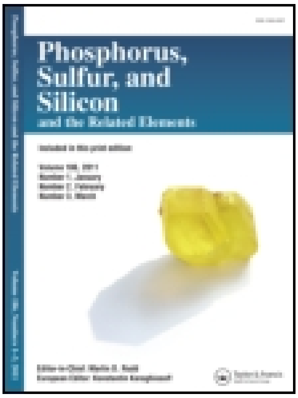

Phosphorus, Sulfur, and Silicon and the Related Elements

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A NEW SOLVATED PHOSPHORIC TRIAMIDE, $[(C_6H_4(3\text{-}CH_3)NH)_3P(O)] \cdot (C_2H_5OH)$: A DATABASE ANALYSIS OF N ATOM GEOMETRY IN COMPOUNDS WITH AN $[N]_3P(O)$ FRAGMENT

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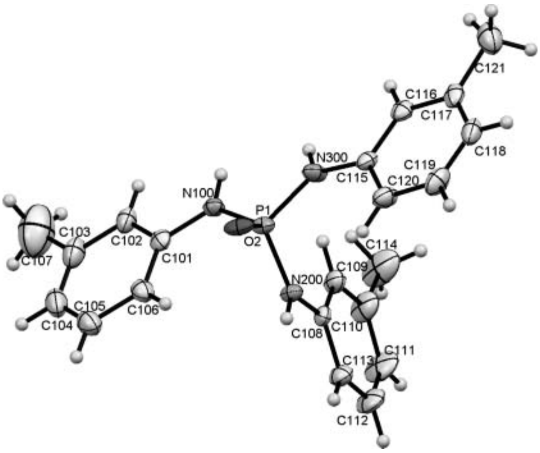
GRAPHICAL ABSTRACT



Abstract *In the crystal structure of the title compound $C_{21}H_{24}N_3OP \cdot C_2H_5OH$, there are three crystallographically independent phosphoric triamide molecules and three ethanol molecules. The environments of the nitrogen atoms are practically planar. The phosphorus atoms display a distorted tetrahedral environment; the maximum and minimum values of angles are observed for one O—P—N and one N—P—N angles, respectively. In this structure, the phosphoramide and ethanol molecules are linked by some different intermolecular O—H···O and N—H···O hydrogen bonds to form chains. The title solvated compound has been further characterized by IR and $^{31}P\{^1H\}$, ^1H and ^{13}C NMR spectroscopy. The geometry of the nitrogen atoms in this compound is analyzed and compared with those of analogous structures deposited in the Cambridge Structural Database (CSD; Allen, Acta Cryst. 2002, B58, 380-388).*

Keywords CSD; crystal structure; phosphoric triamide

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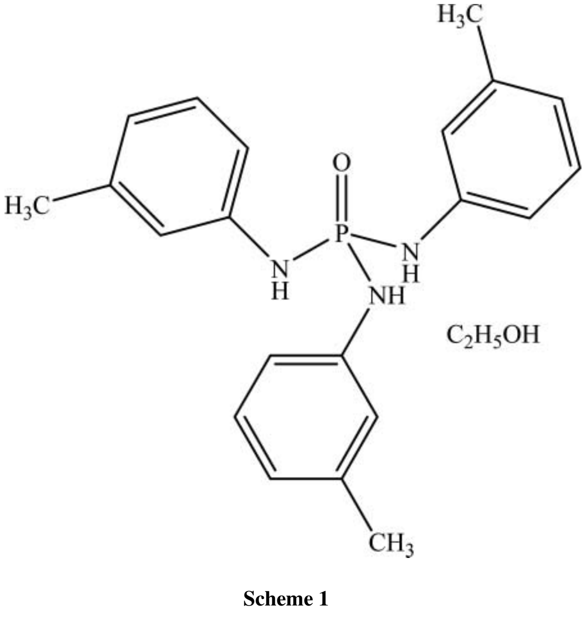
INTRODUCTION

The hybridization of the nitrogen atom bonded to the phosphorus atom in phosphoric triamides with an [N][N'][N"]P=O skeleton tends toward *sp*^{2},[1] similar to nitrogen atoms bonded to carbon atoms in organic amides.[2] This tendency is reflected in the bond-angle sums around such nitrogen atoms, which was recently investigated for $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides[3] through a database analysis of the structures deposited in the Cambridge Structural Database.[4] Here, we continue such analysis for $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides.

