Two Conformers in Solution and Solid State for a Novel Phosphoramidate –
Synthesis, Characterization and Crystal Structures of 
\( \text{C}_6\text{H}_5\text{C}(\text{O})\text{NHP(O)}[\text{NH(tert-C}_4\text{H}_9)]_2 \) and \( \text{CCl}_3\text{C}(\text{O})\text{NHP(O)}[\text{NH(tert-C}_4\text{H}_9)]_2 \)

Khodayar Gholivand* and Mehrdad Pourayoubi

Tehran / Iran, Department of Chemistry, Tarbiat Modarres University

Received March 15th, 2004.

Abstract. Two new phosphoramidates with formula \( \text{RC(O)NHP(O)}[\text{NH(tert-C}_4\text{H}_9)]_2, R = \text{C}_6\text{H}_5, (1) \) and \( \text{CCl}_3, (2) \) were synthesized and characterized by IR, \(^1\text{H}-, \text{ }^13\text{C}-, \text{ }^{31}\text{P NMR, mass}

spectroscopy and elemental analysis. The structures confirmed by X-ray single crystal determination. Compound 1 appears as two conformers (1a and 1b) in solid state as well as solution. Both compounds (1 and 2) exist in the polymeric chains in crystalline lattice produced by hydrogen bonding that for compound 1, there are two independent infinite chains; each of them composed of one of the two conformers.

Keywords: Crystal structure; Phosphoric triamide; NMR spectroscopy

Introducing

This work is a continuation of previous studies about the reaction of halogen-phosphorus compounds with amines to form P-N bonds. Perhaps, they are the most extensively studied inorganic series [1—5].

Despite this, relatively little is known about N-carbonyl-phosphoramidates with \( \text{C(O)N(H)P(O)} \)- skeleton. A few crystal structures of these types of molecules and their complexes were reported [6—10]. In previous synthesized N-carbonyl-phosphoramidates, IR spectroscopy showed two stretching frequencies for PO bonds which were assigned on the presence of two rotamers in solid state, but no report has done on solution, so far [11].

Results and Discussion

The reaction of tert-butyl amine with N-benzoyl and trichloroacetyl phosphoramidic dichloride which lead to corresponding phosphoric triamides, \( \text{C}_6\text{H}_5\text{C}(\text{O})\text{NHP(O)}[\text{NH(tert-C}_4\text{H}_9)]_2, (1) \) and \( \text{CCl}_3\text{C}(\text{O})\text{NHP(O)}[\text{NH(tert-C}_4\text{H}_9)]_2, (2) \). NMR study shows that compound 1 appears as two conformers in solution with the ratio depending on temperature and concentration. X-ray crystallography confirms the existence of two conformers in crystalline lattice which we believe that it is the first example of a conformeric pair examined by X-ray single crystal structure determination techniques so far for a phosphoramidate. Substitution of phenyl for CCl₃ leads to various results. In compound 2, NMR study and X-ray crystallography show just one compound in solution and solid state.

* Dr. Khodayar Gholivand
Department of Chemistry-Tarbiat Modarres University
P. O. Box: 14115-175
Tehran / Iran
Tel.: (+98) 21-8011001-Int.: 3443
Fax: (+98) 21-8006544
E-mail: gholi_kh@modares.ac.ir
Two Conformers in Solution and Solid State for a Novel Phosphoramidate

Scheme 1 Preparation of compounds 1 and 2.

**NMR Study**

The prepared molecules contain two amino and one amidic protons. Usually, it is expected to one signal for amino and one signal for amidic protons. $^1$H NMR spectrum of compound 1 shows three signals at 3.92, 4.00, and 4.43 ppm with integration ratio 1:2:1 in saturated solution, which belongs to amino protons. Also two different signals are revealed for amidic protons at 9.47 and 9.64 ppm with various coupling constants, $^2$J(PNH), in addition to, the corresponding peaks for methyl and phenyl groups.

Unexpectedly, In [D$_6$]DMSO, $^{31}$P{$^1$H} NMR spectra show two peaks at 4.10 and 4.70 ppm with integration ratio 54:46 %, Figure 1 (top) and 41:59 % Figure 1 (below) in saturated solution and the same solution that diluted four times, respectively.

The $^{31}$P{$^1$H} NMR spectra indicate the signals ratio are depend on temperature and concentration.

