

Synthesis and spectroscopic study of (X)(C₆H₅CH₂NH)₂P(O) (X = C₆H₅ and CCl₃C(O)NH)

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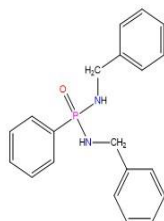
Abstract: The (C₆H₅)(C₆H₅CH₂NH)₂P(O) (I) phosphonicamide and (CCl₃C(O)NH)(C₆H₅CH₂NH)₂P(O) (II) phosphoric triamide were synthesized and studied by spectroscopic methods. All carbon atoms belonging to the phenyl group attached to phosphorus (in I), and the *ipso*-carbon atom of benzyl moiety in both compounds appear doublets due to the coupling with phosphorus nucleus (ⁿJ_{PC}, n = 1 to 4 and ³J_{PC}, respectively).

Keywords: Phosphonicamide; Phosphoric triamide; NMR; Phosphorus-carbon coupling constant.

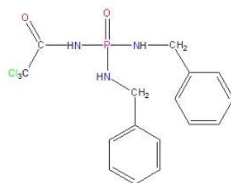
Introduction

Biochemical properties of phosphoramides [1] and fire retardant properties of phosphonamides [2] have been studied in literature.

The CP(O)(NR¹R²)₂ fragment defines phosphonicamide compounds, and phosphoramides are introduced with the X₂P(O)NR¹R² formula (X = nitrogen from amine/amide groups (phosphoric triamide), halogen, and/or oxygen attached to hydrogen or hydrocarbon groups and R¹/R² are H or hydrocarbon fragment). In this research, the synthesis and spectroscopic characterization of two new compounds, (C₆H₅)(C₆H₅CH₂NH)₂P(O) (I) phosphonicamide (Scheme 1) and (CCl₃C(O)NH)(C₆H₅CH₂NH)₂P(O) (II) phosphoric triamide (Scheme 2) are investigated. Some topics related to the phosphorus chemical shifts and phosphorus-carbon coupling constants were addressed.



Scheme 1: Chemical structure of I



Scheme 2: Chemical structure of II

Experimental Section

Synthesis and Identification

(C₆H₅)(C₆H₅CH₂NH)₂P(O) (I)

To a solution of dichlorophenylphosphine oxide in CHCl₃, a solution of benzylamine (1 to 4 mole ratio) in the same solvent was added at 0°C (ice bath) and stirred (4 hours). Then, the solvent was removed and the solid obtained was washed with distilled water. The product was dried in air and recrystallized from chloroform and normal hexane.

³¹P{¹H} (121.76 MHz, DMSO-d₆): δ = 19.80 (s). ¹H NMR (300.81 MHz, DMSO-d₆): δ = 4.00 (m, 4H, CH₂), 5.10 (m, 2H, NH), 7.07–7.54 (m, 13H), 7.83 (m, 2H). ¹³C{¹H} NMR (75.65 MHz, DMSO-d₆): δ = 44.04, 126.86, 127.70, 128.43, 128.43 (d, J = 13.1 Hz), 131.18 (d, J = 2.2 Hz), 131.88 (d, J = 8.0 Hz), 135.38 (d, J = 148.5 Hz), 141.86 (d, J = 6.3 Hz). IR (KBr, cm⁻¹): 3214, 3157, 3066, 2887, 2638, 1962, 1641, 1599, 1455, 1300, 1251, 1176, 1120, 1023, 949, 909, 876, 814, 739, 695.

(CCl₃C(O)NH)(C₆H₅CH₂NH)₂P(O) (II)

The (CCl₃C(O)NH)Cl₂P(O) reagent was obtained from a reaction between 2,2,2-trichloroacetamide and PCl₅ in CCl₄ under reflux condition (2 hours) and then the treatment of HCOOH in ice bath temperature (2 hours) (molar ratio: 1:1:1).

The (CCl₃C(O)NH)Cl₂P(O) reagent was reacted with benzylamine (1 to 4 mole ratio) in CHCl₃ at 0°C (ice bath) for 4 hours. Then, the solvent was removed and the solid obtained was washed with distilled water. The product was dried in air and recrystallized from chloroform and normal hexane.

³¹P{¹H} (121.76 MHz, DMSO-d₆): δ = 7.75 (s). ¹H NMR (300.81 MHz, DMSO-d₆): δ = 4.05 (m, 4H, CH₂), 5.51 (m, 2H, NH), 7.27–7.57 (m, 10H), 9.52 (s, 1H, NH). ¹³C{¹H} NMR (75.65 MHz, DMSO-d₆): δ = 43.54, 93.62 (d, J = 10.2 Hz), 128.41, 129.55, 131.66, 140.33 (d, J = 5.2 Hz), 162.06. IR

(KBr, cm^{-1}): 3328, 3233, 2930, 2866, 1714, 1655, 1556, 1491, 1440, 1214, 1176, 1088, 1014, 884, 826, 677.

