

Synthesis, Spectroscopic Characterization and Crystal Structure of a New Acetyl phosphorylamidate $P(O)[NHC(O)C_6H_4(4-NO_2)][N(CH(CH_3)_2)(CH_2C_6H_5)]_2$

Mehrdad Pourayoubi · Fahimeh Sabbaghi

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Abstract A new acetyl phosphorylamidate $P(O)[NHC(O)C_6H_4(4-NO_2)][N(CH(CH_3)_2)(CH_2C_6H_5)]_2$ has been synthesized and characterized by elemental analysis, 1H , ^{13}C and ^{31}P NMR, IR and single crystal X-ray diffraction. Single crystal X-ray analysis shows that it belongs to triclinic system, space group $P\bar{1}$, with $a = 10.5868(16)$ Å, $b = 11.8058(18)$ Å, $c = 12.4364(19)$ Å, $\alpha = 65.410(3)^\circ$, $\beta = 67.492(4)^\circ$, $\gamma = 85.879(3)^\circ$, $V = 1,298.6(3)$ Å³, and $Z = 2$. The intermolecular $PO \cdots HN$ hydrogen bond makes H-bonded dimer of molecule with Ci symmetry. In the crystal network, the dimers are aggregated in the chain arrays through π -stacking between p -NO₂-C₆H₄-C(O)-NH- moieties. Moreover, weak C-H \cdots O and C-H \cdots π interactions exist in the crystal network.

Keywords Synthesis · Phosphorylamidate · Crystal structure · NMR · Centrosymmetric dimer · N-H \cdots O C-H \cdots O and C-H \cdots π interactions · π - π stacking

Introduction

Acetyl phosphorylamidates, containing C(O)N(H)P(O) moiety have attracted special interest because of bearing a close structural resemblance to the β -diketone frame and acting as effective chelating ligands [1], having biological properties [2, 3] and urea inhibition [4]. In the previous work, the

synthesis and crystal structures of *N*-benzyl-2-propanaminium *O*-methyl trichloroacetamidophosphate, $[NH_2(CH(CH_3)_2)(CH_2C_6H_5)][P(O)(NHC(O)CCl_3)O(OCH_3)]$ and *N*-benzylpropan-2-aminium (benzylisopropylamido)(2,2,2-trifluoroacetamido) phosphate $[NH_2(CH(CH_3)_2)(CH_2C_6H_5)][P(O)(NHC(O)CF_3)O(N(CH(CH_3)_2)(CH_2C_6H_5))]$ have been reported [5, 6]. In this paper, we report on the synthesis of a new acetyl phosphorylamidate $P(O)[NHC(O)C_6H_4(4-NO_2)][N(CH(CH_3)_2)(CH_2C_6H_5)]_2$ (Fig. 1) from the reaction between 4-NO₂-C₆H₄C(O)NHP(O)Cl₂ and NH(CH(CH₃)₂)(CH₂C₆H₅). Characterization was done by elemental analysis, 1H , ^{13}C and ^{31}P NMR, IR and single crystal X-ray diffraction.

Experimental

Instruments and Materials

All chemicals were purchased commercially and used without further purification. 1H , ^{13}C and ^{31}P NMR spectra were determined on a Bruker Avance DRS 500 spectrometer. 1H and ^{13}C chemical shifts were determined relative to internal TMS, ^{31}P chemical shift relative to 85% H₃PO₄ as external standard. Infrared (IR) spectrum was recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

Preparation of the Title Compound

The reaction of phosphorus pentachloride (4.165 g, 20 mmol) and 4-nitrobenzamide (3.323 g, 20 mmol) in dry CCl₄ (70 mL) at 80 °C (3 h) and then the treatment of formic acid (0.921 g, 20 mmol) at room temperature leads

M. Pourayoubi · F. Sabbaghi
Department of Chemistry, Islamic Azad University-Zanjan
Branch, P.O. Box 49195-467, Zanjan, Iran

M. Pourayoubi (✉)
Department of Chemistry, Ferdowsi University of Mashhad,
91779 Mashhad, Iran
e-mail: mehrdad_pourayoubi@yahoo.com