From the point of view of the bonding, the main difference between $RC(O)NHP(O)[NR^1R^2]_2$ and $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides is related to the presence of carbonyl group in the former class. Thus, the lone electron pair (LEP) of the N_{CP} [the nitrogen atom of O=C—NH—P=O fragment] is tending to delocalize over the C=O group. This leads to different strengths for P—N bonds in $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides where the P—N_P [N_P is the nitrogen atom of NR^1R^2] is shorter than P—N_{CP}. Moreover, apart from P—N_{CP}, it is well-known that the P—N bonds in phosphoramides are shorter than the P—N single bond.[3]

It should be noted that in $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides, three N_P atoms compete for electron-donation to the phosphorus atom as compared to two N_P atoms in $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides.

Here, we present the synthesis, spectroscopic characterization and crystal structure of a new solvated phosphoric triamide, $[(C_6H_4(3\text{-}CH_3)NH)_3P(O)] \cdot (C_2H_5OH)$, Scheme 1. Moreover, the geometries of nitrogen atoms bonded to the phosphorus atom in this structure and 59 analogous structures deposited in the CSD are compared to those of $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides.



Scheme 1

RESULTS AND DISCUSSION

Of the numerous known $OP[N(H)R]_3$ phosphoric triamides, structures have been determined only for R = H,[5] phenyl,[6] *m*-tolyl,[7] *p*-tolyl,[8] methyl, *tert*-butyl,[9] 2-pyridyl,[10] benzyl,[11] cyclohexyl,[12] and *p*-methoxyphenyl.[13] A search in the CSD for compounds with a $P(O)[N]_3$ skeleton, without considering complexes, shows that 191 structures have been deposited, so far, belonging to $RC(O)NHP(O)[NR^1R^2]_2$ (93) and $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ (88) and some other families. In these structures, the nitrogen atoms tend towards planarity, which is reflected in the bond angles around the nitrogen atoms (2 × P—N—C + C—N—C or P—N—H + H—N—C + C—N—P). These bond-angle sums usually show a few deviations from the planar value of 360°; however, values in the range of 339.07° to 360.72° for $RC(O)NHP(O)[NR^1R^2]_2$ and 325.2° to 360.4° for $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ were reported. The largest deviations are related to three-membered cyclic amido moiety (phosphoric triamide compounds with three membered cyclic amido moiety were not considered in this analysis). Moreover, some co-crystals and phosphoric triamides with disorder in amido fragments were excluded.

A CSD analysis on $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides shows that the P—N_P bond lengths are in the range of 1.60–1.70 Å; whereas, the P—N_{CP} appears in the range 1.66–1.74 Å.[3] This means that the electron deficiency of phosphorus atom is more provided by two NR^1R^2 groups; whereas, the N_{CP} is involved in resonance interaction with C=O. So, may be the lower availability of electron of N_{CP} leads to more efficient interaction of N_P atoms with P atoms. If it is true, the N_P atoms in $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides should display a more planar environment than the N_P atoms in $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides. This tendency may appear in the average of the sum of the surrounding bond angles at the N_P atoms.

For this purpose, the cif files of all $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides were analyzed and the bond-angle sum (SUM = 2 × P—N—C + C—N—C or P—N—H + H—N—C + C—N—P related to the amido moiety bonded to P) for each N_P atom was considered. Then, $SUM_{av} = 0.5\ (SUM1 + SUM2)$ was calculated. For $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides, $SUM_{av} = 0.33\ (SUM1 + SUM2 + SUM3)$ was considered. These average values are shown in Figure 1, which shows that the $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides, in deposited structures, have relatively lower values than $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides; i.e., the three amido moieties in $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides compete with each other and in overall, they have lower SUM_{av} values or more pyramidal N atoms.

Of course, the bond-angle sum is also related to the type of amido substituent; for example, sum of the three bond angles at the N atoms (of *p*-methoxy phenyl amido substituent) in $C_{18}H_{18}N_3O_1P_1$ (KEQLUO[14]) are about 360°.

In this work, we investigate a new structure, *N*,*N*',*N*''-tris(3-methyl-phenyl) phosph–oric triamide, ethanol solvate (Scheme 1). The asymmetric unit is composed of three independent phosphoric triamide molecules and three ethanol molecules. One of the independent molecule and the asymmetric unit are shown in Figures 2 and 3, respectively. Data collection and structure refinement parameters are given in Table 1. Selected bond distances and bond angles and the hydrogen-bonds geometry are provided in Tables 2 and 3. Figure 4 shows packing of the title solvated compound.