At 298, 313, 323, and 338 K the ratio of them, in diluted solution are 41:59 %, 52:48 %, 44:56 %, and 38:62 % and in saturated solution at the same temperatures are 54:46 %, 54:46 %, 50:50 %, and 50:50 %, respectively.

The $^{13}$C NMR study confirmed $^1$H NMR results, so that three signals appeared at 16.55, 31.60, and 31.74 ppm for methyl groups and three signals at 50.86, 50.90, and 61.20 ppm for tert-carbon atoms whereas two signals are revealed for carbonyl at 168.70 and 168.57 ppm.

These NMR data proposed that two convertible species (conformers) in solution exist. The presence of three signals for amino protons means that one of them has equivalent amino protons (in chemical shift 4.00 ppm with relative intensity 2) and alkyl groups whereas the other one contains two nonequivalent amino protons (in 3.92 and 4.43 ppm with integration ratio 1:1) and alkyl groups, too. It must be mentioned that in saturated solution the conversion of conformers is negligibly small.

Observation in molecule 2 is different from molecule 1. $^1$H NMR spectrum shows one peak at 9.8 ppm for amidic proton and a doublet peak at 4.19 ppm which owing to amine protons and one peak at 1.20 ppm for methyl protons. $^{13}$C NMR confirms $^1$H NMR results, also $^{31}$P{$^1$H} NMR spectrum shows just one peak at 1.00 ppm. Contrast compound 1, there is only one molecule in solution. The coupling constant $^2$J(PNH)$_\text{amide}$ in compound 1 is observed but not in 2.

In compound 2, probably, because of CCl$_3$ group’s steric effect tert-butyl groups can not rotate.

To check and confirmation of NMR observation, we used the X-ray crystallography technique.

**X-ray crystal structure**

Single crystals of 1 and 2 were obtained from a solution of 1-heptane and chloroform (with ratio 1:4), at room temperature. Crystallographic data and structure refinement parameters are listed in Table 1.
Crystallographic data for the structures in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 218879 (C₁₅H₂₆N₃O₂P₁) and 230775 (C₁₀H₂₁Cl₃N₃O₂P₁). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Selected bond lengths and angles are shown in Tables 2 and 3 for compounds 1 and 2, respectively.

Compound 1 exists as two conformers in crystalline lattice. They are due to different spatial orientation of tert-butyl amine groups. One of them has two amino hydrogen atoms which are syn, (Figure 2, top, 1a), but not in the other (Figure 2, below, 1b).

The difference is described by comparison of corresponding torsion angles in two conformers. Torsion angles N(3)-P(1)-N(2)-C(8) and N(2)-P(1)-N(3)-C(12) are 108.6(2)° and 172.5(2)°, whereas N(3')-P(1')-N(2')-C(8') and N(2')-P(1')-N(3')-C(12') are 171.1(2)° and 178.3(2)°, respectively.

Various orientations of amine groups cause for existence of different inter- and intramolecular hydrogen bonds. There are two independent infinite chains in this structure. Each is composed of one of the two independent molecules, (Figure 2, below, 1b).

Figure 4 shows a view of the unit cell packing that the intermolecular hydrogen bonds in 1a are seen. Two syn amino hydrogen atoms in 1a form intermolecular hydrogen...
Two Conformers in Solution and Solid State for a Novel Phosphoramidate

Figure 2 Molecular structure and atom-labeling scheme for \([\text{NH}(t-C_4H_9)]_2\text{P}(\text{O})(\text{NHCOPh}), \text{1a (top), and 1b (below) (50\% probability ellipsoids).}}\)

Figure 3 Two independent infinite chains, each of them composed of one of the two independent molecules (conformers).

Figure 4 A view of the unit cell packing for compound 1 which in the intermolecular hydrogen bonds 1a are seen.

Figure 5 Inter and intramolecular hydrogen bonds in 1b.

bonds only with a carbonyl oxygen atom, O(1'B). Figure 5 indicates hydrogen bonds in other chain. The carbonyl oxygen atom O(1) makes intramolecular hydrogen bond with the proton which is connected to N(2) and makes intermolecular with H(3BB). In both chains, the amidic hydrogen atoms produced hydrogen bonds with oxygen atoms of P(O).

