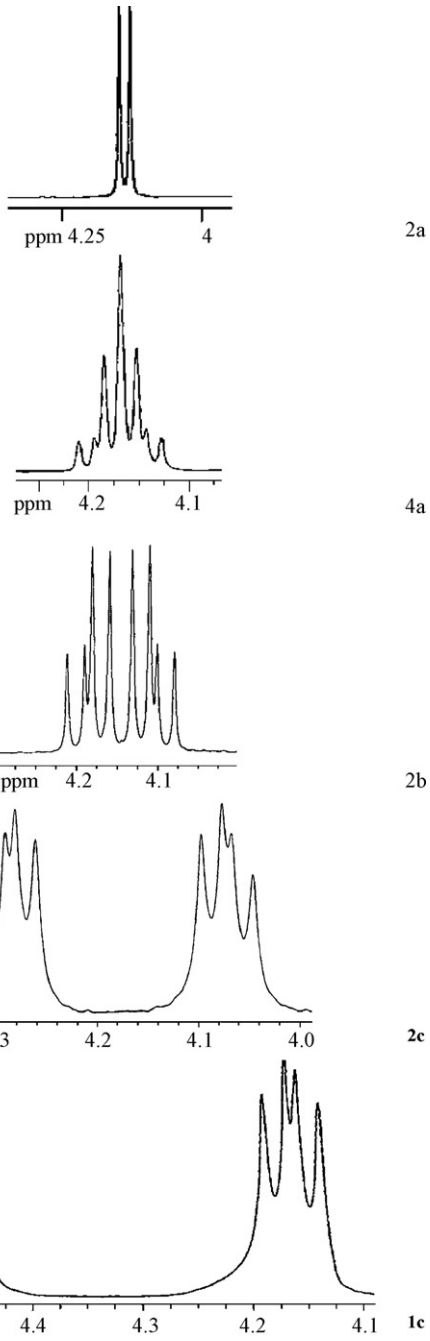


Fig. 1. ^{1}H NMR spectrum of the benzylic CH_2 protons for some synthesized compounds ($CDCl_3$).

$$PCl_5 \xrightarrow{H_2NC(O)R_1} Cl_3P{=}NC(O)R_1 \xrightarrow[\text{donor}]{\text{proton}} Cl_2P(O)NHC(O)R_1$$

$$Cl_2P(O)NHC(O)R_1 \xrightarrow[-2HCl]{+4\text{amine}} ((C_6H_5CH_2)(R_2)N)P(O)NHC(O)R_1$$

Scheme 2.

The main absorption bands in the IR spectra of the synthesized compounds, together with their assignments are given in Table 3. The IR spectra of these compounds exhibit the characteristic band corresponding to carbonyl group (C=O), which appears in the 1652–1719 cm^{-1} region. The stretching vibrations of phosphoryl group (P=O) appear in the 1169–1208 cm^{-1} region. A shift to a low frequency region is observed for both phosphoryl and the carbonyl groups in the N-benzoyl relative to the N-acetyl derivatives. The degree of interaction of the amide and amine nitrogen atoms with the neighboring phosphoryl centers in **1b**, **3b**, **1c** and **2c** can be inferred from X-ray crystallography data. The structure of these compounds reveals that the P–N_{amide} bond is longer than the

Table 3
Vibrational frequencies (cm^{-1}) in the infrared spectra and their assignments.

Assignment	1a	2a	3a	4a	1b	2b	3b	4b	1c	2c	3c	4c
υ(P=O)	1208	1193	1188	1184	1185	1177	1173	1169	1172	1175	1169	1167
υ(C=O)	1714	1666	1652	1669	1711	1662	1669	1661	1719	1665	1666	1669
$\delta(N–H)_{amide}$	1452	1446	1445	1449	1444	1441	1449	1440	1440	1444	1441	1440
$\upsilon(P–N)_{amine}$	1008	1005	1008	1011	1017	1015	1022	1029	1019	1023	1028	1042
$\upsilon(P–N)_{amide}$	834	799	785	801	855	794	802	811	821	804	812	799
$\upsilon(N–H)_{amide}$	3396	3415	3402	3411	3411	3392	3414	3401	3409	3398	3405	3409

Table 4
Selected geometrical parameters (Å,°) for **1b, 3b** and **1c** with standard uncertainties in parentheses.

