

## Three new [3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)NH]P(O)[NRR']<sub>2</sub> (NRR' = N(C<sub>2</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>11</sub>), NC<sub>4</sub>H<sub>8</sub>O & NC<sub>5</sub>H<sub>9</sub>-4-CH<sub>3</sub>) phosphoric triamide structures

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### ABSTRACT

In this work, we report on the synthesis, spectroscopic characterization and X-ray crystal structure determination of three new [3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)NH]P(O)[NRR']<sub>2</sub> [NRR' = N(C<sub>2</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>11</sub>) (1), NC<sub>4</sub>H<sub>8</sub>O (2) and NC<sub>5</sub>H<sub>9</sub>-4-CH<sub>3</sub> (3)] phosphoric triamides. In all three compounds, the P-N<sub>CP</sub> bond length (N<sub>CP</sub> is the nitrogen atom of the C(O)NHP(O) segment) is longer than the two other P-N bond lengths, because of the resonance interaction of the N<sub>CP</sub> lone pair with the π system of C=O group that causes a partial multiple bond character in C-N<sub>CP</sub> (the C-N<sub>CP</sub> bond length is shorter than the other C-N bond lengths in each structure). The OPN<sub>CP</sub> angle is less than the two OPN angles. All of the compounds are aggregated as centrosymmetric dimers via pairs of intermolecular N<sub>CP</sub>-H...O=P hydrogen bonds.

**Keywords:** Phosphoric triamide, Hydrogen bond, Structural feature, X-Ray crystallography.

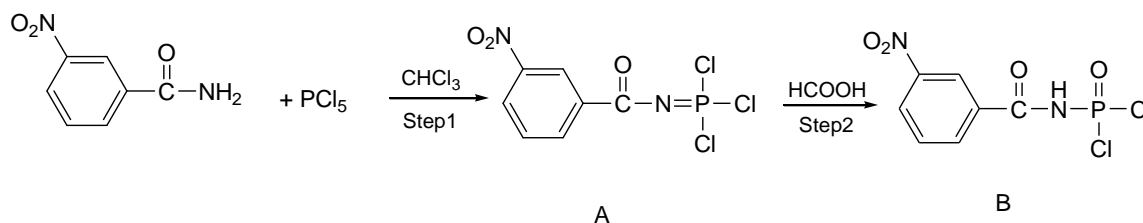
### 1. INTRODUCTION

The chemistry of phosphoramides has been developed recently due to their biological activity [1] and complexation reactions [2]. In this paper, we synthesized three new compounds of this family (containing a [C(O)N(H)]P(O)[N]<sub>2</sub> segment) as well as spectroscopic characterization and X-ray crystallography investigation.

### 2. EXPERIMENTAL

#### 2.1. Syntheses

The reagent [3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)]NHP(O)Cl<sub>2</sub> was prepared according to the schematic procedure shown in Scheme 1, according to the literature method described for the synthesis of [4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)]NHP(O)Cl<sub>2</sub> [3], by using of 3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)NH<sub>2</sub> instead of 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)NH<sub>2</sub>.



**Scheme 1.** Schematic procedure for [3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)]NHP(O)Cl<sub>2</sub>

#### 2.1.1. Synthesis of (1)

To a solution of [3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C(O)NH]P(O)Cl<sub>2</sub> (2 mmol) in dry acetonitrile, a solution of N-ethylcyclohexylamine (4 mmol) and triethylamine (4 mmol) in the same solvent was added at 273 K under stirring. After 4 h, the solvent was evaporated and the solid obtained was washed with distilled water. Single crystals were obtained from a mixture of CH<sub>3</sub>OH/C<sub>7</sub>H<sub>16</sub> (5:1 v/v) by slow evaporation at room temperature. IR (KBr, cm<sup>-1</sup>): 3104, 2935, 2859, 1674, 1535, 1455, 1348, 1268, 1199, 1121, 1028, 989, 854. Selected crystal data: Triclinic, *P*-1, *a* = 8.3499(3) Å, *b* = 10.6515(4) Å, *c* = 14.5012(5) Å, β = 93.042(3)°, *Z* = 2, *V* = 1197.21(8) Å<sup>3</sup>, Mo *K*α Radiation, μ = 0.15 mm<sup>-1</sup>, *T* = 120 K, 0.79×0.55×0.43 mm,

