

Syntheses, spectroscopic study and crystal structures of some new *N*-benzoylphosphoric triamides

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Abstract The reaction of *N*-benzoylphosphoramidic dichloride with amines afforded some new *N*-benzoylphosphoric triamides with formula $C_6H_5C(O)NHP(O)(X)_2$, $X = NH-CH(CH_3)_2$ (**1**), $NH-CH_2-CH(CH_3)_2$ (**2**), $NH-CH_2-CH(OCH_3)_2$ (**3**), $N(CH_3)[CH_2CH(OCH_3)_2]$ (**4**) and $N(CH_3)(C_6H_{11})$ (**5**) that were characterized by 1H , ^{13}C , ^{31}P NMR, IR spectroscopy and elemental analysis. The structures have been determined for compounds **4** and **5** by X-ray crystallography. These compounds contain one amidic hydrogen atom and form centrosymmetric dimmers via intermolecular $-P=O \cdots H-N-$ hydrogen bonds besides weak $C-H \cdots O$ hydrogen bonds that lead to three-dimensional polymeric clusters in the crystalline lattice.

Keywords Phosphoric triamides · NMR · X-ray crystallography · Hydrogen bonds

Introduction

In recent years, investigations on *N*-benzoylphosphoric triamides are an important part of phosphoramidate chemistry due to their synthetic and structural [1–3], coordination [4–8] and biological [9] applications. These molecules have $-C(O)NHP(O)-$ skeleton and the existence of peptide group in these derivatives cause them biologically active anticancer drugs [10]. Moreover, applications of other phosphoramidates in chemical reactions have been reported [11–13]. Compound $C_6H_5C(O)NHP(O)[NH-C(CH_3)_3]_2$ showed two conformers in solution NMR spectra and solid

state [14]. Moreover, compounds $C_6H_5C(O)NHP(O)X_2$, $X = NC_3H_6$ [15], NC_4H_8 [16] $4-CH_3-C_6H_4OP(O)(NH-CH(CH_3)(CH_2C_6H_5))$ [17] and $C_6H_5C(O)NHP(O)(NC_5H_{10})_2$ [18] $4-F-C_6H_4C(O)NH P(O)(NC_5H_{10})_2$ [19] exhibited two and four conformers, respectively, only in their crystalline states. The synthesis and structure of compound $\{(1R, 2S)-N-^iPr\text{-ephedrine}\}P(S)NH[(Si(CH_3)_3)]$, which is an oxaphosphole molecule with three independent molecules in the crystalline lattice, was reported [20]. The spectra and structure of some organophosphorus compounds (that are analogues of phosphoramidates) [21] and also of a polymorph $Mo_2(CO)_8(\mu-PPh_2)_2$ complex have been investigated [22]. Herein, we have considered the synthesis and spectroscopic characterization of several new *N*-benzoylphosphoric triamides with formula $C_6H_5C(O)NHP(O)(X)_2$, $X = NH-CH(CH_3)_2$ (**1**), $NH-CH_2-CH(CH_3)_2$ (**2**), $NH-CH_2-CH(OCH_3)_2$ (**3**), $N(CH_3)[CH_2CH(OCH_3)_2]$ (**4**) and $N(CH_3)(C_6H_{11})$ (**5**). The solid-state crystal structures of compounds **4** and **5** were investigated by means of X-ray crystallography technique.

Experimental

Crystal structure determination

X-ray data of compounds **4** and **5** were collected on a Bruker SMART 1000 CCD area detector [23] single crystal diffractometer with graphite monochromated $Mo K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were refined with SHELXL-97 [24] by full-matrix least-squares on F^2 . The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program [25].

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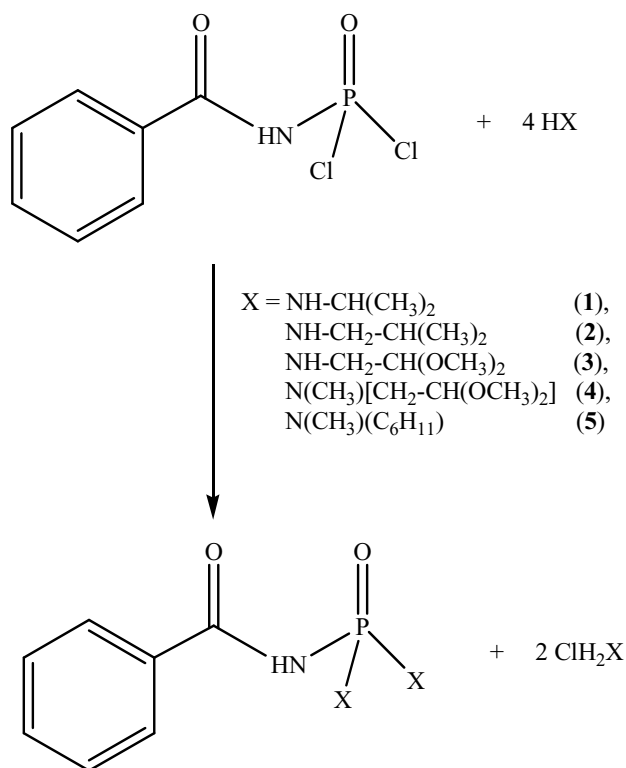
Spectroscopic measurements