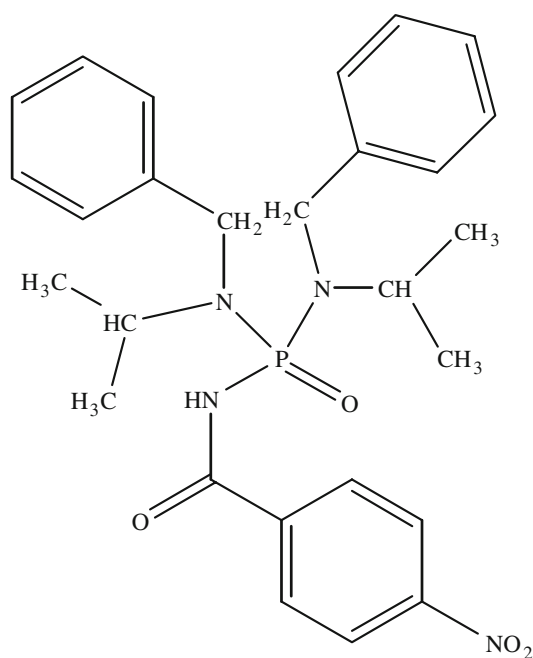


Fig. 1 Chemical formula of title compound

to 4-NO₂-C₆H₄C(O)NHP(O)Cl₂. The solid (4-NO₂-C₆H₄C(O)NHP(O)Cl₂) was washed with dry CCl₄. To a solution of (0.708 g, 2.5 mmol) 4-NO₂-C₆H₄C(O)NHP(O)Cl₂ in CCl₄ (40 mL), a solution of *N*-isopropylbenzylamine (1.492 g, 10 mmol) in CCl₄ (10 mL) was added dropwise at 0 °C. After 24 h, the solvent was removed in vacuum and the solid was washed with distilled water. The residue recrystallized in CH₃CN-CH₃OH. *Anal. Calc.* for C₂₇H₃₃N₄O₄P: C, 63.77; H, 6.54; N, 11.02. Found: C, 63.85; H, 6.51; N, 11.06%. ³¹P NMR ([D₆]DMSO): δ 14.29. ¹³C NMR ([D₆]DMSO): δ 21.46 (d, ³J(P,C) = 2.7 Hz, 2 C, CH₃), 21.90 (d, ³J(P,C) = 2.8 Hz, 2 C, CH₃), 45.53 (d, ²J(P,C) = 5.1 Hz, 2 C, CH), 47.64 (d, ²J(P,C) = 5.0 Hz, 2 C, CH₂), 123.26 (s), 126.54 (s), 127.66 (s), 127.90 (s), 129.37 (s), 139.69 (d, ³J(P,C) = 8.9 Hz), 141.11 (d, ³J(P,C) = 2.4 Hz), 149.30 (s), 167.04 (s, 1 C, C=O). ¹H NMR ([D₆]DMSO): δ 0.98 (d, ³J(H,H) = 6.4 Hz, 6 H, 2 CH₃), 0.99 (d, ³J(H,H) = 6.5 Hz, 6 H, 2 CH₃), 3.89 (m, 2 H, 2 CH), 4.31 (m, 4 H, 2 CH₂), 7.17–7.96 (m, 10 H, Ar-H), 8.21 (d, ³J(H,H) = 7.0 Hz, 2 H, Ar-H), 8.26 (d, ³J(H,H) = 7.0 Hz, 2 H, Ar-H), 9.65 (b, 1 H, NH). IR (KBr, cm⁻¹): 3,050, 2,971, 2,701, 1,661 (νC=O), 1,601, 1,520, 1,456, 1,346, 1,275, 1,217, 1,064, 944, 849, 787, 712.

Crystal Structure Determination and Refinement

A colorless prismatic crystal (0.4 mm × 0.24 mm × 0.2 mm) was selected for X-ray crystallography experiment. Crystal data and refinement details for the structure

Table 1 Crystal data and structure refinement for P(O)[NHC(O)C₆H₄(4-NO₂)][N(CH(CH₃)₂)(CH₂C₆H₅)]₂

Empirical formula	C ₂₇ H ₃₃ N ₄ O ₄ P
Molecular weight	508.54
CCDC deposit no.	696934
Temperature (K)	120 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.5868 (16)
<i>b</i> (Å)	11.8058 (18)
<i>c</i> (Å)	12.4364 (19)
α (°)	65.410 (3)
β (°)	67.492 (4)
γ (°)	85.879 (3)
<i>V</i> (Å ³)	1,298.6 (3)
<i>Z</i>	2
<i>D_x</i> (g cm ⁻³)	1.301
μ (Mo K α) (mm ⁻¹)	0.146
<i>F</i> (000)	540
Crystal size (mm ³)	0.4 × 0.24 × 0.2
θ range (°)	1.91–27.00
Limiting indices	−13 ≤ <i>h</i> ≤ 13, −15 ≤ <i>k</i> ≤ 15, −15 ≤ <i>l</i> ≤ 15
Reflections collected/unique	12,532/5,667 [<i>R</i> (int) = 0.0305]
Completeness to $\theta = 27.00^\circ$	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.975 and 0.961
Refinement method	Full-matrix least-squares on <i>F</i> ²
GOF on <i>F</i> ²	1.004
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0589, <i>wR</i> ₂ = 0.1149
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0846, <i>wR</i> ₂ = 0.1281
Largest diff. peak and hole (e Å ⁻³)	0.346 and −0.317