1b		**3b**		**1c**	
Bond lengths (Å)					
P1-O1	1.482(1)	P1-O2	1.475(1)	P1-O1	1.469(2)
P1-N1	1.627(2)	P1-N3	1.636(1)	P1-N1	1.635(2)
P1-N2	1.629(2)	P1-N2	1.642(1)	P1-N2	1.640(2)
P1-N3	1.694(2)	P1-N1	1.678(1)	P1-N3	1.694(2)
C17-N3	1.355(2)	C7-N1	1.373(2)	C29-N3	1.363(3)
O2-C17	1.205(2)	O1-C7	1.221(2)	O2-C29	1.213(3)
Bond angles (°)					
O1-P1-N1	109.8(8)	O2-P1-N3	110.2(7)	O1-P1-N1	110.3(9)
O1-P1-N2	119.4(8)	O2-P1-N2	118.6 (7)	O1-P1-N2	119.8(9)
N1-P1-N2	105.7(9)	N3-P1-N2	104.2(7)	N1-P1-N2	106.6(9)
O1-P1-N3	104.2(7)	O2-P1-N1	105.7(7)	O1-P1-N3	105.6(8)
N1-P1-N3	113.6(9)	N3-P1-N1	112.9(8)	N1-P1-N3	111.5(9)
N2-P1-N3	104.3(8)	N2-P1-N1	105.5(7)	N2-P1-N3	102.9(9)
C8-N1-C1	115.0(2)	C7-N1-P1	128.2 (1)	C8-N1-C1	114.6(2)
C8-N1-P1	122.9(1)	C7-N1-H1	115.9	C8-N1-P1	124.7(1)
C1-N1-P1	120.5(1)	P1-N1-H1	115.9	C1-N1-P1	120.1(1)
C16-N2-C9	113.6(2)	C15-N2-C14	113.7 (1)	C15-N2-C22	112.9(2)
C16-N2-P1	125.4(2)	C15-N2-P1	116.6 (1)	C15-N2-P1	119.9(1)
C9-N2-P1	119.9(1)	C14-N2-P1	122.3(1)	C22-N2-P1	121.6(1)
C17-N3-P1	130.4(1)	C16-N3-C17	114.3(1)	C29-N3-P1	128.0(2)
C17-N3-H3	114.8	C16-N3-P1	125.5(1)	C29-N3-H3N	116.0
P1-N3-H3	114.8	C17-N3-P1	120.2(1)	P1-N3-H3N	116.0

P–N_{amine} bond (Table 4). Therefore, the medium absorption band observed around 785 to 834 cm^{-1} corresponds to the stretching vibrations of P–N_{amide} bond while presence of an intense band at 1005–1042 cm^{-1} is associated with the P–N_{amine} stretching vibrations. This assignment is arrived at by comparing the spectra of synthesized compounds with those of similar phosphoramidate molecules [29].

3.2. Structural studies

The molecular structures of **1b**, **3b**, **1c** and **2c** with the atom numbering schemes are presented in Figs. 2–5 and selected interatomic parameters are collected in Tables 4 and 5. As shown in Fig. 4, compound **2c** exists as two independent molecules (**$2c_1$** and **$2c_2$**) in a crystalline lattice.

The crystal structures of **1b**, **3b**, **1c** and **2c** consist of a core unit containing phosphoryl, nitrogen and carbonyl groups in the =P(O)N(H)C(O)– fashion. In all structures, the P(O) and C(O) groups are in anti-position with respect to each other.

The coordination environment around the phosphorus atoms of these compounds is approximately tetrahedral since the average values of six angles involving P are 109.5°, 109.5°, 109.4°, 109.43° and 109.5° for **1b**, **3b**, **1c**, **$2c_1$** and **$2c_2$**, respectively. However, the coordination is clearly distorted, arising from the presence of different substituents at phosphorus center. For **1b**, the angles N2-P1-N3 and O1-P1-N2 are 104.3(8)° and 119.4(8)°, respectively. This is also the case in **3b**, **1c**, and **2c**.