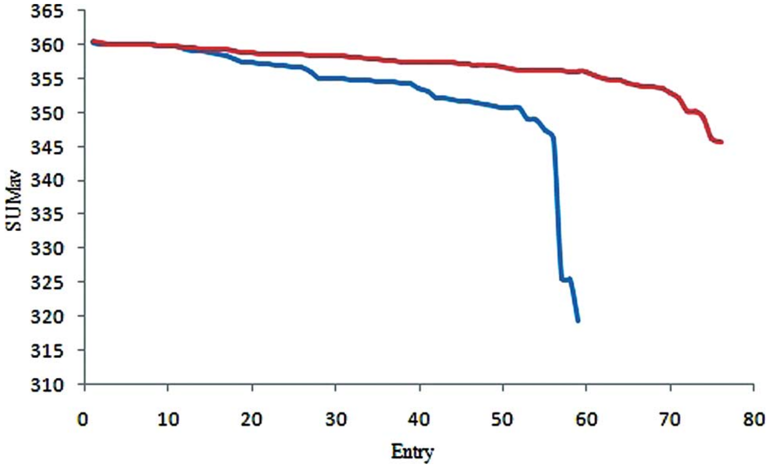


Figure 1 The SUM_{av} values at the N atoms of $[R^1R^2N]P(O)[NR^3R^4][NR^5R^6]$ phosphoric triamides (bottom line, brown in the electronic version of paper) and $RC(O)NHP(O)[NR^1R^2]_2$ phosphoric triamides (top line, blue) (Color figure available online).

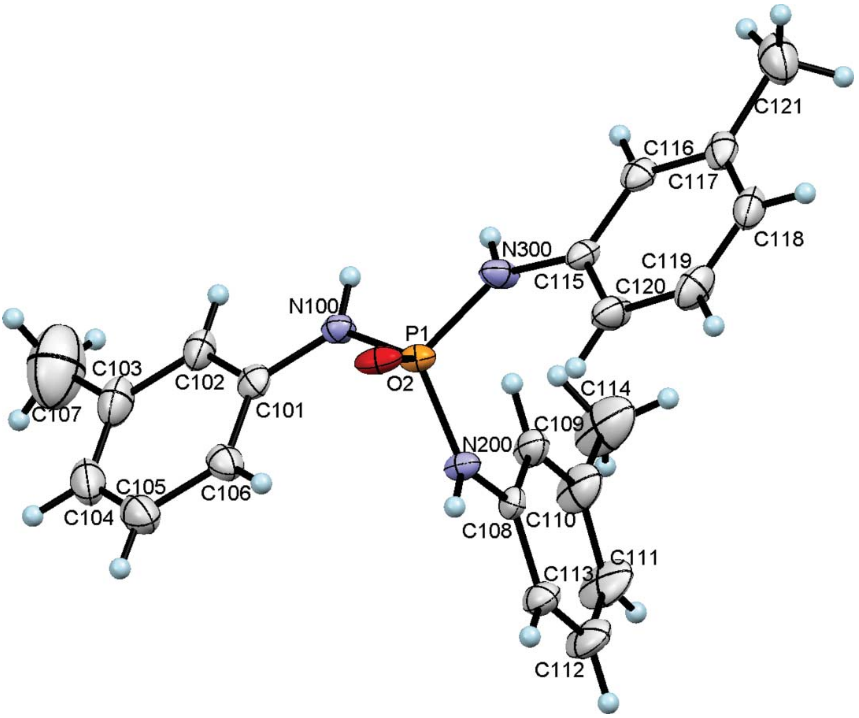


Figure 2 ORTEP diagram of one of the independent phosphoric triamide molecules; thermal ellipsoids are at 30% probability level (Color figure available online).

Table 1 Crystal data and structure refinement

Empirical formula	$C_{21}H_{24}N_3OP,C_2H_6O$
Formula weight	411.47
Temperature	150(1)K
Wavelength	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 12.5401(11)$ Å, $b = 12.8961(7)$ Å, $c = 23.8258(10)$ Å $\alpha = 92.411(4)^\circ$, $\beta = 101.934(5)^\circ$, $\gamma = 114.075(6)^\circ$
Volume	3407.2(4)
Z	6
Density (calculated)	1.203
Absorption coefficient	0.144
F(000)	1320
Crystal size	$0.40 \times 0.36 \times 0.26$ mm^3
Theta range for data collection	1.83 to 27.50
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-30 \leq l \leq 29$
Reflections collected	66369
Independent reflections	15486 [$R_{int} = 0.094$]

The P=O (1.488(4) Å, 1.489(3) Å and 1.487(4) Å) and P—N (in the range of 1.633(4) Å to 1.642(4) Å) bond lengths are within the expected values.[14] The bond angles around P atoms are in the range of 98.0(2)° to 116.5(2)°. The P—N—C bond angles are in the range of 126.3(3) to 130.8(4)° (Table 2).