Results and Discussion

NMR spectroscopy

The phosphorus signals (in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra) of compounds **I** and **II** appear at 19.80 and 7.75 ppm, respectively. The more value of chemical shift of **I** is related to the anisotropic effect of phenyl ring directly attached to phosphorus.

In the ^1H NMR spectra, the CH_2 and NH protons of $\text{C}_6\text{H}_5\text{CH}_2\text{NH}$ moieties are revealed as multiplets at 4.00 and 5.10 ppm for **I** and at 4.05 and 5.51 ppm for **II**. The NH proton of the $\text{C}(\text{O})\text{NHP}(\text{O})$ moiety of compound **II** appears as broad signal at 9.52 ppm.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **I**, all carbon atoms of the phenyl group directly attached to phosphorus show coupling with phosphorus (^1J , ^2J , ^3J and ^4J). The doublet signal at 131.18 ppm ($^4\text{J} = 2.2$ Hz) is assigned to the *para*-carbon atom of the noted phenyl ring with four bonds separation from phosphorus. The doublet centered at 135.38 ppm ($^1\text{J} = 148.5$ Hz) is related to carbon atom directly attached to phosphorus. The doublets at 128.43 ppm ($\text{J} = 13.1$ Hz) and 131.88 ppm ($\text{J} = 8.0$ Hz) are assigned to the *ortho*- and *meta*-carbon atoms. There is also one singlet at 128.43 ppm which is situated in the center of doublet at 128.43 ppm. The *ipso*-carbon atom of benzyl moiety shows a doublet at 141.86 ppm ($^3\text{J} = 6.3$ Hz) (Fig. 1 and Fig. 2).

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **II**, the doublets at 93.62 ppm ($\text{J} = 10.2$ Hz) and 140.33 ppm ($\text{J} = 5.2$ Hz) associate to the carbon atoms of CCl_3 and phenyl moieties, both with three bonds separation from phosphorus (Fig. 3).

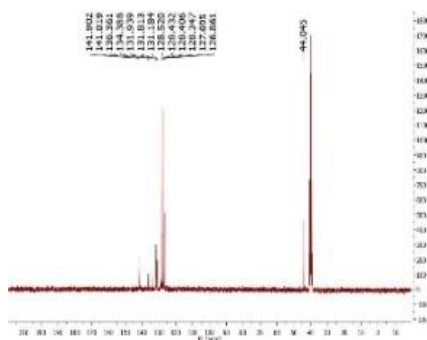


Fig. 1: $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **I**

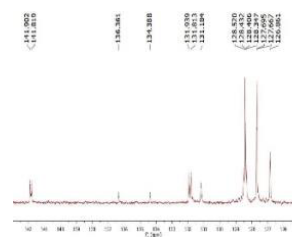


Fig. 2: $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **I** (aromatic region)

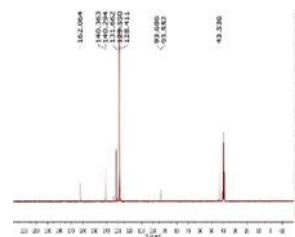


Fig. 3: $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **II**

Conclusion

The $(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2\text{NH})_2\text{P}(\text{O})$ phosphonicamide (**I**) and $(\text{CCl}_3\text{C}(\text{O})\text{NH})(\text{C}_6\text{H}_5\text{CH}_2\text{NH})_2\text{P}(\text{O})$ phosphoric triamide (**II**) were synthesized and studied by IR, ^1H -NMR, $^{31}\text{P}\{^1\text{H}\}$ -NMR and $^{13}\text{C}\{^1\text{H}\}$ -NMR. The phenyl group attached to phosphorus atom in **I** shows the doublet signals for all carbon atoms ($^n\text{J}_{\text{CP}}$, $n = 1, 2, 3$ and 4 coupling constants), and the ^1J and ^4J values are 148.5 and 2.2 Hz, respectively. The *ipso*-carbon atoms of benzyl moieties in two compounds are also revealed as doublets $^3\text{J}_{\text{CP}} = 6.3$ Hz in **I** $> ^3\text{J}_{\text{CP}} = 5.2$ Hz in **II**. The CCl_3 moiety in **II** appears a doublet ($^3\text{J}_{\text{CP}} = 10.2$ Hz). The phosphorus signal in **I** is revealed in a higher value of chemical shift ($^{31}\text{P}\{^1\text{H}\}$ NMR) with respect to the phosphorus signal in **II**, due to the anisotropic effect of phenyl ring directly attached to phosphorus in **I**.

References

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- [2] Li, Z., Liu, C., Cao, W. & Yao, Q. (2018). *J. Appl. Polym. Sci.* 135, 47411.