Amine P–N bonds in all studied compounds (**1b** 1.63(2) and 1.63(2), **3b** 1.64(1) and 1.64(1), **1c** 1.64(2) and 1.64(2), **$2c_1$** 1.64(2) and 1.65(2), **$2c_2$** 1.64 (2) and 1.65(2) Å) are of interest when compared with the typical P–N bond distance of 1.77 Å [6]. In all

Table 5
Selected geometrical parameters (Å,°) for **$2c_1$** and **$2c_2$** with standard uncertainties in parentheses.

$2c_1$		**$2c_2$**	
Bond lengths (Å)			
P1-O2	1.479(2)	P2-O4	1.483(2)
P1-N3	1.643(2)	P2-N6	1.640(2)
P1-N2	1.647(2)	P2-N5	1.649(2)
P1-N1	1.692(2)	P2-N4	1.691(2)
O1-C7	1.221(3)	O3-C42	1.225(3)
N1-C7	1.372(3)	N4-C42	1.373(3)
Bond angles (°)			
O2-P1-N3	111.3(1)	O4-P2-N6	110.8(1)
O2-P1-N2	118.0(1)	O4-P2-N5	118.7(9)
N3-P1-N2	106.8(9)	N6-P2-N5	106.0(9)
O2-P1-N1	104.5(9)	O4-P2-N4	105.1(9)
N3-P1-N1	111.0(9)	N6-P2-N4	112.2(9)
N2-P1-N1	105.1(1)	N5-P2-N4	104.2(1)
C7-N1-P1	127.4(2)	C42-N4-P2	124.9(2)
C7-N1-H1	116.3	C42-N4-H4	117.5
P1-N1-H1	116.3	P2-N4-H4	117.5
C15-N2-C8	115.8(2)	C43-N5-C50	114.5(2)
C15-N2-P1	118.5(2)	C43-N5-P2	118.5(1)
C8-N2-P1	121.8(2)	C50-N5-P2	120.4(2)
C22-N3-C29	115.7(2)	C57-N6-C64	114.6(2)
C22-N3-P1	124.2(2)	C57-N6-P2	125.3(2)
C29-N3-P1	118.9(2)	C64-N6-P2	119.5(2)
Torsion angles (°)			
O2-P1-N2-C8	−88.9(2)	O4-P2-N5-C43	−71.7(2)
O2-P1-N2-C15	67.9(2)	O4-P2-N5-C50	78.0 (2)
O2-P1-N3-C22	166.4(2)	O4-P2-N6-C57	−158.8(2)
O2-P1-N3-C29	−0.5 (2)	O4-P2-N6-C64	11.4(2)

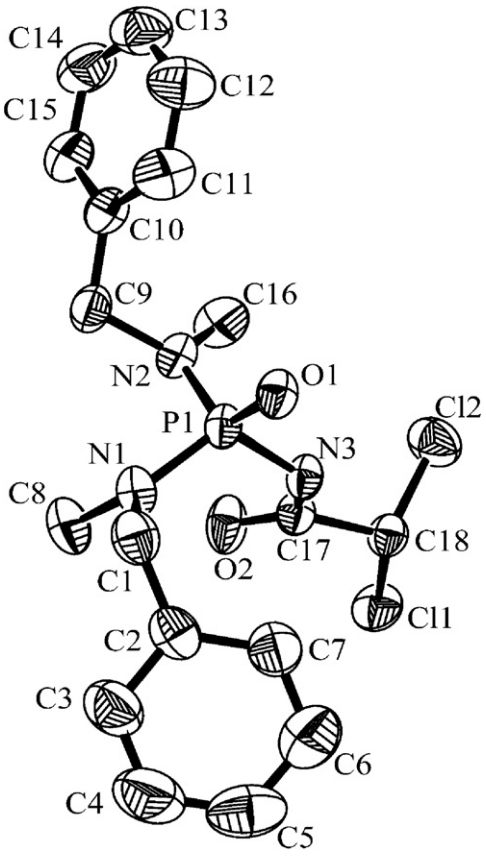


Fig. 2. Crystallogeraphically determined molecular structure of **1b** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clearer view).