determination are presented in Table 1. Data were collected at 120 K on a Bruker SMART 1000 CCD [7] single crystal diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) in the range of 1.91° < θ < 27.00°. The structure was refined with SHELXL-97 [8] by full matrix least squares on *F*². The hydrogen atom of NH group was found in difference Fourier synthesis. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the *U*_{iso}(H) parameters equal to 1.2 *U*_{eq}(C_i), for methyl groups equal to 1.5 *U*_{eq}(C_{ii}), where *U*(C_i) and *U*(C_{ii}) are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded. A semi-empirical absorption correction was performed using the SADABS program [9].

Results and Discussion

Description of the Crystal Structure

Single crystals of title compound were obtained from a solution of $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ after slow evaporation at room temperature. The final atomic coordinates and equivalent isotropic displacement parameters and selected geometric parameters are given in Tables 2 and 3. The phosphoryl

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{P}(\text{O})[\text{NHC}(\text{O})\text{C}_6\text{H}_4(4\text{-NO}_2)][\text{N}(\text{CH}(\text{CH}_3)_2)(\text{CH}_2\text{C}_6\text{H}_5)]_2$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
P(1)	8,354(1)	8,299(1)	1,253(1)	29(1)
O(1)	9,287(2)	9,014(2)	1,435(2)	31(1)
O(2)	7,182(2)	7,794(2)	-427(2)	42(1)
O(3)	9,917(2)	12,642(2)	-6,854(2)	50(1)
O(4)	8,441(2)	11,389(2)	-6,748(2)	53(1)
N(1)	8,561(2)	9,088(2)	-304(2)	29(1)
N(2)	9,046(2)	11,744(2)	-6,262(2)	39(1)
N(3)	8,646(2)	6,865(2)	1,431(2)	32(1)
N(4)	6,773(2)	8,239(2)	2,254(2)	30(1)
C(1)	7,942(2)	8,754(2)	-931(2)	30(1)
C(2)	8,248(2)	9,621(2)	-2,328(2)	29(1)
C(3)	9,044(3)	10,766(2)	-2,988(2)	36(1)
C(4)	9,289(3)	11,480(3)	-4,280(2)	38(1)
C(5)	8,718(2)	11,021(2)	-4,866(2)	33(1)
C(6)	7,901(3)	9,909(2)	-4,228(2)	34(1)
C(7)	7,674(3)	9,203(2)	-2,945(2)	34(1)
C(8)	8,143(3)	5,815(2)	2,737(2)	39(1)
C(9)	7,481(3)	4,697(3)	2,745(3)	53(1)
C(10)	9,220(3)	5,451(3)	3,323(3)	52(1)
C(11)	9,703(3)	6,595(3)	393(2)	36(1)
C(12)	11,172(3)	6,650(2)	291(2)	36(1)
C(13)	11,892(3)	7,790(3)	-109(2)	38(1)
C(14)	13,225(3)	7,845(3)	-197(3)	46(1)
C(15)	13,877(3)	6,754(3)	100(3)	49(1)
C(16)	13,183(3)	5,636(3)	449(3)	49(1)
C(17)	11,843(3)	5,579(3)	545(3)	42(1)
C(18)	5,582(3)	7,620(3)	2,282(2)	38(1)
C(19)	4,784(3)	8,581(3)	1,606(3)	52(1)
C(20)	4,620(3)	6,756(3)	3,645(3)	51(1)
C(21)	6,486(3)	9,012(2)	2,970(2)	34(1)
C(22)	6,234(2)	8,284(2)	4,378(2)	31(1)
C(23)	7,176(3)	7,515(2)	4,743(2)	35(1)
C(24)	6,932(3)	6,816(3)	6,031(3)	42(1)
C(25)	5,734(3)	6,895(3)	6,963(2)	45(1)
C(26)	4,804(3)	7,687(3)	6,613(2)	42(1)
C(27)	5,047(3)	8,367(3)	5,329(2)	36(1)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor