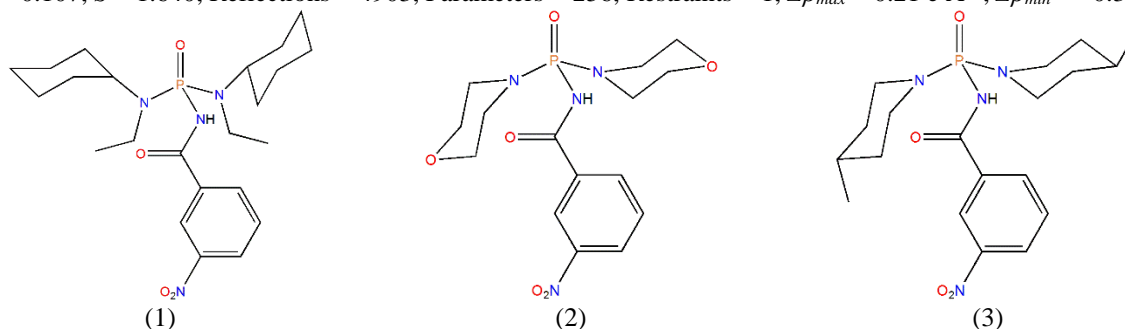
$R_{int} = 0.022$ ,  $R[F^2 > 3\sigma(F^2)] = 0.035$ ,  $wR(F^2) = 0.104$ ,  $S = 1.560$ , Reflections = 5490, Parameters = 292, Restraints = 0,  $\Delta\rho_{max} = 0.28 \text{ e } \text{\AA}^{-3}$ ,  $\Delta\rho_{min} = -0.31 \text{ e } \text{\AA}^{-3}$ .

### 2.1.2. Synthesis of (2)

Compound (2) was obtained in a similar procedure to (1), but by using morpholine instead of N-ethylcyclohexylamine. Single crystals were obtained from a mixture of  $\text{CH}_3\text{OH}/\text{C}_7\text{H}_{16}$  (5:1 v/v) by slow evaporation at room temperature. IR (KBr,  $\text{cm}^{-1}$ ): 3084, 2969, 2891, 2852, 1681, 1614, 1532, 1489, 1446, 1353, 1265, 1194, 1118, 970, 868. Selected crystal data: Monoclinic,  $P2_1/n$ ,  $a = 10.4702(6) \text{ \AA}$ ,  $b = 16.9847(7) \text{ \AA}$ ,  $c = 10.7105(6) \text{ \AA}$ ,  $\beta = 110.901(5)^\circ$ ,  $Z = 4$ ,  $V = 1779.35(17) \text{ \AA}^3$ , Mo  $K\alpha$  Radiation,  $\mu = 0.2 \text{ mm}^{-1}$ ,  $T = 120 \text{ K}$ ,  $0.9 \times 0.71 \times 0.49 \text{ mm}$ ,  $R_{int} = 0.020$ ,  $R[F^2 > 3\sigma(F^2)] = 0.040$ ,  $wR(F^2) = 0.119$ ,  $S = 1.810$ , Reflections = 4097, Parameters = 251, Restraints = 4,  $\Delta\rho_{max} = 0.36 \text{ e } \text{\AA}^{-3}$ ,  $\Delta\rho_{min} = -0.34 \text{ e } \text{\AA}^{-3}$ .