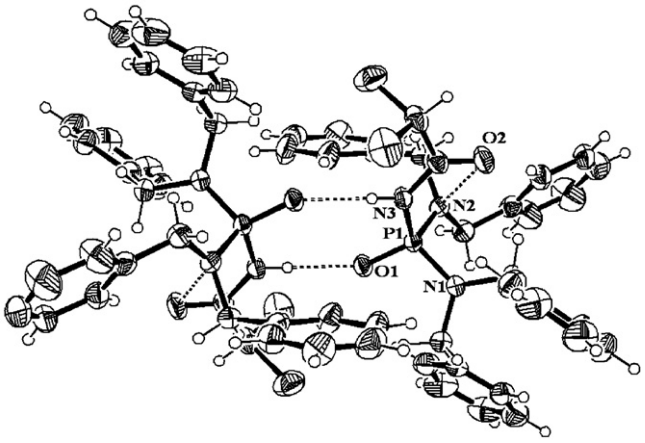


Fig. 4. The hydrogen bonding (NH···O=P) and N···O=C interaction in the compound **1c** with ellipsoid probability of 50% (hydrogen atoms shown as circles of arbitrary radii).

structures, amine groups are nearly planar as measured by the sums of three bond angles around nitrogen atoms (ΣN). Furthermore, the planarity around the amidic nitrogen is also reflected in the distances around this atom, being rather shorter than normal P–N bond (Tables 4 and 5).

The Ph ring and –C–C(O)N– unit connecting the ring in **3b** and **2c** are coplanar. The angle between the plane of the Ph ring and the plane subtended by –C–C(O)N– for **3b** is 27.1(1) and 30.4(2) and 18.9(2)° for two conformers of **2c**. This degree of coplanarity allows for increased π-conjugation between phenyl and amide groups.

As shown in Fig. 4, the $\mathbf{2c_1}$ and $\mathbf{2c_2}$ are nearly identical in their distances and angles as well as configurations. The main distinctions between these conformers exist in the different orientations of the dibenzyl amine group. The difference is described by comparison of corresponding torsion angles O–P–N–CH_2 in two conformers (Table 5). The various orientations of the dibenzyl

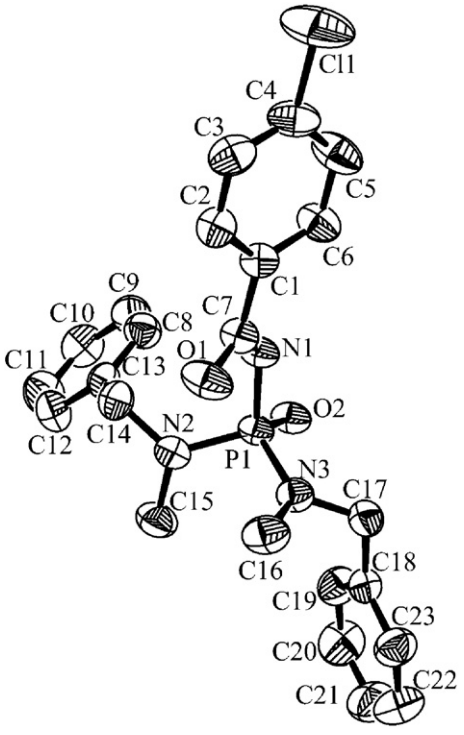


Fig. 3. Crystallogeraphically determined molecular structure of **3b** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clearer view).

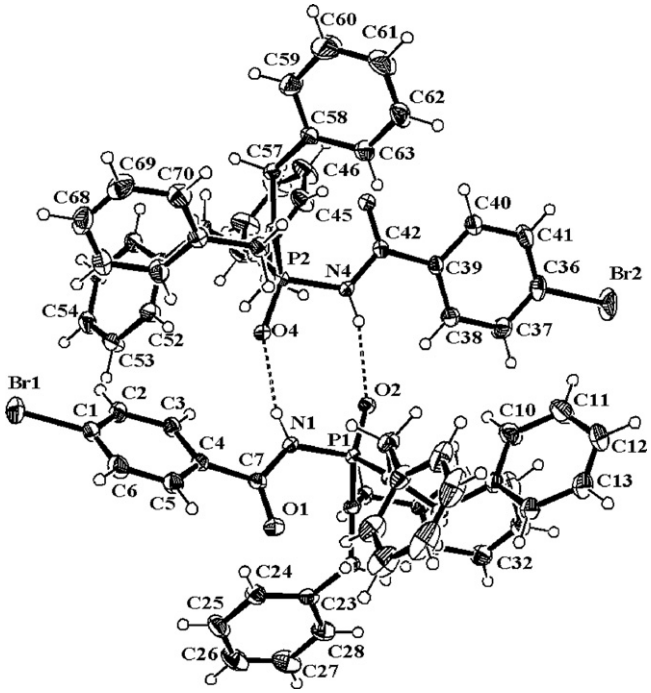


Fig. 5. The hydrogen bonding in the compound **2c** with ellipsoid probability of 50% (hydrogen atoms shown as circles of arbitrary radii).