Table 2 Selected geometric parameters

P2-O4	1.489(3)	P3-N800	1.639(4)
P2-N400	1.640(4)	P3-N900	1.634(6)
P2-N500	1.640(5)	P1-N100	1.642(4)
P2-N600	1.640(4)	P1-N200	1.633(5)
P3-O5	1.487(4)	P1-O2	1.488(4)
P3-N700	1.638(5)	P1-N300	1.641(4)
O4-P2-N400	105.46(19)	N800-P3-N900	98.0(2)
O4-P2-N500	115.5(2)	C315-N900-P3	130.8(4)
O4-P2-N600	115.1(2)	C301-N700-P3	129.5(3)
N400-P2-N500	110.5(2)	C308-N800-P3	129.0(3)
N400-P2-N600	111.0(2)	O2-P1-N300	114.4(2)
N500-P2-N600	99.3(2)	O2-P1-N100	115.6(2)
C201-N400-P2	130.8(3)	O2-P1-N200	105.4(2)
C208-N500-P2	127.3(3)	N100-P1-N200	111.1(2)
C215-N600-P2	127.6(4)	N100-P1-N300	99.6(2)
O5-P3-N700	116.5(2)	N200-P1-N300	110.9(2)
O5-P3-N900	115.1(2)	C101-N100-P1	126.3(3)
O5-P3-N800	116.5(2)	C108-N200-P1	129.5(3)
N700-P3-N800	110.7(2)	C115-N300-P1	127.2(4)
N700-P3-N900	111.1(3)		

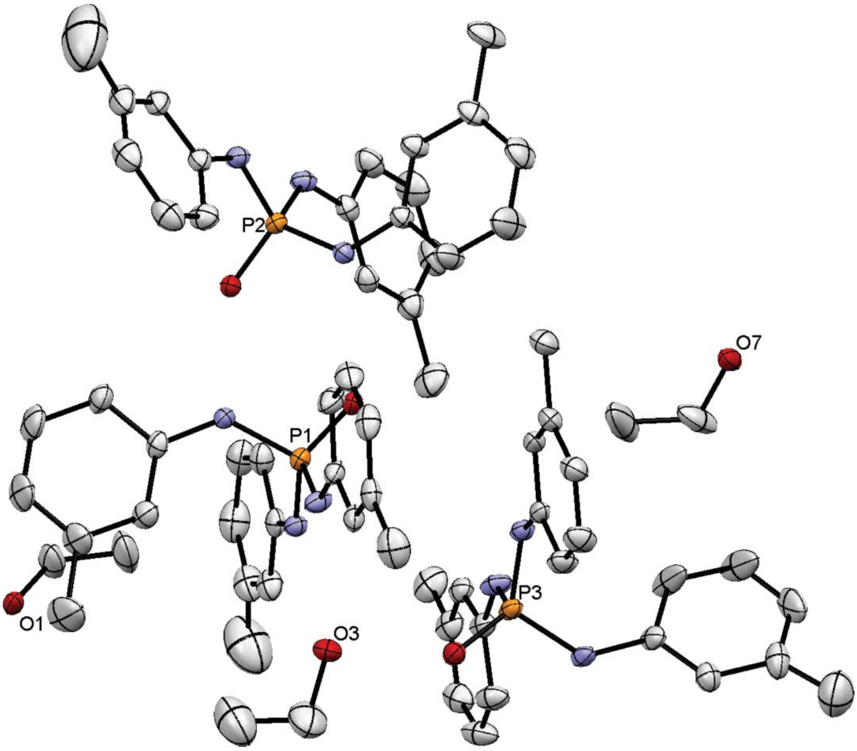


Figure 3 The asymmetric unit of $[(C_6H_4(3\text{-}CH_3)NH)_3P(O)].(C_2H_5OH)$; the hydrogen atoms are omitted for clarity and only the P atoms of phosphoric triamide molecules and the O atoms of C_2H_5OH molecules are labeled. Thermal ellipsoids are at 30% probability level (Color figure available online).