### 2.1.3. Synthesis of (3)

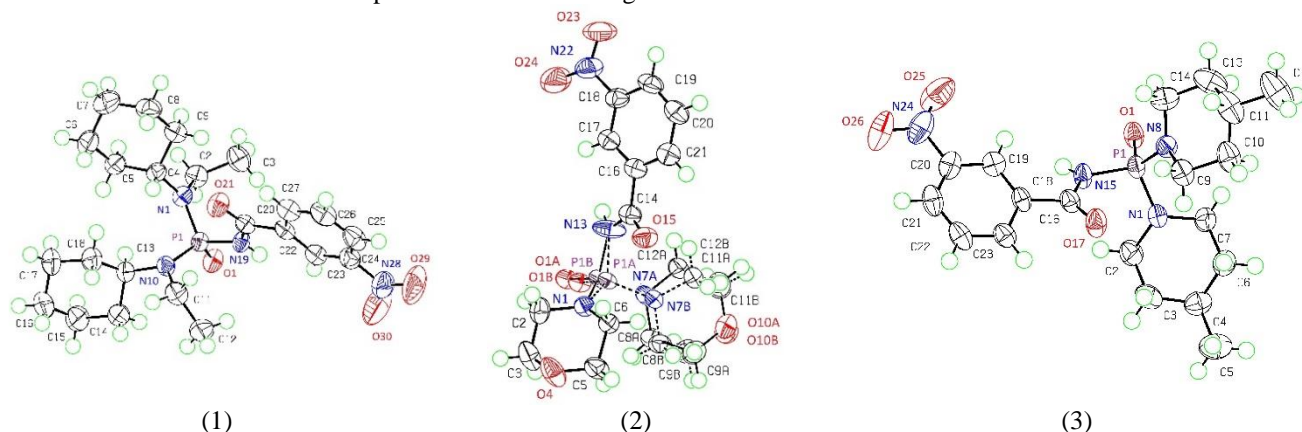
Compound (3) was obtained in a similar procedure to (1), but by using 4-methylpiperidine instead of N-ethylcyclohexylamine. Single crystals were obtained from a mixture of  $\text{CH}_3\text{OH}/\text{C}_7\text{H}_{16}$  (5:1 v/v) by slow evaporation at room temperature. IR (KBr,  $\text{cm}^{-1}$ ): 3090, 2920, 2855, 1685, 1618, 1535, 1472, 1355, 1265, 1197, 1093, 917, 817, 734. Selected crystal data: Monoclinic,  $C2/c$ ,  $a = 18.8320(8) \text{ \AA}$ ,  $b = 8.4148(3) \text{ \AA}$ ,  $c = 26.6633(11) \text{ \AA}$ ,  $\beta = 94.844(3)^\circ$ ,  $Z = 8$ ,  $V = 4210.2(3) \text{ \AA}^3$ , Mo  $K\alpha$  Radiation,  $\mu = 0.16 \text{ mm}^{-1}$ ,  $T = 120 \text{ K}$ ,  $0.66 \times 0.43 \times 0.27 \text{ mm}$ ,  $R_{int} = 0.023$ ,  $R[F^2 > 3\sigma(F^2)] = 0.035$ ,  $wR(F^2) = 0.107$ ,  $S = 1.640$ , Reflections = 4903, Parameters = 256, Restraints = 1,  $\Delta\rho_{max} = 0.21 \text{ e } \text{\AA}^{-3}$ ,  $\Delta\rho_{min} = -0.35 \text{ e } \text{\AA}^{-3}$ .



**Scheme 2.** Chemical structures of 1 – 3

## 3. DISCUSSION

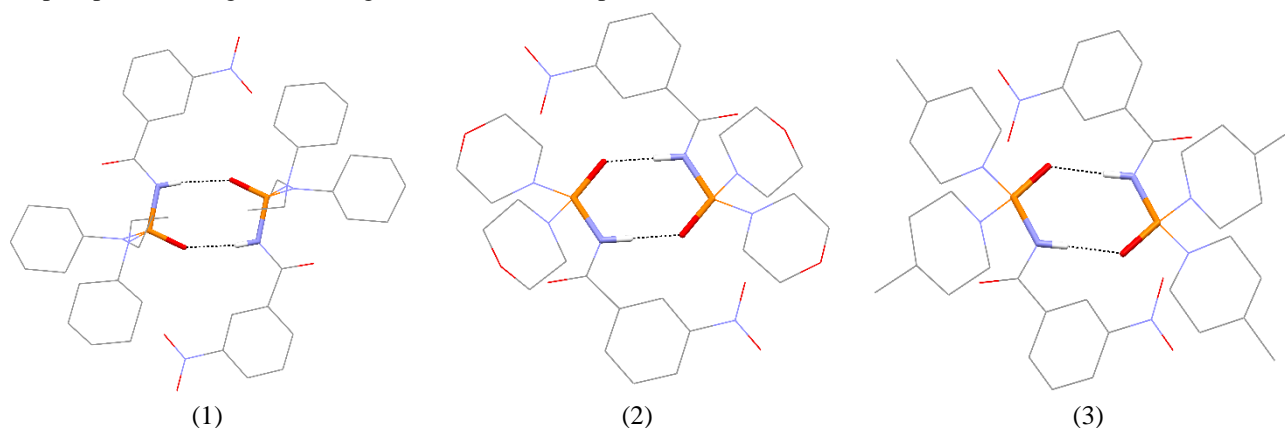
Single crystals of compounds 1–3 were obtained from a solution of methanol and 1-heptane after slow evaporation at room temperature. Selected bond lengths and angles are given in Table 1 and Hydrogen bonding data are listed in Table 2. The molecular structures of compounds are shown in Fig. 1.



**Fig 1.** Displacement ellipsoid plots (50% probability) of structures (1) – (3) showing the atom-numbering schemes. H atoms are drawn as spheres of arbitrary radii.

The phosphorus atoms in the structures 1–3 have a distorted tetrahedral configuration. For a typical example, in compound 1 the minimum and maximum values of bond angles at the phosphorus atoms are  $104.32(5)^\circ$  [ $\angle N10-P1-N19$ ] and  $117.67(6)^\circ$  [ $\angle O1-P1-N10$ ], respectively. In all structures, the phosphoryl and the NH groups are *syn* with respect to each other, Fig. 1. The nitrogen atoms adopt a practically planar environment, which are reflected in the bond angles around the nitrogen atom. For example, in compound 1 the bond angles C2–N1–C4, C2–N1–P1 and C4–N1–P1 are  $117.26(10)$ ,  $117.25(7)$  and  $125.35(8)^\circ$ , respectively. Similar results were obtained for compounds 2 and 3. These results confirm the  $sp^2$  hybridization states for the nitrogen atoms.