All reactions were performed under argon atmosphere and in dry solvents. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to internal TMS, ^{31}P chemical shifts relative to 85% H_3PO_4 as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. $\text{C}_6\text{H}_5\text{C}(\text{O})\text{NHP}(\text{O})\text{Cl}_2$ was prepared according to the literature method [26].

Results and discussion

Spectroscopic study

Synthesis of compounds **1–5** was performed by the reaction of *N*-benzoylphosphoramidic dichloride [26] with corresponding amines, Scheme 1. The spectroscopic data of these molecules are summarized in Table 1. ^1H NMR spectra of compounds **1**, **2** and also of **4** indicate two separate signals for the two non-equivalent CH_3 and OCH_3 groups, respectively. In these compounds, the existence of prochiral CH group leads to different methyl and methoxy groups. $^2J(\text{PNH})_{\text{amine}}$ coupling constant for amine protons in compound **1** is 9.1 Hz in d_6 -DMSO and 13.2 Hz in CDCl_3 . This



Scheme 1 Synthesis pathway of compounds **1–5**

constant in both similar compounds **2** (containing isobutyl groups) and **3** (containing 2,2-dimethoxy-ethyl groups) is 16.1 Hz that is higher than those observed for acyclic phosphoramidates [14, 27, 28]. $^3J(\text{PNCH})$ coupling constant in molecule **4** is 16.3 Hz, which is higher than the observed values for our previously reported acyclic phosphoramidates [27–29]. This constant is 10.9 Hz in molecule **5** (for the splitting of *N*-methyl protons with phosphorus atom). The CH_2 protons in compound **4** are diastereotopic and exhibit two ddd coupling patterns in ^1H NMR spectrum due to the coupling of each of these protons with another one, with CH proton and phosphorus atom. The amidic proton splits with phosphorus atom in compounds **1** and **5** with $^2J(\text{PNH})_{\text{amide}} = 5.7$ and 5.9 Hz, respectively.

^{13}C NMR spectra of compounds **1** and **2** display two distinct signals for the two non-equivalent methyl carbon atoms. The related $^3J(\text{P}, \text{C})$ coupling constants for the methyl carbon atoms in **1** are 4.8 and 6.6 Hz. The *ipso* carbon atoms of phenyl rings in compounds **1–5** show $^3J(\text{P}, \text{C})_{\text{aromatic}}$ coupling constants in the range of 7.5 Hz (in **3**) to 8.7 Hz (in **4**). The coupling between $\text{C}=\text{O}$ carbon atom and phosphorus atom have been observed only in compound **5** (2.9 Hz). The only difference between compounds **3** and **4** is the replacement of amino proton in $\text{NH-CH}_2\text{CH}(\text{OCH}_3)_2$ chains (**3**) with CH_3 group (**4**). A comparison between compounds **3** and **4** indicates that the $^3J(\text{P}, \text{C})_{\text{aliphatic}}$ for the splitting of carbon atom in CH moiety with phosphorus atom is nearly twice in **3** (6.7 Hz) relative to that of in **4** (3.1 Hz). The $\delta(^{31}\text{P})$ of compounds **1–5** are in the range of 13.75 ppm (in **5**) to 8.22 ppm (in **1**).

IR spectra of compounds **1–5** showed that the $\nu_{\text{P}=\text{O}}$ and $\nu_{\text{C}=\text{O}}$ frequencies are in the range of 1182 cm^{-1} (in **4**) to 1215 cm^{-1} (in **2**) and 1635 cm^{-1} (**2**) to 1670 cm^{-1} (**5**), respectively. The $\nu_{\text{P}=\text{O}}$ bond frequency in compound **2** (containing isobutyl substituent) is stronger than in **1** (containing isopropyl substituent), but for the $\text{C}=\text{O}$ frequency an opposite result was obtained. A comparison between similar compounds **2** and **3** indicates that $\nu_{\text{P}=\text{O}}$ in **2** is stronger than in **3** in contrary to the result for $\nu_{\text{C}=\text{O}}$. This is also observed for compounds **3** and **4** in which the $\nu_{\text{P}=\text{O}}$ in **3** is stronger than in **4**. The $\nu_{\text{P}=\text{O}}$ in compounds **4** and **5**, 1182 and 1183 cm^{-1} , are very close to each other that shows the $\text{P}=\text{O}$ bond lengths in these molecules are nearly the same. This is confirmed by X-ray crystal structures of **4** and **5** indicate that the $\text{P}=\text{O}$ bond lengths are 1.4818(11) and 1.4842(12) Å, respectively.