Table 3 Selected bond lengths (\AA) and angles ($^\circ$) for $\text{P}(\text{O})[\text{NHC}(\text{O})\text{C}_6\text{H}_4(4\text{-NO}_2)][\text{N}(\text{CH}(\text{CH}_3)_2)(\text{CH}_2\text{C}_6\text{H}_5)]_2$

P(1)–O(1)	1.4801(17)	O(4)–N(2)	1.223(3)
P(1)–N(3)	1.636(2)	N(1)–C(1)	1.370(3)
P(1)–N(4)	1.644(2)	N(2)–C(5)	1.486(3)
P(1)–N(1)	1.694(2)	N(3)–C(11)	1.485(3)
O(2)–C(1)	1.216(3)	N(3)–C(8)	1.488(3)
O(3)–N(2)	1.219(3)	N(4)–C(21)	1.466(3)
O(1)–P(1)–N(3)	118.24(10)	C(11)–N(3)–C(8)	116.2(2)
O(1)–P(1)–N(4)	108.78(10)	C(11)–N(3)–P(1)	121.79(17)
N(3)–P(1)–N(4)	107.25(10)	C(8)–N(3)–P(1)	120.08(17)
O(1)–P(1)–N(1)	105.31(10)	C(21)–N(4)–C(18)	117.67(19)
N(3)–P(1)–N(1)	104.71(11)	C(21)–N(4)–P(1)	119.18(16)
N(4)–P(1)–N(1)	112.63(10)	C(18)–N(4)–P(1)	122.15(16)
C(1)–N(1)–P(1)	126.67(17)	O(2)–C(1)–N(1)	123.1(2)
O(3)–N(2)–O(4)	124.1(2)	O(2)–C(1)–C(2)	119.0(2)
O(3)–N(2)–C(5)	117.9(2)	N(1)–C(1)–C(2)	117.9(2)

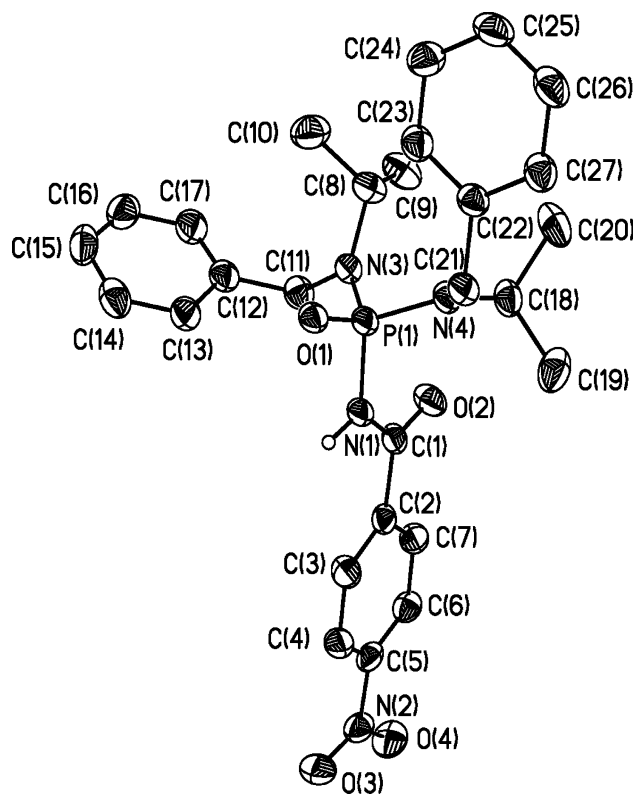


Fig. 2 Molecular structure of $\text{P}(\text{O})[\text{NHC}(\text{O})\text{C}_6\text{H}_4(4\text{-NO}_2)][\text{N}(\text{CH}(\text{CH}_3)_2)(\text{CH}_2\text{C}_6\text{H}_5)]_2$ in representation of atoms via thermal ellipsoids at 50% probability level (all hydrogen atoms except H(1N) are omitted for clarity)

and the carbonyl groups are *anti* and the phosphorus atom has a slightly distorted tetrahedral configuration (Fig. 2). The bond angles around the P atom are in the range of $104.71(11)^\circ$ – $118.24(10)^\circ$. P(1)–N(3) and P(1)–N(4) bond lengths (1.636(2) \AA and 1.644(2) \AA) are significantly