Table 6
Hydrogen bond D–H···A for **1b**, **3b**, **1c** and **3c**.

	D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1b	N3–H3···O1[1 − *x*, 1 − *y*, 1 − *z*]	0.880	1.912	2.772	165.114
3b	N1–H1···O1[1 − *x*, 1 − *y*, 1 − *z*]	0.860	1.986	2.835	169.029
1c	N3–H3N···O1[0.5 + *x*, 0.5 − *y*, 0.5 + *z*]	0.860	1.983	2.824	165.223
2c	N1–H1···O4	0.859	1.994	2.832	164.617
	N4–H4···O2	0.860	2.091	2.927	163.888

amine group seem to be greatly influenced by restricted rotation of the P–N bond in solid state.

The crystal structure of **1c** reveals N···O=C interamolecular interaction in a five-membered ring (Fig. 5). The N(2)···O(2) = C(29) distance is 3.066(2) Å, which is slightly shorter than the sum of the van der Waals radii [30]. The decrease in electron density on the carbonyl group by electron withdrawing groups in the amide function (chlorine atoms) and the highly restricted rotation of the P–N_{amine} bond, may facilitate the formation of this unusual interaction.

Molecules **1b**, **3b** and **1c** (Fig. 5) form centrosymmetric dimers in eight-membered rings held together in the crystals by the >P(O)HN– functional group as a simultaneous hydrogen bonding donor and acceptor. In **2c**, two independent molecules are connected to each other via two different –P=O···HN– hydrogen bonds and form a non-centrosymmetric dimer (Fig. 5). Based on the parameters shown in Table 6, the hydrogen bonding interactions for **1b**, **3b**, **1c** and **2c** are considerably strong.

4. Conclusions

^{1}H NMR investigation of 12 new N-acetyl and N-benzoyl phosphoramidates derivatives indicates that the presence of bulky groups in phosphorus center and the electron withdrawing group in amide moiety lead to a large chemical-shift non-equivalence of the diastereotopic methylene protons. The crystal structures of **1b**, **3b**, **1c** and **2c** show approximately tetrahedral coordination of the phosphorus atom. The amine and amide groups are nearly planar and the P–N bond lengths are shorter than normal. The examination of intermolecular distance indicates that the crystals of **1b**, **3b** and **1c** are composed of centrosymmetric dimers by N–H···O hydrogen bond. However, two independent molecules in **2c** form non-centrosymmetric dimers via two different N–H···O hydrogen bond. The structural and spectroscopic (NMR) study of **1c** demonstrate that the N···O=C interaction between the carbonyl group and the benzylic nitrogen can occur intramolecularly and can be retained in solution leading to a high non-equivalence of the diastereotopic methylene protons.

Acknowledgement

S. D. would like to acknowledge the Alzahra University Research Council for partial support of this work.

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures **1b**, **3b**, **1c** and **2c** reported in this paper have been deposited with the *Cambridge Crystallographic Data Center*, CCDC no. 704317–704320 for **1b**, **1c**, **2c** and **3b**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