X-ray crystallography investigation

Single crystals of compound **4** were obtained from a mixture of diethylether/*n*-heptane and of **5** from a mixture of dichloromethane/*n*-hexane/diethylether at room temperature. The crystal data and the details of the X-ray analysis are

Table 1 Spectroscopic NMR and IR data of compounds 1–5

No.	$\delta(^{31}\text{P})$ (ppm)	$^2J(\text{PNH})_{\text{amine}}$ (Hz)	$^2J(\text{PNH})_{\text{amide}}$ (Hz)	$^2J(\text{P, C})_{\text{aliphatic}}$ (Hz)	$^3J(\text{P, C})_{\text{aliphatic}}$ (Hz)	$^3J(\text{P, C})_{\text{aromatic}}$ (Hz)	$\nu(\text{C=O})$ (cm^{-1})	$\nu(\text{P=O})$ (cm^{-1})
1	8.22	9.1 (d_6 -DMSO), 13.2 (CDCl_3)	— (d_6 -DMSO), 5.7 (CDCl_3)	—	4.8 (CH_3), 6.6 (CH_3)	7.8	1640	1203
2	9.68	16.1	—	—	6.1 (CH)	7.9	1635	1215
3	9.54	16.1	—	5.6 (CH_2)	6.7 (CH)	7.5	1645	1208
4	13.75	—	—	4.3 (CH_3)	3.1 (CH)	8.7	1666	1182
5	13.56	—	5.9	2.9 (C=O), 4.8 (CH_3), 5.2 (CH)	3.1, 3.9 (CH_2)	8.6	1670	1183

given in Table 2, selected bond lengths and angles in Table 3. Molecular structures (ORTEP view) of these compounds are shown in Figs. 1 and 4, the unit cells are presented in Figs. 3 and 6.

As we observed in NMR section, the two methoxy groups of one chain in molecule 4 are not equivalent with each other due to their different spatial orientations. This matter can be attributed to the existence of prochiral CH group in this compound and it can be shown by the differences in their sim-

ilar torsion angles. The torsion angles O(1)–P(1)–N(2)–C(9) and O(1)–P(1)–N(3)–C(14) of the two amine chains are $114.01(14)^\circ$ and $-34.21(14)^\circ$, respectively, (similarly, compare the torsion angles P(1)–N(2)–C(9)–C(10) and P(1)–N(3)–C(14)–C(15) that are $-87.10(16)^\circ$ and $97.12(15)^\circ$, respectively). The two *N*-methyl groups have different orientations relative to each other that can be displayed by the differences in their related torsion angles. The torsion angles O(1)–P(1)–N(2)–C(8) and O(1)–P(1)–N(3)–C(13)

Table 2 Crystallographic data for compounds 4 and 5

	Compound 4	Compound 5
Empirical formula	$\text{C}_{17}\text{H}_{30}\text{N}_3\text{O}_6\text{P}$	$\text{C}_{21}\text{H}_{34}\text{N}_3\text{O}_2\text{P}$
Formula weight	403.41	391.48
Temperature (K)	120(2)	120(2)
Wavelength (\AA)	0.7173	0.7173
Crystal system, space group	Triclinic, <i>P</i> -1	Orthorhombic, <i>Pbca</i>
Unit cell dimensions		
<i>a</i> (\AA)	10.2760(9)	18.2690(13)
<i>b</i> (\AA)	10.4970(9)	11.5500(8)
<i>c</i> (\AA)	11.1259(10)	20.0921(15)
α ($^\circ$)	91.924(2)	90.0
β ($^\circ$)	104.352(2)	90.0
γ ($^\circ$)	116.338(2)	90.0
<i>V</i> (\AA^3)	1027.63(16)	4239.6(5)
<i>Z</i> , Calculated density (Mg. m^{-3})	2, 1.304	8, 1.227
Absorption coefficient (mm^{-1})	0.171	0.150
<i>F</i> (0 0 0)	432	1696
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.20$	$0.45 \times 0.40 \times 0.30$
θ range for data collection ($^\circ$)	2.31–28.50	2.03–29.02
Limiting indices	$-13 \leq h \leq 13$ $-14 \leq k \leq 14$ $-14 \leq l \leq 14$	$-24 \leq h \leq 24$ $-15 \leq k \leq 15$ $-27 \leq l \leq 27$
Reflections collected/unique	9582/5158 [<i>R</i> (int) = 0.0239]	44016/5572 [<i>R</i> (int) = 0.0417]
Completeness to theta	98.9%	98.8%
Absorption correction	Semi-empirical from equivalents	None
Max. and min. transmission	0.960 and 0.950	—
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5158/0/251	5572/0/246
Goodness-of-fit on <i>F</i> ²	0.978	1.003
Final <i>R</i> indices	$R_1 = 0.0456$, $wR_2 = 0.0970$	$R_1 = 0.0529$, $wR_2 = 0.1221$
<i>R</i> indices (all data)	$R_1 = 0.0583$, $wR_2 = 0.1034$	$R_1 = 0.0683$, $wR_2 = 0.1322$
Largest diff. peak and hole (e. \AA^{-3})	0.376 and -0.363	0.469 and -0.270