shorter than the typical P–N single bond length (1.77 Å) [10]. The shortening of P–N bond lengths is likely related to an electrostatic effect (polar bond) which overlaps with P–N σ bond [11]. The P(1)–N(1) bond length (1.694(2) Å) is longer than the P(1)–N(3) and P(1)–N(4) bond lengths due to the resonance interaction of N(1) nitrogen atom lone pair with the C=O system (and less interaction with P=O) that causes a partial multiple bond character in N(1)–C(1) (compare N(1)–C(1) with other N–C bond lengths (Table 3). The environment of the nitrogen atoms is practically planar. In the title compound, the angles C(11)–N(3)–C(8), C(11)–N(3)–P(1) and C(8)–N(3)–P(1) are 116.2(2)°, 121.79(17)° and 120.08(17)°, respectively (with average 119.4°). A similar result was obtained for the bond angles around N(4) atom (average = 119.7°). Furthermore, the angle C(1)–N(1)–P(1) is 126.67(17)°. These results confirm the sp^2 hybridization for the nitrogen atoms, although due to repulsion and steric interactions and electronic effect, some angles are greater and the others are smaller than 120°. The P=O bond length, 1.4801(17) Å, is longer than the normal P=O bond length (1.45 Å) [10]. The amidic hydrogen atom of title compound is involved in intermolecular –P=O...H–N– hydrogen bond (Fig. 3; Table 4) to form a dimer with Ci symmetry (centrosymmetric dimer). The donor...acceptor distances for the –P=O...H–N hydrogen bond in the title compound is in the range of the values which have been observed for the other phosphoramidate compounds, Table 5. H-bonded dimers in the crystal structure form chains through π -stacking between *p*-NO₂–C₆H₄–C(O)–NH– moieties (see the

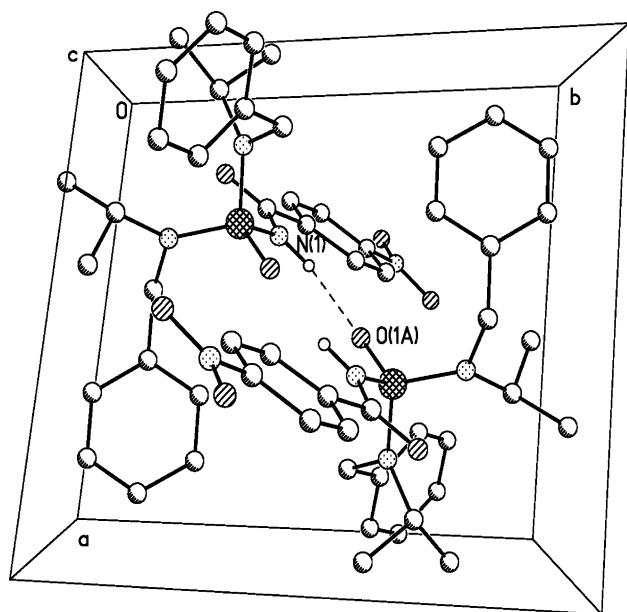


Fig. 3 The fragment of crystal packing of P(O)[NHC(O)C₆H₄(4-NO₂)] [N(CH(CH₃)₂)(CH₂C₆H₅)]₂ along the crystallographic plane *ab* (all hydrogen atoms except H(1N) are omitted for clarity)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
N(1)–H(1N)...O(1)#1	0.91(4)	1.91(4)	2.801(3)	168(3)

Symmetry transformations used to generate equivalent atoms: #1 –*x* + 2, –*y* + 2, –*z*

