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A novel tubular hydrogen bond pattern in the crystal structure of a new diazaphosphole oxide: (4-Cl-C_6H_4NH)P(O)(1,2-NH)$_2C_6H_4$

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ABSTRACT

In this work, we report on the synthesis, spectroscopic characterization and X-ray crystal structure determination of a new diazaphosphole oxide, (4-Cl-C_6H_4NH)P(O)(1,2-NH)$_2C_6H_4$ namely 2-[para-chloroanilino]-1,3,2λ^4-diazaphosphol-2-one. This compound was synthesized in a two-step reaction, from $POCl_3$ and 4-chloroaniline for the preparation of (4-Cl-C_6H_4NH)P(O)Cl_2 phosphorus-chlorine reagent in the first step and then the reaction of 1,2-phenylenediamine with the phosphorus-chlorine compound. In the molecule, the P atom is bonded in a distorted tetrahedral P(O)[N]$_3$ environment, with one of the O═P—N angle as the maximum angle at the P atom and the N—P—N angle within the ring as minimum angle. In the crystal packing, each molecule is surrounded with four neighbouring molecules through (N—H)$_2$…O═P hydrogen bonds. These interactions form a tubular arrangement of fused hydrogen-bonded rings, of $R^3_3(12)$ and $R^3_4(14)$ graph-set motifs, along [001]. An N—H…π interaction exists in the tubular shape which does not change the dimension of hydrogen bond pattern.

Keywords: Diazaphosphole oxide, (N—H)$_2$…O═P, N—H…π interaction, X-Ray crystallography.

1. INTRODUCTION

Organophosphorus compounds, especially of the pentavalent type, are extremely versatile and have prevalent environmental and industrial applications [1]. Among them, a diazaphosphole compound (including a five-membered ring with one P, two C and two N atoms in the P(O)(N)$_2C_2$ segment) seems to be interesting for study from the crystal engineering viewpoint, due to the existence of a rigid five membered ring with the less bulk effect at the P(O) group caused by the N_2C_2 segment. So, it is possible to design different molecules with versatile exocyclic groups with different flexibilities bonded to the rigid P(O)(N)$_2C_2$ system and also to change the atoms bonded to the nitrogen and carbon atoms in the N_2C_2 segment.

In a previous work, the synthesis and spectroscopic features of an (R^1NH)P(O)(NH)$_2R^2$ diazaphosphole (4-CH_3-C_6H_4NH)P(O)(NH)$_2C_6H_4$ was studied [2]. Here, we represent the synthesis of the title compound namely 2-[*para*-chloroanilino]-1,3,2λ^4-diazaphosphol-2-one, $C_{12}H_{11}ClN_3OP$ (I). Compound (I) was studied by the NMR investigations and X-ray diffraction experiment. A survey on the Cambridge Structural Database (CSD) shows that the structure (I) is the first diffraction study of an (R^1NH)P(O)(NH)$_2R^2$ diazaphosphole (R^1 and R^2 = H or a hydrocarbon segment).

2. EXPERIMENTAL

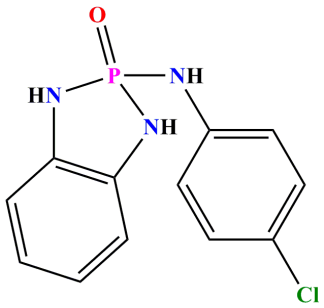
2.1. Synthesis

The starting phosphorus–chlorine compound (4-Cl-C_6H_4NH)P(O)Cl_2 was synthesized by a reaction of 4-Cl-$C_6H_4NH_2$ (20 mmol) dissolved in dry acetonitrile (10 ml) with a solution of P(O)Cl_3 (10 mmol) in the same solvent (20 ml) at 273 K.

After stirring for 4 h, the solid which formed, *i.e.* 4-Cl-$C_6H_4NH_2$.HCl, was filtered off and the (4-Cl-C_6H_4NH)P(O)Cl_2 reagent was obtained as solid from the filtrate after removing of the solvent *in vacuo*.