Table 3 Selected bond lengths (Å) and angles (°) of compounds **4** and **5**

Compound 4		Compound 5	
Bond lengths (Å)			
P(1)–O(1)	1.4818(11)	P(1)–O(1)	1.4842(12)
P(1)–N(2)	1.6286(14)	P(1)–N(2)	1.6344(14)
P(1)–N(3)	1.6314(13)	P(1)–N(3)	1.6368(14)
P(1)–N(1)	1.6801(14)	P(1)–N(1)	1.6980(14)
O(2)–C(1)	1.2234(19)	O(2)–C(1)	1.218(2)
O(3)–C(15)	1.4079(19)	N(1)–C(1)	1.377(2)
O(3)–C(17)	1.425(2)	N(1)–H(1A)	0.8800
O(4)–C(15)	1.409(2)	N(2)–C(8)	1.466(2)
O(4)–C(16)	1.428(2)	N(2)–C(9)	1.4848(19)
O(5)–C(10)	1.4142(19)	N(3)–C(15)	1.469(2)
O(5)–C(11)	1.434(2)	N(3)–C(16)	1.481(2)
O(6)–C(10)	1.4031(18)	C(1)–C(2)	1.504(2)
O(6)–C(12)	1.422(2)	C(2)–C(3)	1.390(2)
N(1)–C(1)	1.3721(19)	C(2)–C(7)	1.391(2)
Bond angles (°)			
O(1)–P(1)–N(2)	116.97(7)	O(1)–P(1)–N(2)	117.30(7)
O(1)–P(1)–N(3)	110.47(7)	O(1)–P(1)–N(3)	111.71(7)
N(2)–P(1)–N(3)	105.30(7)	N(2)–P(1)–N(3)	106.22(7)
O(1)–P(1)–N(1)	106.28(7)	O(1)–P(1)–N(1)	105.92(7)
N(2)–P(1)–N(1)	106.36(7)	N(2)–P(1)–N(1)	105.14(7)
N(3)–P(1)–N(1)	111.48(7)	N(3)–P(1)–N(1)	110.30(7)
C(15)–O(3)–C(17)	113.49(14)	C(1)–N(1)–P(1)	131.08(11)
C(15)–O(4)–C(16)	115.07(14)	C(1)–N(1)–H(1A)	114.5
C(10)–O(5)–C(11)	114.87(13)	P(1)–N(1)–H(1A)	114.5
C(10)–O(6)–C(12)	113.22(13)	C(8)–N(2)–C(9)	117.26(13)
C(1)–N(1)–P(1)	126.47(11)	C(8)–N(2)–P(1)	117.50(11)
C(1)–N(1)–H(1N)	117.4	C(9)–N(2)–P(1)	121.53(11)
P(1)–N(1)–H(1N)	116.1	C(15)–N(3)–C(16)	118.80(13)
C(9)–N(2)–C(8)	116.86(13)	C(15)–N(3)–P(1)	118.41(11)
C(9)–N(2)–P(1)	125.40(11)	C(16)–N(3)–P(1)	119.00(11)
C(8)–N(2)–P(1)	117.59(11)	O(2)–C(1)–N(1)	123.95(15)
C(14)–N(3)–C(13)	115.29(12)	O(2)–C(1)–C(2)	120.88(15)
C(14)–N(3)–P(1)	119.26(10)	N(1)–C(1)–C(2)	115.13(14)
C(13)–N(3)–P(1)	124.35(11)	C(3)–C(2)–C(7)	119.40(15)
O(2)–C(1)–N(1)	122.51(15)	C(3)–C(2)–C(1)	123.46(15)
O(2)–C(1)–C(2)	121.00(14)	C(7)–C(2)–C(1)	117.13(15)
N(1)–C(1)–C(2)	116.49(13)	C(2)–C(3)–C(4)	120.05(16)