orientation of these moieties in crystal packing, Fig. 4). The planes of *p*-NO₂–C₆H₄–C(O)–NH– moieties of neighboring molecules are parallel (0.0(1)°) and are situated at 3.36(2) Å from each other; compare it with the distance between the planes of *p*-H₃C–C₆H₄–NH moieties (3.26(1) Å [20]) in [(CH₃)₂N][*p*-H₃C–C₆H₄–O]P(O)[*p*-H₃C–C₆H₄–NH]. The π -stacking between *p*-NO₂–C₆H₄–C(O)–NH– moieties is off-center stacking, the distance between the centers of the interacting phenyl rings is 4.046(4) Å. The concept of H bonds has been extended to C–H...Y bonding (where Y is an electronegative atom or the π system [21, 22]). Previous studies have suggested that C–H...O hydrogen bonds occur in the range of 3.0–4.0 Å for C...O distances and more than 110° for the bond angles [23, 24]. Figure 5 indicates a view of normal N(1)–H(1N)...O(1) and weak C(3)–H(3A)...O(1) and C(15)–H(15A)...O(2) hydrogen bonds. The weak C–H...O hydrogen bonds in the title compound [C(3)...O(1) = 3.165(3) Å, ∠C–H–O = 155.6° and C(15)...O(2) = 3.517(3) Å, ∠C–H–O = 157.7°] are in the range of the previous results for the phosphoryl compounds, for example in P(O)(OCH₃)₂(NHC₆H₄(4-NO₂)): C(sp²)...O(phosphoryl) = 3.352 Å and C(sp³)...O(nitro) = 3.302 Å [25] and in P(O)[4-CH₃–C₅H₉N]₂[NHC₆H₄(4-NO₂)]: C(sp²)...O(phosphoryl) = 3.288 Å, C(sp³)...O(nitro) = 3.429 and 3.435 Å [13]. A view of C(7)–H(7A)... π and C(25)–H(25A)... π interactions is given in Fig. 6 [r(C(7)...meanplane) = 3.562(3) Å, r(H(7A)–C(25)) = 2.854 Å, ∠C–H–C = 137.2° and r(C(25)...meanplane) = 3.467(4) Å, r(H(25)–C(15)) = 2.884 Å, ∠C–H–C = 131.7°]. The C–H bond points away from the ring although the hydrogen is close to a carbon (type VI C–H... π interaction according to the classification of Malone et al. [26]). The distances of interacting H atoms to phenyl ring centroid (3.44 and 3.53 Å) in P(O)[NHC(O)C₆H₄(4-NO₂)] [N(CH(CH₃)₂)(CH₂C₆H₅)]₂ are more than the values for [P(O)(O)(NHC(O)CF₃)(N(CH(CH₃)₂)(CH₂C₆H₅))] [NH₂(CH(CH₃)₂)(CH₂C₆H₅)] (3.26 Å [6]) and [(CH₃)₂N]P(O)[NH(*iso*-C₃H₇)] [*p*-OC₆H₄–CH₃] (3.31 Å) [19].

Spectroscopic Characterization

As can be seen in X-ray structure of the title compound, the P=O...H–N_{amide} hydrogen bond leads to a dimeric aggregate in the solid state, which means the phosphoryl oxygen

Table 5 Donor...acceptor (N...O) distances for N–H...O=P hydrogen bonds in some phosphoramidate compounds