2.1.1. Synthesis of (4-Cl-C_6H_4NH)P(O)(1,2-NH)$_2C_6H_4$

For the synthesis of (I), a solution of 1,2-phenylenediamine (2 mmol) and triethylamine (4 mmol) in dry $CHCl_3$ (10 ml) was added to a solution of (4-Cl-C_6H_4NH)P(O)Cl_2 (2 mmol) in the same solvent (20 ml) at 273 K. After stirring for 4 h, the product as precipitate was filtered and washed with chloroform. Single crystals of (I) suitable for X-ray crystallography were obtained from CH_3OH by slow evaporation at room temperature. $^{31}P\{^1H\}$ NMR (DMSO-d_6, 121.49 MHz, 300 K): 11.74 (s). ^1H NMR (DMSO-d_6, 300.13 MHz, 300 K): 6.54 (d, $^3J(H,H)$ = 8.5 Hz, 2H), 6.71 (s, 4H), 7.10 (d, $^3J(H,H)$ = 8.6 Hz, 2H), 8.15 (d, $^2J(H,P)$ = 8.3 Hz, 1H), 8.53 (d, $^2J(H,P)$ = 17.2 Hz, 2H). ^{13}C NMR (DMSO-d_6, 75.47, 300 K): 109.67 (d, J(C,P) = 12.6 Hz), 118.47 (d, J(C,P) = 7.8 Hz), 119.14 (s), 123.95 (s), 128.59 (s), 131.78 (d, J(C,P) = 13.6 Hz), 141.27 (s). Selected crystal data: Trigonal, *P*3*c*1, a = 15.8635(2) Å, b = 15.8635(2) Å, c = 8.97540(10) Å, γ = 120°, Z = 6, V = 1956.06(5) Å^3, Mo $K\alpha$ Radiation, μ = 0.406 mm^{-1}, T = 293(2) K, 0.3553 × 0.2183 × 0.1454 mm, R_{int} = 0.048, $R[F^2 > 2\sigma(F^2)]$ = 0.0407, $wR(F^2)$ = 0.1072.



Scheme 1. *Chemical structure of (4-Cl-C_6H_4NH)P(O)(1,2-NH)$_2C_6H_4$*

3. DISCUSSION

The (R^1R^2N)P(O) segment (R^1 & R^2 = H or a hydrocarbon group) is called the phosphoramide group [3] due to its similarity to the (R^1R^2N)C(O) segment [4] in organic amides, and also due to the fact that the (R^1R^2N)$^-$ anion obtained from the NHR^1R^2 amine in the (R^1R^2N)P(O) segment can be considered as an amide group. So, compounds with the general formula (R^1R^2N)(R^3R^4N)(R^5R^6N)P(O), where $R^{1–6}$ is either an H atom or a hydrocarbon group, are called phosphoric triamides. If the R^1R^2N and R^3R^4N groups belong to an initial R^1R^2NHXNHR^3R^4 diamine (X may be any linker, such as a hydrocarbon segment), the linking of two N atoms to one P atom (and the loss of two NH protons) forms a ring. In this case, the compound, although formally considered a phosphoramide, is usually named according to different nomenclature. An example of such nomenclature is the structure with CSD refcode SAYJIM namely 2-(N-*p*-fluorobenzoyl)-2-oxo-1,3,2-benzodiazaphosphole, with a ring containing one P, two N and two C atoms [2].

In this work, we synthesized the title compound (Scheme 1) and examined its crystal structure (Fig. 1). Selected bond lengths and angles are given in Table 1. The P═O bond length of 1.484 (2) Å is within the expected range for compounds with a P(O)[N]$_3$ skeleton. The P atom is bonded in a distorted tetrahedral P(O)[N]$_3$ environment, with the bond angles at the P atom within 92.49 (12)° to 116.94 (12)°. The minimum angle is related to the N1-P1-N3 within the five member ring. Moreover, all of the angles within the five member ring are contracted with respect to the same angles in acyclic structures. For example, the P1-N1-C1 angle, being 112.45 (18)° shows a deviation from sp^2 angle observed in acyclic analogous structures [5]. The N1 and N3 atoms are placed in the plane constructed from C1/C2/C3/C4/C5/C6 atoms of phenylene segment, while the P1 atom shows a few distance from this plane. The P-N bonds within the rings are longer than the exocyclic P-N bond.

In the crystal, each molecule is surrounded with four neighbouring molecules through (N—H)$_2$…O hydrogen bonds. These interactions form a tubular arrangement of fused hydrogen-bonded rings along [001] (Fig. 2). The entrance of this pattern is an $R^3_3(12)$ ring [6] formed through the NH units of three 4-Cl-C_6H_4NH segments (N2-H5A), belonging to three adjacent molecules, hydrogen bonded to the oxygen atoms of phosphoryl groups. The other hydrogen-bonded ring motif in

this pattern, $R^3_4(14)$, is formed through two N1-H4A and two N2-H5A units hydrogen-bonded to the three oxygen atoms of phosphoryl groups. The tubular shape is completed with extending the noted motifs. One of the NH units of diazaphosphole ring (N3-H3A) does not take part in the N—H…O hydrogen bond. Surprisingly this N—H unit takes part in an N—H…π interaction which is another novel feature of the crystal structure (N3…Cg^{iii} = 3.303(3) Å, Cg is the centroid of C7/C8/C9/C10/C11/C12 ring, symmetry code (iii) x, $x - y$, $z - 1/2$). The N—H…π interactions are within the tubular pattern discussed and do not extend the dimensionality of hydrogen bond pattern.