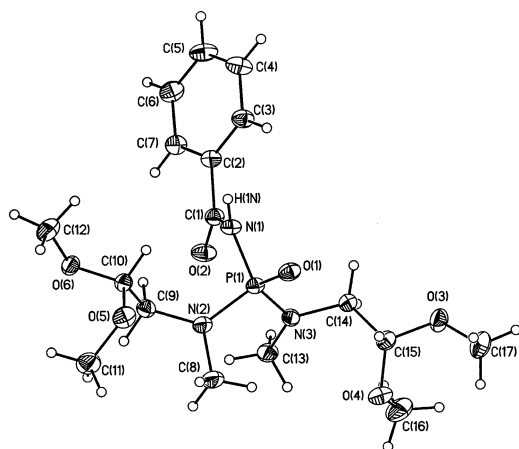


Fig. 1 Molecular structure and atom labelling scheme for compound **4** (50% probability ellipsoids)

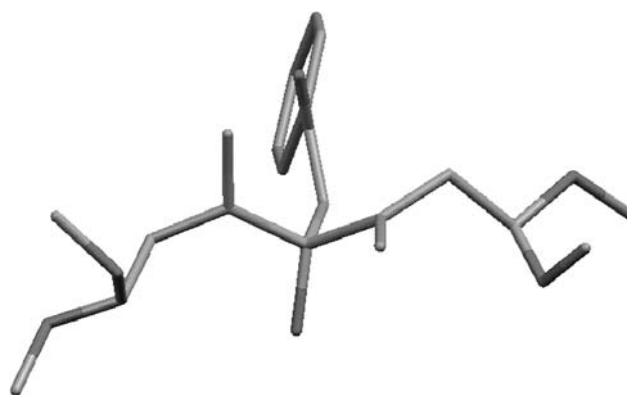
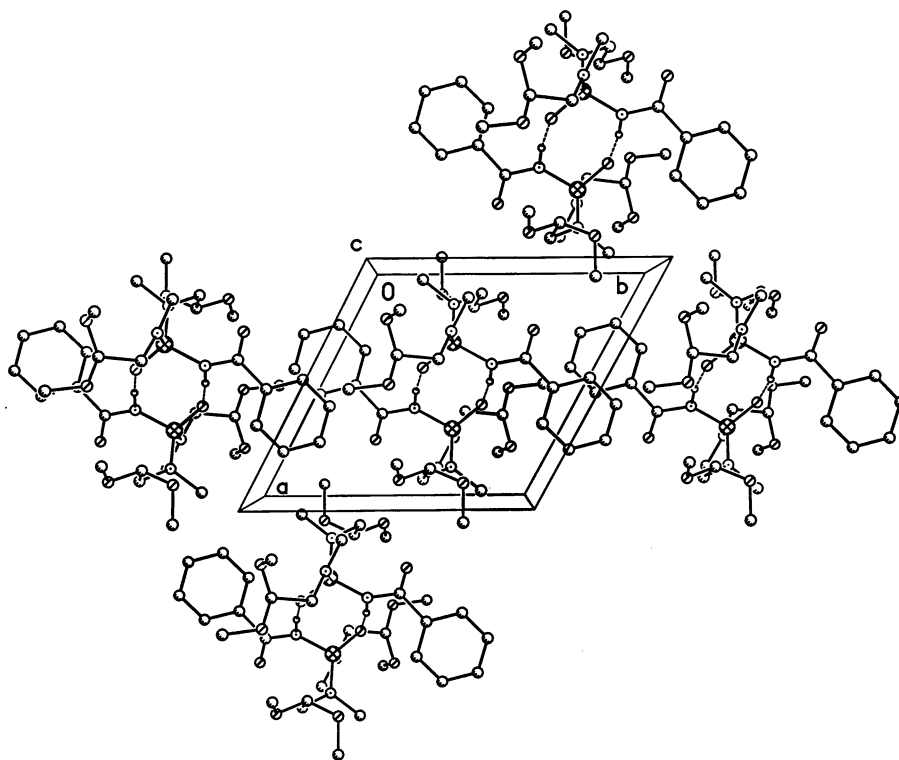


Fig. 2 The two non-equivalent $N(\text{CH}_3)[\text{CH}_2\text{CH}(\text{OCH}_3)_2]$ groups in structure of **4** that indicates different spatial orientations of *N*-methyl groups and two OCH_3 moieties

Fig. 3 A view of the unit cell packing of compound **4**



are $-61.38(15)^\circ$ and $158.33(13)^\circ$, respectively, Fig. 2. Also, in compound **5**, the two *N*-methylcyclohexyl moieties are not equivalent (Fig. 5) and their similar torsion angles are different. The torsion angles $O(1)-P(1)-N(2)-C(8)$ and $O(1)-P(1)-N(3)-C(15)$ are $-63.86(14)^\circ$ and $167.69(12)^\circ$,

respectively. Moreover, the torsion angles $O(1)-P(1)-N(2)-C(9)$, $O(1)-P(1)-N(3)-C(16)$ and $N(3)-P(1)-N(2)-C(8)$, $N(2)-P(1)-N(3)-C(15)$ are $93.85(13)^\circ$, $167.69(12)^\circ$ and $170.43(12)^\circ$, $-63.27(14)^\circ$, respectively.