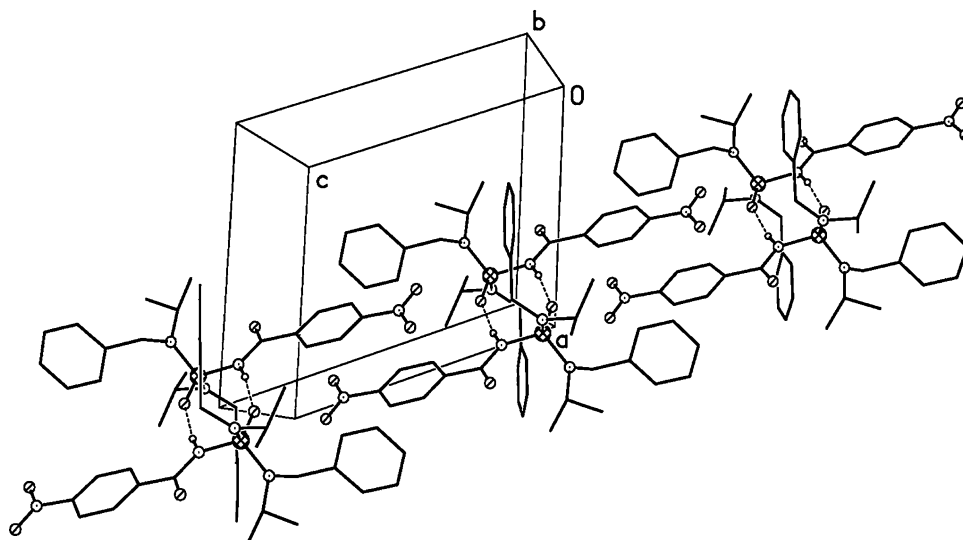
No.	Compound	D...A (Å)	Ref.
1	P(O)(C ₆ H ₅ C(O)NH)[N(CH ₃)(CH ₂ C ₆ H ₅) ₂]	2.809(3)	[12]
2	P(O)(CCl ₃ C(O)NH)[N(CH ₃)(CH ₂ C ₆ H ₅) ₂]	2.794(2)	[12]
3	P(O)(CF ₃ C(O)NH)[N(CH ₃)(CH ₂ C ₆ H ₅) ₂]	2.747(4)	[13]
4	P(O)(4-NO ₂ -C ₆ H ₄ NH)[4-CH ₃ -NC ₅ H ₉] ₂	2.770(2)	[13]
5	P(O)(4-F-C ₆ H ₄ C(O)NH)[NC ₄ H ₈] ₂	2.842(2)	[14]
6	P(O)(4-F-C ₆ H ₄ C(O)NH)[NC ₅ H ₁₀] ₂ ^a	2.818(4), 2.886(4), 2.912(4), 2.916(4)	[14]
7	P(O)(4-F-C ₆ H ₄ C(O)NH)(NC ₄ H ₈ O) ₂	2.904(3)	[14]
8	P(O)(4-F-C ₆ H ₄ C(O)NH)(NC ₆ H ₁₂) ₂	2.820(4)	[14]
9	P(O)(C ₆ H ₅ C(O)NH)(NC ₄ H ₈) ₂ ^b	2.855(6), 2.886(5)	[15]
10	P(O)(4-F-C ₆ H ₄ C(O)NH)[NH-C(CH ₃) ₃] ₂	2.774(2)	[16]
11	P(O)(4-F-C ₆ H ₄ C(O)NH)[NH-CH ₂ C ₆ H ₅] ₂	2.834(2), 3.015(2), 2.937(2)	[16]
12	P(O)(4-F-C ₆ H ₄ C(O)NH)[N(CH ₃)(CH ₂ C ₆ H ₅) ₂]	2.8055(14)	[16]
13	P(O)(C ₆ H ₅ C(O)NH)(NC ₃ H ₆) ₂ ^b	2.817(1), 2.815(1)	[17]
14	P(O)(C ₆ H ₅ C(O)NH)(NC ₆ H ₁₂) ₂	2.816(3)	[17]
15	P(O)[(C ₆ H ₅)(CH ₃)CH-NH](<i>p</i> -OC ₆ H ₄ CH ₃) ₂ ^b	2.839(6), 2.817(6)	[18]
16	[NH ₂ (CH(CH ₃) ₂)(CH ₂ C ₆ H ₅)] ₂ [P(O)(NHC(O)CCl ₃)O(OCH ₃)]	2.811(2), 2.727(2), 2.743(2)	[5]
17	P(O)[NHCH(CH ₃) ₂][(CH ₃) ₂ N][<i>p</i> -H ₃ C-C ₆ H ₄ -O]	2.849(4)	[19]

^a Compound contains four independent molecules in crystal lattice

^b Two independent molecules

^c The first D...A distance in the table is related to P=O...H-N_{amide}, two others are related to P=O...H-N_{amine}

Fig. 4 A view of H-bonded dimers with C_i symmetry and the chain array through π -stacking between *p*-NO₂-C₆H₄-C(O)-NH- moieties



atom is the better H-acceptor than the carbonyl oxygen atom. This finding is in agreement with the theoretical studies on compounds with -P(O_P)XC(O_C)- system. The theoretical investigation shows that the O_P atom is a better electron donor relative to the O_C counterpart as a result of the more partial negative charge (δ^-) on the O_P atom relative to the O_C [27]. In title compound, the $\nu(\text{C}=\text{O})$ stretching frequency appears at 1,661 cm⁻¹ wave number. The frequency of the N-H stretching vibration ($\tilde{\nu}_{\text{N-H}}$) is

very sensitive to the formation of hydrogen bonding (red-shift of the absorption band, band broadening or intensification). For N-H...O hydrogen bonds, the $\tilde{\nu}_{\text{N-H}}$ is depending on the H-bond strength or donor...acceptor distance (N...O). For title compound, the band at 3,050 cm⁻¹ is assigned to N-H_{amide}. The wave number is close to the ones which have been observed for ClF₂CC(O)NHP(O)Cl₂ and CF₃C(O)NHP(O)Cl₂ (3,064 and 3,093 cm⁻¹) [28, 29]. This relative low wave number for

Fig. 5 A view of normal N–H···O and weak C–H···O hydrogen bonds in the crystal network