References

[1] M.D. Swerdloff, J.F. Kolc, M.M. Rogic, L.L. Hendrikson, U.S. Patent 4,517,007 (1985).
[2] D. Abbott, H. Slamon, R. Sattergood, Brit. Patent. 1,558,462 (1980).
[3] G. Zon, Prog. Med. Chem. 19 (1982) 205–246.
[4] S. Dehghanpour, Y. Rasmi, M. Bagheri, Mol. Divers. 11 (2007) 47–57.
[5] S.E. Denmark, X. Su, Y. Nishigaichi, D.M. Coe, L.T. Wong, S.B.D. Winter, J.Y. Choi, J. Org. Chem. 64 (1999) 1958–1967.
[6] D.E.C. Corbridge, Phosphorus: An Outline of its Chemistry, Biochemistry and Technology, fifth ed., Elsevier, The Netherlands, 1995.
[7] K.E. Gubina, V.M. Amirkhanov, Z. Naturforsch. 55b (2000) 1015–1019.
[8] K. Gholivand, M. Pourayoubi, Z. Shariatinia, H. Mostaanzadeh, Polyhedron 24 (2005) 655–662.
[9] K. Gholivand, Z. Shariatinia, M. Pourayoubi, Z. Anorg. Allgem. Chem. 631 (2005) 961–967.
[10] K. Gholivand, C.O. Vedova, A.A. Firooz, A.M. Alizadehgan, M.C. Michelini, R.P. Diez, J. Mol. Struct. 750 (2005) 67–71.
[11] K. Gholivand, F. Mojahed, A.M. Alizadehgan, H.R. Bijanzadeh, Z. Anorg. Allg. Chem. 632 (2006) 1570–1577.
[12] K. Gholivand, F. Mojahed, A.M. Alizadehgan, Pol. J. Chem. 81 (2007) 393–402.
[13] K. Gholivand, C.O.D. Védova, M.F. Erben, F. Mojahed, A.M. Alizadehgan, J. Mol. Struct. 840 (2007) 66–70.
[14] W.D. Mallender, T. Szegletes, T.L. Rosenberry, Biochemistry 39 (2000) 7753–7763.
[15] O.N. Rebrova, V.N. Biiushkin, T.I. Malinovskii, L.D. Protsenko, T.N. Dneprova, Dokl. USSR 266 (1982) 1391–1395.
[16] D. Barak, A. Ordentlich, D. Kaplan, R. Barak, D. Mizrahi, C. Kronman, Y. Segall, B. Velan, A. Shaferman, Biochemistry 39 (2000) 1156–1161.
[17] N.U. Mohe, K.J. Padiya, M.M. Salunkhe, Bioorg. Med. Chem. 11 (2003) 1419–1431.
[18] E.A. Trush, V.M. Amirkhanov, V.A. Ochynnikov, J. Swiatek-Kozlowska, K.A. Lanikina, K.V. Domasevitch, Polyhedron 22 (2003) 1221–1229.
[19] E.A. Trush, V.A. Ochynnikov, K.V. Domasevitch, J. Swiatek-Kozlowska, V.Y. Zub, V.M. Amirkhanov, Z. Naturforsch. 57b (2002) 746–750.
[20] V.V. Skopenko, V.M. Amirkhanov, V.A. Ovchynnikov, A.V. Turov, Russ. J. Inorg. Chem. 41 (1996) 611–616.
[21] V.M. Amirkhanov, V.A. Ovchinnikov, A.V. Turov, V.V. Skopenko, Russ. J. Coord. Chem. 23 (1997) 139–142.
[22] V.A. Trush, K.V. Domasevitch, V.M. Amirkhanov, J. Sieler, Z. Naturforsch. 54b (1999) 451–455.
[23] V.V. Skopenko, V.M. Amirkhanov, T.Yu. Sliva, I.S. Vasilchenko, E.L. Anpilova, A.D. Garnovski, Russ. Chem. Rev. 73 (2004) 797–813.
[24] O.N. Rebrova, V.N. Biyushkin, T.I. Malinovski, V.M. Ovrucki, L.D. Procenko, T.N. Dneprova, Dokl. USSR 324 (1992) 103–106.
[25] K.E. Gubina, V.A. Ovchynnikov, V.M. Amirkhanov, H. Fischer, R. Stumpf, V.V. Skopenko, Z. Naturforsch. 55b (2000) 576–582.
[26] V.A. Ovchynnikov, V.M. Amirkhanov, T.P. Timoshenko, T. Glowiak, H. Kozlowski, Z. Naturforsch. 53b (1998) 481–484.
[27] V.M. Amirkhanov, V.A. Ovchynnikov, T. Glowiak, H. Kozlowski, Z. Naturforsch. 52b (1997) 1331–1336.
[28] G.M. Sheldrick, SHELX97, University of Göttingen, Germany, 1997.
[29] K. Nakamato, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, New York, 1962.
[30] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.