In the crystal, adjacent molecules are linked *via* (O−H)(N−H)···O=P and $(N{-}H)_2\cdots O{-}C$ groups in a linear arrangement (O···O in the range of 2.655(5) Å to 2.704(5) Å and N···O in the range of 2.854(5) Å to 2.997(5) Å) (Table 3) in which the oxygen atoms of phosphoryl groups and ethanol molecules act as a

Table 3 Hydrogen bonds

D−H···*A*	*D*−H	H···*A*	*D*···*A*	*D*−H···*A*
N400−H400···O2	0.86	2.02	2.854(5)	164
N100−H100···O3	0.86	2.14	2.963(5)	161
N700−H700···O5	0.86	2.25	2.958(5)	140
N500−H500···O7	0.86	2.17	2.997(5)	160
N200−H200···O4	0.86	2.10	2.905(5)	155
N300−H300···O3	0.86	2.08	2.912(6)	163
N600−H600···O7	0.86	2.03	2.865(6)	165
N800−H800···O1	0.86	2.11	2.946(5)	163
N900−H900···O1	0.86	2.04	2.881(5)	167
O1−H1···O2	0.82	1.84	2.655(5)	174
O3−H3···O5	0.82	1.90	2.704(5)	167
O7−H7···O4	0.82	1.89	2.690(5)	166

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $x, -y+1/2, z+1/2$.

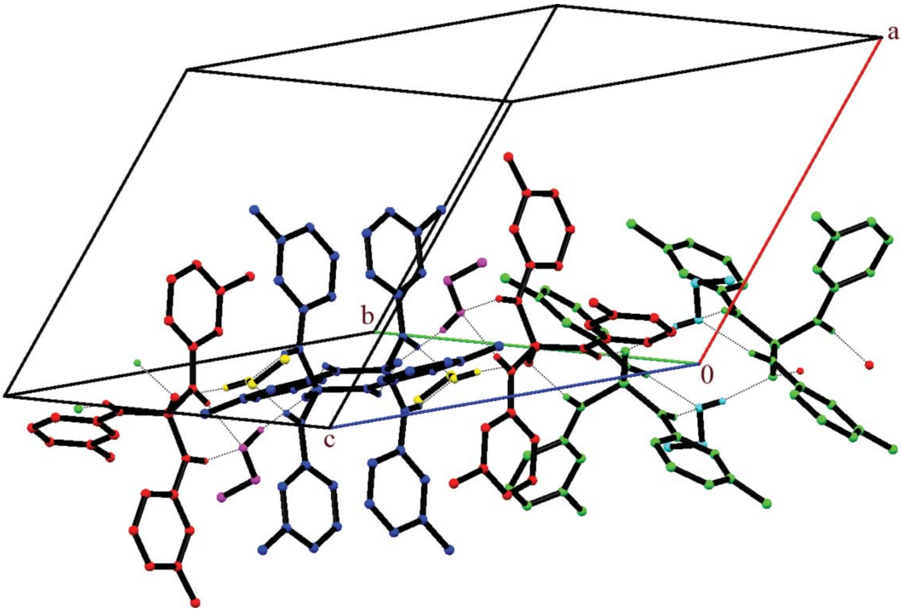


Figure 4 Partial packing view showing the formation of the chain through N—H···O and O—H···O hydrogen bonds which are shown as dotted lines. H atoms not involved in hydrogen bonding have been omitted for the sake of clarity. (Color figure available online).

double-H bond acceptor, for a definition of double-H bond acceptor, see: Reference paper.[15]

Synthesis

To a solution of phosphoryl chloride (6.63 mmol, 1.017 g) in dry chloroform, 3-methyl toluidine (39.78 mmol, 4.263 g) was added dropwise at 0°C. After 4h, the solvent was removed in vacuum and the solid was washed with H_2O. Suitable single crystals for X-ray crystallography were obtained at room temperature from a mixture of C_2H_5OH/CH_3CN (4:1 ratio).

$^{31}P\{^1H\}$ NMR (202.45 MHz, DMSO-d6, 300.0 K, H_3PO_4 external): $\delta = -3.95$, ^1H NMR (500.13 MHz, DMSO-d6, 300.0 K, TMS): $\delta = 1.14$ (t, 3H, CH_3), 2.16 (s, 3H, CH_3), 3.56 (q, 2H, CH_2), 6.70 (d, $^2J_{P\text{-}H} = 7.0$ Hz, 3H, NH), 6.86–7.05 (m, 4H, Ar-H), ^{13}C NMR (125.75 MHz, DMSO-d6, 300.0 K, TMS): $\delta = 18.76$ (s, CH_3), 18.76 (s, CH_3), 57.96 (s, CH_2), 115.72 (d, $J_{P\text{-}C} = 6.6$ Hz), 118.25 (s), 119.40 (d, $J_{P\text{-}C} = 7.2$ Hz), 122.90 (s), 129.85 (s), 139.87 (s), IR (KBr, cm^{-1}): 3378, 2964, 2789, 1714, 1495, 1378, 1203, 1174, 1033, 882, 790.

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