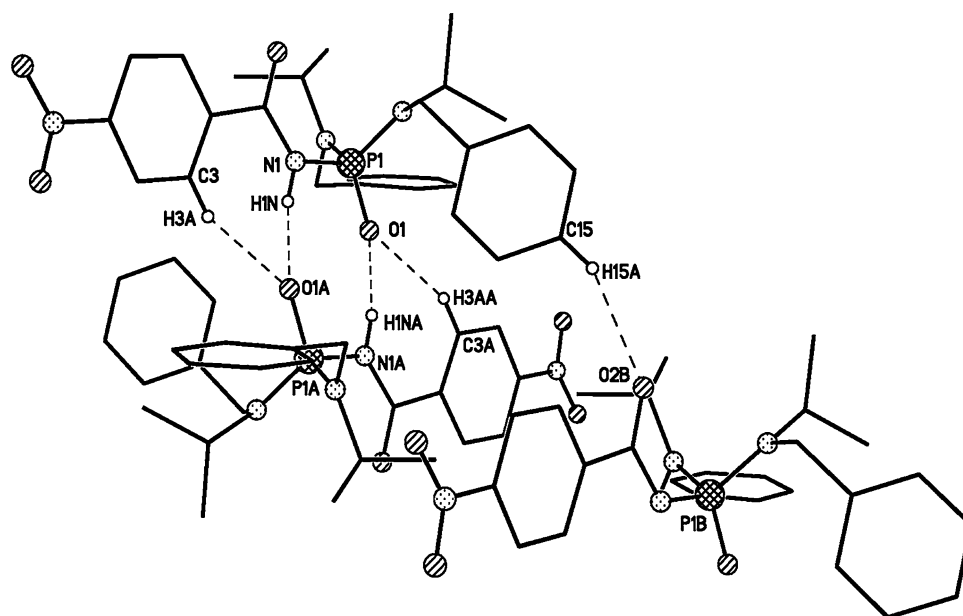
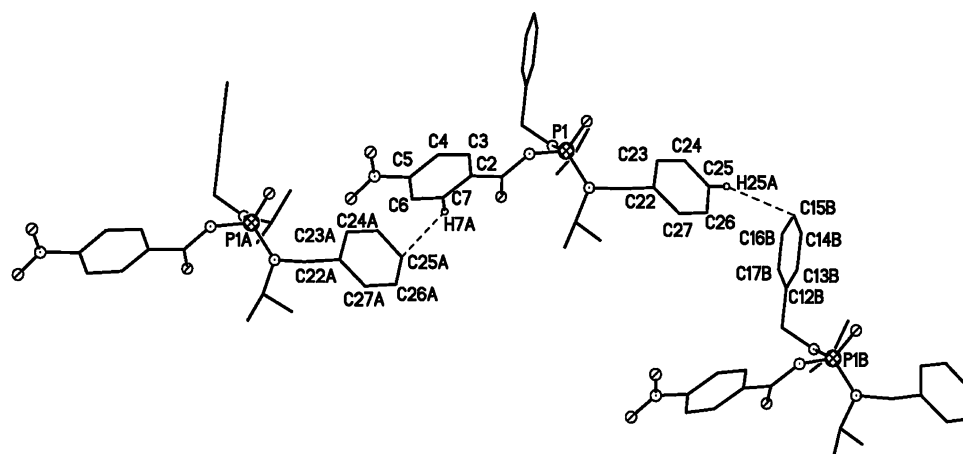


Fig. 6 A view of C–H··· π interactions in the crystal network



an N–H stretching vibrational mode can be explained by the N–H···O intermolecular interactions as reported on related acetyl phosphorylamidate compounds [28]. The NH_{amide} is placed between two withdrawing groups (PO and CO) which causes an increase in the acidity of the H atom. Appearance of the NH_{amide} signal at 9.65 ppm in ^1H NMR spectrum confirms this fact. Moreover, the phosphorus–hydrogen coupling constant, $^2J(\text{PNH})$ was not observed. The P–C coupling constants give rise to two doublet signals for two non-equivalent methyl carbon atoms of *isopropyl* moieties at 21.46 ppm ($^3J(\text{P,C}) = 2.7$ Hz) and 21.90 ppm ($^3J(\text{P,C}) = 2.8$ Hz). Moreover, the CH and CH_2 carbon atoms show P–C coupling constants at 45.53 ppm ($^2J(\text{P,C}) = 5.1$ Hz) and 47.64 ppm ($^2J(\text{P,C}) = 5.0$ Hz), which means that for these aliphatic carbon atoms $^2J(\text{P,C}) > ^3J(\text{P,C})$. Also, the *ipso* C atoms of the phenyl moieties show P–C coupling constants ($^3J(\text{P,C}) = 2.4$ and 8.9 Hz). Phosphorus chemical shift in the title compound was observed at 14.29 ppm in ^{31}P NMR spectrum.

Supplementary Material

CCDC 696934 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1BZ, UK, Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk.

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