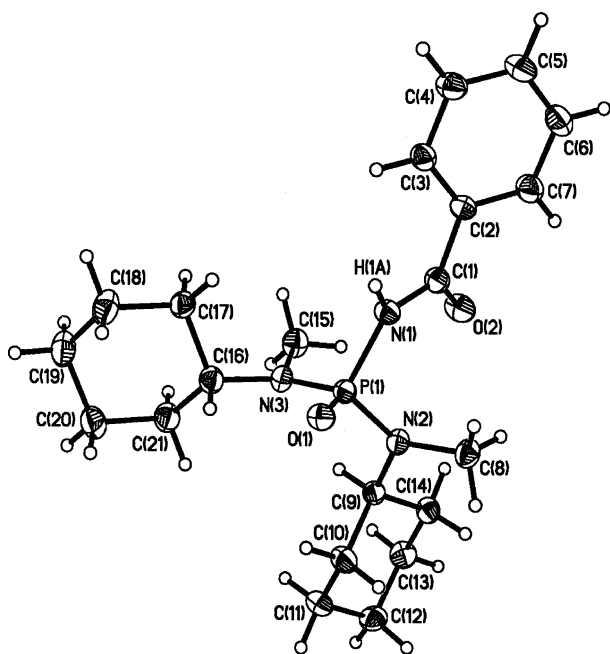


Fig. 4 Molecular structure and atom labelling scheme for compound **5** (50% probability ellipsoids)

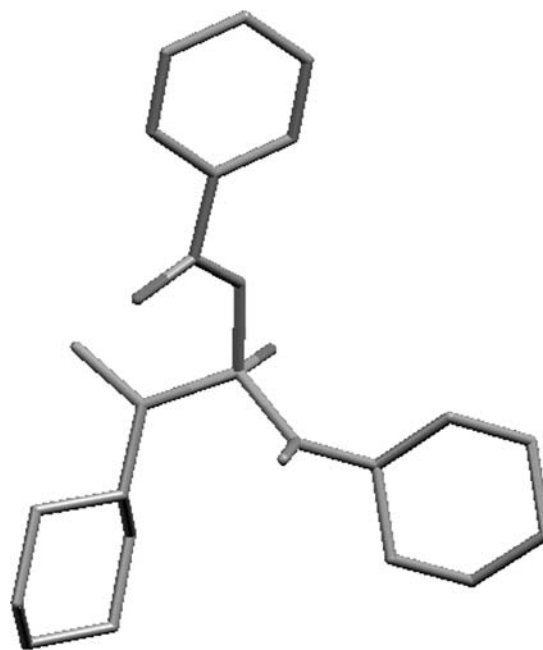
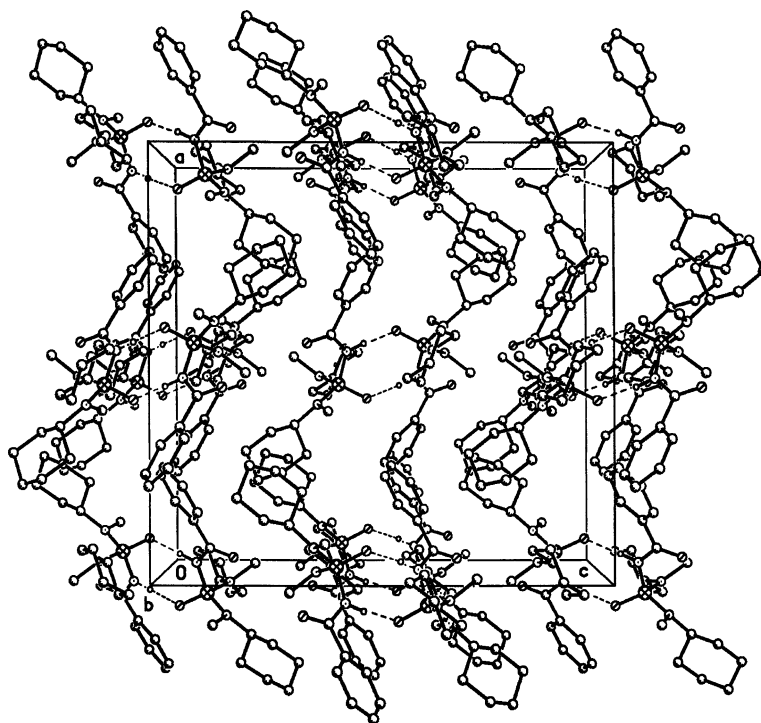