In compound 1, the P1–N19 bond length ( $1.6950(12)$  Å) is longer than the P1–N1 and P1–N10 bond lengths ( $1.6367(11)$  Å and  $1.6355(11)$  Å, respectively) due to the resonance interaction of the N19 nitrogen lone pair with the  $\pi$  system of C=O group that causes a partial multiple-bond character in N19–C20 (Table 1). Similar results were obtained for the phosphorus-nitrogen bond lengths for the other compounds.



**Fig. 2.** Views of the centrosymmetric dimers in structures (1)–(3), produced by pairs of  $N-H \dots O=P$  hydrogen bonds.

In the structures of 1–3, pairs of  $N_{CP}-H \dots O=P$  hydrogen bonds (Table 2) form centrosymmetric dimers as  $R_2^2(8)$  ring motif (Fig. 2).

#### 4. ACKNOWLEDGMENTS

Support of this investigation by Ferdowsi University of Mashhad is gratefully acknowledged.

#### 5. REFERENCES

- [1] Domínguez, M. J., Sanmartín, C., Font, M., Palop, J. A., San Francisco, S., Urrutia, O., Houdusse, F. & García-Mina, J. M. (2008). *J. Agric. Food Chem.* **56**, 3721–3731.
- [2] Saneei, A., Pourayoubi, M., Crochet, A. & Fromm, K. (2016). *Acta Cryst.* **C72**, 230–233.
- [3] Sabbaghi, F., Rostami Chaijan, M., & Pourayoubi, M. (2010). *Acta Cryst.* **E66**, o1754.

**Table 1** Selected bond lengths (Å) and bond angles (°) for compounds 1–3.

(1)			
P1—O1	1.4817(9)	P1—N10	1.6355(11)
P1—N1	1.6367(11)	P1—N19	1.6950(12)
O1—P1—N1	109.25(5)	N1—P1—N10	107.77(5)
O1—P1—N10	117.67(6)	N1—P1—N19	113.17(6)
O1—P1—N19	104.73(5)	N10—P1—N19	104.32(5)
C2—N1—C4	117.26(10)	P1—N1—C2	117.25(7)
P1—N1—C4	125.35(8)		
(2)			
P1a—O1a	1.482(7)	P1b—O1b	1.475(8)
P1a—N1	1.6309(13)	P1b—N1	1.6336(14)
P1a—N13	1.6935(18)	P1b—N13	1.695(2)
P1a—N7a	1.627(3)	P1b—N7b	1.631(3)
O1a—P1a—N1	112.8(3)	O1b—P1b—N1	106.4(4)
O1a—P1a—N13	110.0(3)	O1b—P1b—N13	103.0(4)
O1a—P1a—N7a	119.2(3)	O1b—P1b—N7a	106.9(3)
N1—P1a—N13	112.10(10)	N1—P1b—N13	111.90(13)
N1—P1a—N7a	102.58(12)	N1—P1b—N7b	108.76(17)
N13—P1a—N7a	99.20(13)	N13—P1b—N7a	111.42(15)
N13—P1b—N7b	110.86(17)	O1b—P1b—N7b	115.8(3)
P1a—P1b—N7b	153.2(5)		
(3)			
P1—N1	1.6325(11)	P1—N15	1.6859(10)
P1—N8	1.6342(10)		
O1—P1—N1	118.42(5)	N1—P1—N8	104.19(5)
O1—P1—N8	110.67(5)	N1—P1—N15	105.60(5)
O1—P1—N15	105.83(5)	N8—P1—N15	112.18(5)

**Table 2** Hydrogen bond parameters for compounds 1–3 (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
(1)				
N19—H1n19...O1 <sup>i</sup>	0.800(13)	1.999(13)	2.7937(12)	171.7(18)
(2)				
N13—H1n13...O1a <sup>ii</sup>	0.908(17)	1.809(19)	2.706(8)	169(2)
N13—H1n13...O1b <sup>ii</sup>	0.908(17)	1.968(19)	2.870(9)	172.4(17)
(3)				
N15—H1n15...O1 <sup>ii</sup>	0.870(3)	1.951(3)	2.8123(14)	170.5(13)

Symmetry code: (i)  $-x, -y, -z$ ; (ii)  $-x + 1, -y + 1, -z$ .