Torsion angles N(1)-C(1)-C(2)-C(3), O(1)-C(1)-C(2)-C(7) and P(1)-N(1)-C(1)-C(2) in conformer 1b are 4.6(4), 3.9(4)° and −178.6(2)°, respectively. It shows phenyl ring approximately placed on the plane of C(1)-N(1)-P(1), i.e. phenyl ring is nearly the symmetry plane of this conformer, Figure 6 (top). For other conformer, torsion angles N(1')-C(1')-C(2')-C(3') , O(1')-C(1')-C(2')-C(7') and P(1')-N(1')-C(1')-C(2') are 9.6(4), 8.9(4) and −169.9(2)°, respectively, that show more deviation than 1a, Figure 6 (below). Also see the tert-butyl amine group’s orientation in Figure 6, up and down. In both cases, the phenyl ring position allows the various orientations of tert-butyl groups in two conformers to be done.

Both P(1)-N(2) and P(1)-N(3) bond lengths are 1.629(2) Å, whereas P(1')-N(2') and P(1')-N(3') are not identical, 1.619(3) Å and 1.629(2) Å, respectively. These data certainly demonstrated two different amino protons, P-N bonds and tert-butyl groups in compound 1a. In 1b tert-butyl groups are almost always equivalent but not in 1a. It seems that due to the restricted rotation of tert-butyl amine groups, the presence of two conformers is observable in solution, too.

The P(1)-N(2), P(1)-N(3), P(1')-N(2'), and P(1')-N(3') bond lengths are significantly shorter than the typical P-N single bond length (1.77 Å) [15] but longer than the PN
double bond length (1.57 Å, in Ph$_3$P=N-). The shortening of PN bond lengths is likely related to an electrostatic effect (polar bond) which overlaps with P-N σ bond [16]. The angles C(12)-N(3)-P(1), C(8)-N(2)-P(1), C(12′)-N(3′)-P(1′), and C(8′)-N(2′)-P(1′) are 126.9(2)°, 125.9(2)°, 127.2(2)° and 127.4(2)° that show hybridization is nearly sp$^2$ for amino nitrogen atoms. The same observation for amidic nitrogen atoms is done due to the resonance interaction of non-bonding electrons of N(1) and N(1′) with C(1) and C(1′). Therefore the existence of two conformers, which we suggested by NMR spectroscopy are confirmed by X-ray crystallography.

Finally, replacing phenyl ring by electronegative CCl$_3$ group suggests notable results. The molecular structure and atomic numbering scheme are shown in Figure 7. Compound 2 forms a one-dimensional chain in which two syn amino protons are hydrogen-bonded to carbonyl oxygen atom of an adjacent molecule and amidic proton with oxygen atom of phosphoryl group. Figure 8. Similar to 1a and 1b, the P-N(amine) distances are shorter than the typical P-N single bond length and the nitrogen atoms are surrounded relatively planar. The C=O bond length in compound 2 is shortened about 0.02 and 0.03 Å in comparison with two conformers (1a and 1b), respectively. The P-N(amine) bond lengths are shorter than similar P-N bonds in 1a and 1b. Despite this a longer bond length revealed for amidic P-N bond in compound 2. Perhaps this increasing of P-N amidic bond length in compound 2 is the reason for vanishing of the coupling between phosphorus and amidic proton (2J$_{PNH}$ = 0 Hz). There are anti orientation of the P=O relative to C=O group in both compounds 1 (1a and 1b) and 2. Drastically difference is obtained between amidic and amino P-N bond lengths in compound 1 and 2. The amino P-N bond lengths in both molecules are considerably shorter than amidic P-N bonds. It means that the restricted rotation can be performed around the P-N amine bond and the rotation around P-N amide at normal temperature can not restricted.

**Experimental Section**

Tert-butyl amine(>99 %), benzamide(>98 %), 2, 2, 2-trichloroacetamide(>98 %) (Merck), phosphorus pentachloride(≥98 %) (Fluka), were used as supplied. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker (Avance DRS) 500 spectrometer. $^1$H and $^{13}$C and $^{31}$P chemical shifts were determined relative to TMS and 85 % H$_3$PO$_4$ as external standards, respectively. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. High-resolution mass spectra were obtained with a Shimadzu model QP-1100EX spectrometer (EI, 20 ev).
Two Conformers in Solution and Solid State for a Novel Phosphoramidate

C₂H₅C(O)NHP(O)Cl₂ was prepared similar to the procedure by Kirsanov [17] from the reaction of phosphorus pentachloride and benzamide in CCl₄ and then the treatment of formic acid.