Fig. 5 The two non-equivalent $N(CH_3)(C_6H_{11})$ groups in compound **5** that indicates different spatial orientations of *N*-methyl groups and two cyclohexyl moieties

Fig. 6 The unit cell packing of molecule **5** (intermolecular hydrogen bonds are shown by dashed lines)



In molecules **4** and **5** the phosphoryl and the carbonyl groups show anti configuration, Figs. 1 and 4. The phosphorus atoms in these structures have distorted tetrahedral configuration. The bond angles around P(1) atoms in these compounds are in the range of $105.14(7)^\circ$ to $117.30(7)^\circ$ (both of them have been observed in **5**), for the angles N(2)–P(1)–N(1) and O(1)–P(1)–N(2), respectively, Table 3. In compounds **4** and **5**, the angles $\text{OPN}_{\text{amide}}$ (N_{amide} is the nitrogen atom of P(O)N(H)C(O) moiety) are lower than the angles $\text{OPN}_{\text{amine}}$ (N_{amine} is the nitrogen atom of P(O)NR moiety). This was also observed in our previously reported compounds [28, 29, 31]. The P=O bond lengths in molecules **4** and **5** are 1.4818(11) and 1.4842(12) Å that are larger than the normal P=O bond length (1.45 Å) [30].

Compounds **4** and **5** each contain one amidic hydrogen atom and form centrosymmetric dimmers via intermolecular $\text{P}=\text{O} \cdots \text{H}-\text{N}-$ hydrogen bonds (Table 4). Considering weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds leads to three-dimensional polymeric clusters in the crystalline network of these molecules. The earlier studied *N*-benzoyl- and *N*-4-fluorobenzoylphosphoric triamides exist either in the form of dimeric aggregates [15, 19, 29] or as polymeric chains [28, 31].

The P– N_{amide} bond lengths are longer than the P– N_{amine} bond lengths, because of the resonance interaction of the N_{amide} with the C=O π system that cause a partial multiple bond character in C– N_{amide} (the C– N_{amide} bond lengths are shorter than the C– N_{amine} bond lengths, Table 3). All of these P–N bonds are shorter than the typical P–N single bond length (1.77 Å [30]). This is probably due to the electrostatic effects (polar bonds) which overlap with P–N σ bond [32]. The P=O, P= N_{amine} and P= N_{amide} bond lengths in compound **5** are slightly longer than in **4**. These bond lengths in our previously reported structures were in the range of 1.406(12) Å (in **8**) to 1.488(1) Å (in **9**), 1.527(12) Å (in **10**) to 1.658(11) Å (in **10**), and 1.661(13) Å (in **8**) to 1.747(9) Å (in **10**), respectively (Table 5). The environment of the nitrogen atoms is practically planar. In compound **5**, the angles C(8)–N(2)–C(9), C(8)–N(2)–P(1) and C(9)–N(2)–P(1) are $117.26(13)^\circ$, $117.50(11)^\circ$ and $121.53(11)^\circ$, respectively with average 118.8° . The sum of surrounding angles around N(1) and N(3) atoms are 360.08° and 356.21° , respectively. Similar results were obtained for the nitrogen atoms of structure **4** that confirm the sp^2 hybridization for the N atoms, although due to the repulsion and steric interactions, some angles are greater, and the others are smaller than 120° .

Table 4 Hydrogen bonds in compounds **4** and **5** (Å and $^\circ$)

Compound	D–H–A	$d(\text{D}-\text{H})$	$d(\text{H} \cdots \text{A})$	DHA	$d(\text{D} \cdots \text{A})$
4	N(1)–H(1N) \cdots O(1) [$-x + 1, -y + 1, -z + 1$]	0.95	1.90	164	2.823(3)
5	N(1)–H(1A) \cdots O(1) [$-x, -y, -z + 1$]	0.880	2.040	156.29	2.868(2)

Table 5 P=O, P–N_(amine), P–N_(amide) bond lengths (Å) in some *N*-carbonylphosphoric triamides