In the NMR experiment, the nitrogen-bound proton of the diazaphosphole ring manifests a high value ^2J(H,P) = 17.2 Hz coupling constant.

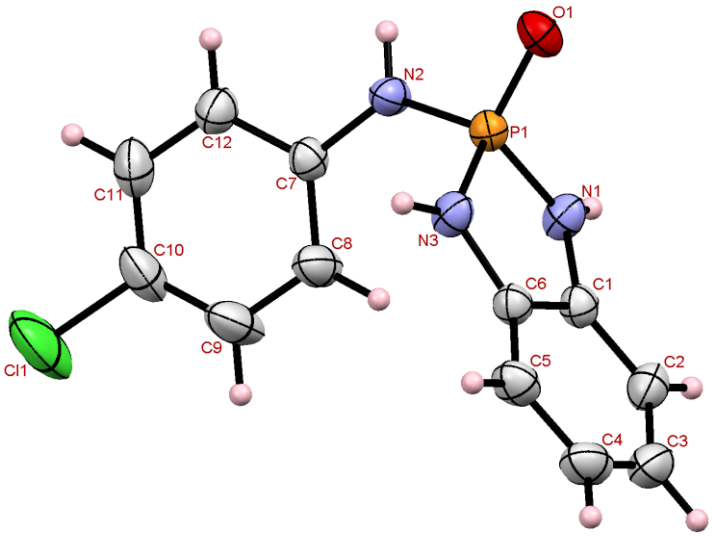


Fig. 1. *Displacement ellipsoid plots (50% probability) of the title structure showing the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.*

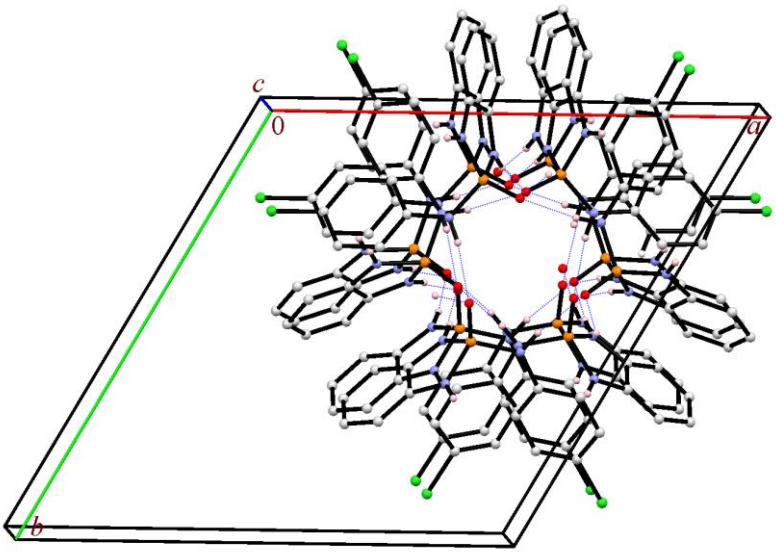


Fig. 2. *A partial view of the crystal packing of the title structure, showing a tubular arrangement of fused hydrogen-bonded rings along [001].*

Table 1. *Selected bond lengths (Å) and bond angles (°) for the title compound.*

P1-O1	1.484(2)	C1-N1	1.404(3)
P1-N1	1.653(2)	C6-N3	1.403(3)
P1-N2	1.633(2)	C7-N2	1.413(3)
P1-N3	1.657(2)		
O1-P1-N3	116.94(12)	N1-P1-N3	92.49(12)
O1-P1-N1	116.40(13)	C6-N3-P1	112.48(18)
O1-P1-N2	107.08(12)	N2-P1-N1	112.70(13)
C1-N1-P1	112.45(18)	N2-P1-N3	110.87(13)
C7-N2-P1	128.32(18)		

4. CONCLUSION

The synthesis, spectroscopic characterization and crystal structure determination of (4-Cl-C_6H_4NH)P(O)(1,2-NH)$_2C_6H_4$ was investigated. A survey on the Cambridge Structural Database (CSD) shows that this structure is the first diffraction study of an (R^1NH)P(O)(NH)$_2R^2$ diazaphosphole (R^1 and R^2 = H or a hydrocarbon segment) and there is no report of (R^1NH)P(O)(NH)$_2R^2$ diazaphosphole in the CSD. There are three hydrogen bond donor sites in the molecules and the P═O group takes part in the (N—H…)$_2$O═P hydrogen bonds forming a novel tubular hydrogen bond pattern. The remaining N—H group takes part in the N—H…π interaction.

5. ACKNOWLEDGMENTS

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