C₆H₅C(O)NHP(O)Cl₂ was prepared in the same way as C₂H₅C(O)NHP(O)Cl₂ by using 2, 2- trichloroacetamide instead of benzamide [18].

N-benzoyl, N,N-bis(tert-butyl)phosphoric triamide (two conformers, 1a + 1b): Tert-butyl amine (0.298 g, 4 mmol) was added to a solution of N-benzoyl phosphoramidic dichloride (0.238 g, 1 mmol) in chloroform (15 mL) and stirred at 13°C for 5 h. After the solvent removed and the residue that formed was stirred in H₂O. Product was filtered off and then washed with H₂O and recrystallized from chloroform and n-heptane. Elemental analysis (%) calcd. for C₁₃H₂₃N₃O₂P: C 34.06, H 6.00, N 11.92; found: C 34.08, H 6.01, N 11.89.

1H NMR (500.13 MHz, [D₆]DMSO, 25 °C, TMS), δ = 1.17 (s, 27 H, C₃H₇), 1.20 (s, 9 H, C₆H₅), 3.92 (br, 1 H, NH amine), 4.00 (d, 2J(PNH) = 9.1 Hz, 2 H, NHamine), 9.8 (s, NHamide).

13C NMR (125.77 MHz, [D₆]DMSO, 25 °C, TMS), δ = 16.80 (d, C, C₆H₅), 168.75 (s, C, C = O), 134.62 (d, 3J(PC) = 7.7 Hz, C₈H₈), 133.95 (d, 3J(PC) = 8.6 Hz, C₈H₈), 132.34 (s), 128.84 (s), 128.72 (s), 128.56 (s), 128.47 (s), 61.20 (s, C₆H₅), 50.90 (s, C₆H₅), 50.86 (s, C₆H₅), 31.74 (d, 3J(PC) = 4.8 Hz, CH₃), 31.60 (d, 3J(PC) = 4.9 Hz, CH₃), 16.55 (d, 3J(PC) = 7.5 Hz, CH₃).

13P NMR (102.46 MHz, [D₆]DMSO, 25 °C, H₃PO₄ external), δ = 3290 (NH, 5 %), 311 (M-C₆H₅)²⁻, 16 %), 105 (P[CO]³⁻), 15 %), 77 (C₅H₅)²⁻, 15 %), 58 (C₆H₆)²⁻, 100 %), 57 (C₅H₅)²⁻, 14 %).

N-trichloroacetetyl, N,N-bis(tert-butyl)phosphoric triamide: Tert-butyl amine (0.298 g, 4 mmol) was added to a solution of trichloroacetyl phosphoramidic dichloride (0.279 g, 1 mmol) in acetonitrile (15 mL) and stirred at −5 °C. After 5 h the solvent removed and the residue that formed was stirred in H₂O. Product was filtered off and then washed with H₂O and recrystallized from chloroform and n-heptane. Elemental analysis (%) calcd. for C₁₁H₂₁Cl₃N₃O₂P: C 34.06, H 6.00, N 11.92; found: C 34.08, H 6.01, N 11.89.

1H NMR (500.13 MHz, [D₆]DMSO, 25 °C, TMS), δ = 1.20 (s, 18 H, C₃H₇), 4.19 (d, 3J(PNH) = 9.1 Hz, 2H, NH₅n), 9.8 (s, NH₅n), 13C NMR (125.77 MHz, [D₆]DMSO, 25 °C, TMS), δ = 162.28 (s, C, C = O), 51.95 (s, C₆H₅), 32.65 (d, 3J(PC) = 4.9 Hz, CH₃).

31P NMR (202.46 MHz, [D₆]DMSO, 25 °C, H₃PO₄ external), δ = 1.00. IR (KBr): δ = 3345 (NH), 3045 (NH), 2860, 1683 (C=O), 1437, 1385, 1262, 1212, 1018, 837, 844, 795, 677. MS (20 eV, EI): m/z = 357 ([C₁₀H₉O₂P]⁺, 1 %), 355 ([C₄H₅N]²⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[O]⁻), 353 ([C₄H₅N]²⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[O]⁻), 280 ([M-C₄H₅N]²⁻, 45 %), 191 ([C₄H₅N]²⁻[O]⁻, 11%), 119 ([Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[Cl]⁻[O]⁻), 65 %), 57 ([C₅H₅]²⁻, 21 %).

References