No.	Compound	P=O	P–N _(amine)	P–N _(amide)	Reference
4	C ₆ H ₅ C(O)N(H)P(O)[N(CH ₃)(CH ₂ CH(OCH ₃) ₂)] ₂	1.4818(11)	1.6286(14), 1.6314(13)	1.6801(14)	^a
5	C ₆ H ₅ C(O)N(H)P(O)[N(CH ₃)(C ₆ H ₁₁) ₂] ₂	1.4842(12)	1.6344(14), 1.6368(14)	1.6980(14)	^a
6	C ₆ H ₅ C(O)N(H)P(O)(NC ₃ H ₆) ₂	1.484(1), 1.484(2)	1.624(2), 1.634(2), 1.614(2), 1.639(2)	1.681(2), 1.682(2)	[15]
7	C ₆ H ₅ C(O)N(H)P(O)(NC ₄ H ₈) ₂	1.487(3), 1.485(3)	1.615(4), 1.618(4), 1.618(3), 1.625(4)	1.679(4), 1.687(4)	[16]
8	C ₆ H ₅ C(O)N(H)P(O)(NC ₅ H ₁₀) ₂	1.472(13), 1.425(12), 1.463(11), 1.406(12)	1.642(14), 1.619(17), 1.631(14), 1.614(13), 1.589(15), 1.624(13), 1.603(15), 1.646(14)	1.661(13), 1.685(14), 1.690(13), 1.671(13)	[18]
9	C ₆ H ₅ C(O)N(H)P(O)(NC ₆ H ₁₂) ₂	1.488(1)	1.635(2), 1.637(2)	1.692(2)	[15]
10	C ₆ H ₅ C(O)N(H)P(O)(4-CH ₃ -NC ₃ H ₆) ₂	1.444(10), 1.470(11)	1.653(14), 1.658(11), 1.527(12), 1.612(9)	1.747(9), 1.669(12)	[18]
11	C ₆ H ₅ C(O)N(H)P(O)[N(CH ₃)(CH ₂ C ₆ H ₅)] ₂	1.476(2)	1.629(2), 1.630(3)	1.676(2)	[27]
12	C ₆ H ₅ C(O)N(H)P(O)(NH-C(CH ₃) ₃) ₂	1.473(2), 1.476(2)	1.629(2), 1.629(2), 1.619(3), 1.629(2)	1.711(2), 1.704(2)	[14]
13	4-F-C ₆ H ₄ C(O)N(H)P(O)(NC ₄ H ₈) ₂	1.4863(10)	1.6239(12), 1.6390(12)	1.6899(11)	[19]
14	4-F-C ₆ H ₄ C(O)N(H)P(O)(NC ₅ H ₁₀) ₂	1.480(2), 1.479(2), 1.471(2), 1.475(3)	1.625(3), 1.636(3), 1.618(3), 1.632(3), 1.625(3), 1.633(3), 1.626(3), 1.633(3)	1.683(3), 1.681(3), 1.670(3), 1.678(4)	[19]
15	4-F-C ₆ H ₄ C(O)N(H)P(O)(NC ₄ H ₈ O) ₂	1.4801(17)	1.6246(18), 1.6318(18)	1.6839(16)	[19]
16	4-F-C ₆ H ₄ C(O)N(H)P(O)(NC ₆ H ₁₂) ₂	1.472(2)	1.626(4), 1.634(3)	1.675(3)	[19]
17	4-F-C ₆ H ₄ C(O)N(H)P(O)(NHCH ₂ C ₆ H ₅) ₂	1.474(1)	1.628(1), 1.635(1)	1.705(1)	[31]
18	4-F-C ₆ H ₄ C(O)N(H)P(O)[N(CH ₃)(CH ₂ C ₆ H ₅)] ₂	1.4825(9)	1.633(1), 1.643(1)	1.686(1)	[31]
19	4-F-C ₆ H ₄ C(O)N(H)P(O)(NH-C(CH ₃) ₃) ₂	1.478(1)	1.629(1), 1.632(1)	1.701(1)	[31]

^aThis work.

Conclusion

The NMR spectra of compounds **1–5** indicated some interesting points that are due to the existence of prochiral carbon atoms (in **1–4**). In compound **5**, the different spatial orientations of *N*-methyl and cyclohexyl groups of the two chains cause asymmetry in this compound. ¹H NMR spectra of compounds **1**, **2** and **4** indicate two separate signals for the two non-equivalent CH₃ and OCH₃ groups, respectively. Crystal structures of molecules **4** (and **5**) showed that the two methoxy groups (and the two *N*-methylcyclohexyl moieties) are not equivalent with each other due to their different spatial orientations.

Supplementary data

Spectroscopic data of compounds **1–5** can be found online as Supplementary material. Crystallographic data for the structures **4** and **5** have been deposited with Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 292744 (C₁₇H₃₀N₃O₆P) and CCDC 292754 (C₂₁H₃₄N₃O₂P). Copies of the data may 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 www: <http://www.ccdc.cam.ac.uk>).

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