# Synthesis and Spectroscopic Characterization of $P(O)(OC_6H_5)_2(NHC_6H_4\text{-}4\text{-}Cl)$ and $P(O)(OC_6H_5)_2(NHC_6H_4\text{-}4\text{-}C_2H_5)$

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**Abstract:** The $P(O)(OC_6H_5)_2(NHC_6H_4\text{-}4\text{-}Cl)$ (I) and $P(O)(OC_6H_5)_2(NHC_6H_4\text{-}4\text{-}C_2H_5)$ (II) phosphoramides were synthesized and characterized. In the IR spectra, the bands centered at 3180 $cm^{-1}$ for (I) and at 3172 $cm^{-1}$ for (II) associate to the NH stretching frequencies, and the P=O stretching bands appear at 1231 and 1195 $cm^{-1}$, respectively. In the mass spectra, the molecular ion peaks are revealed (m/z = 359 for (I) and 353 for (II)). Phosphorus signals for (I) and (II) appear at –6.96 and –6.36 ppm, respectively.

**Keywords:** NMR Spectroscopy; Synthesis; Diphenyl Phosphoryl Chloride.

## Introduction

Phosphoramides are commonly used as insecticides and acaricides in agriculture as well as antiviral and anticancer agents in pharmaceutical research. Some derivates are used as flame retardants in plastics and textiles [1,2]. Here, the synthesis and characterization of two ($P(O)(OC_6H_5)_2(NHC_6H_4\text{-}4\text{-}Cl)$ (I) and $P(O)(OC_6H_5)_2(NHC_6H_4\text{-}4\text{-}C_2H_5)$ (II), Fig. 1) phosphoramides are investigated.

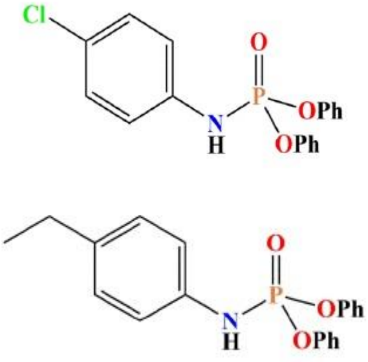

**Fig. 1:** Chemical structures of (I) (left) and (II) (right).

## Experimental Section

For the synthesis of (I), a solution of 4-chloroaniline (2 mmol) in dry chloroform was added dropwise to a solution of diphenyl phosphoryl chloride (1 mmol) in the same solvent. After stirring for 4 hours, the reaction was stopped, the solvent was removed and the obtained solid was washed with distilled water. The crystallization solvent was chloroform and n-heptane (5:1 *v*/*v*). The formulation is $C_{18}H_{15}ClNO_3P$.

**MW:** 359.75 g/mol. **m.p:** 112 °C. **IR** (KBr disc, υ, $cm^{-1}$): 3180, 3147, 3057, 2948, 1592, 1231, 1179, 979, 758. **MS** (70 eV, EI: m/z (%)) = 361 (18) $[M]^+$ ($^{37}Cl$), 359 (93) $[M]^+$ ($^{35}Cl$), 126 (10) $[NC_6H_5{}^{35}Cl]^+$, 94 (12) $[C_6H_6O]^+$, 77 (7) $[C_6H_5]^+$. **$^{31}P\{^1H\}$ NMR** (DMSO-$d_6$, 121 MHz, 297.4 K, 85% $H_3PO_4$): $\delta$ (ppm) = –6.96 (*s*). **$^1H$ NMR** (DMSO-$d_6$, 301 MHz, TMS): $\delta$ (ppm) = 9.08 (*d*, $^2J_{H\text{-}P}$ = 10.1 Hz, 1H), 7.45 – 7.37 (*m*, 6H), 7.29 – 7.22 (*m*, 8H). **$^{13}C\{^1H\}$ NMR** (DMSO-$d_6$, 75 MHz, 297.9 K, TMS): $\delta$ (ppm) = 150.45 (*d*, $^2J_{C\text{-}P}$ = 6.4 Hz), 139.34 (*s*), 130.49 (*s*), 129.66 (*s*), 126.07 (*s*), 125.87 (*s*), 120.59 (*d*, $^3J_{C\text{-}P}$ = 4.7 Hz), 119.84 (*d*, $^3J_{C\text{-}P}$ = 8.2 Hz).

For the synthesis of (II), to a solution of diphenyl phosphoryl chloride (1 mmol) in dry chloroform, a solution of 4-ethyl aniline (2 mmol) in the same solvent was added under stirring. After 4 hours, the solvent was removed and the obtained solid was washed with distilled water. The crystallization solvent was chloroform and n-heptane (4:1 *v*/*v*). The formulation is $C_{20}H_{20}NO_3P$.

**MW:** 353.36 g/mol. **m.p:** 115°C. **IR** (KBr disc, υ, $cm^{-1}$): 3475, 3172, 2956, 1593, 1492, 1294, 1195, 992, 773. **MS** (70 eV, EI: m/z (%)) = 353 (60) $[M]^+$, 352 (89) $[M-1]^+$, 351 (98) $[M-2]^+$, 337 (88) $[M-CH_4]^+$, 93 (48) $[C_6H_5O]^+$, 29 (60) $[C_2H_5]^+$. **$^{31}P\{^1H\}$ NMR** (DMSO-$d_6$, 121 MHz, 297.4 K, 85% $H_3PO_4$): $\delta$ (ppm) = –6.36 (*s*). **$^1H$ NMR** (DMSO-$d_6$, 301 MHz, TMS): $\delta$ (ppm) = 8.82 (*d*, $^2J_{H\text{-}P}$ = 10.7 Hz, 1H), 7.44 – 7.39 (*m*, 4H), 7.29 – 7.16 (m, 10H), 2.54 (*q*, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H), 1.16 (*t*, $^3J_{H\text{-}H}$ = 7.6 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (DMSO-$d_6$, 75 MHz, 297.9 K, TMS): $\delta$ (ppm) = 150.62 (*d*, $^2J_{C\text{-}P}$ = 6.2 Hz), 137.84 (*s*), 137.44 (*s*), 130.42 (*s*), 128.98 (*s*), 125.70 (*s*), 120.60 (*d*, $^3J_{C\text{-}P}$ = 4.8 Hz), 118.32 (*d*, $^3J_{C\text{-}P}$ = 7.8 Hz), 27.90 (*s*), 16.18 (*s*). The mass and NMR spectra are given in Figures 2 to 5.

## Results and Discussion

The N-H protons of (I) and (II) appear as doublets at 9.08 ppm ($^2J_{H\text{-}P}$ = 10.1 Hz) and 8.82 ppm ($^2J_{H\text{-}P}$ = 10.7 Hz), respectively. The fourteen hydrogen atoms of arene rings are revealed in the range of 7.22 to 7.29 ppm and 7.37 to 7.45 ppm for (I), and 7.16 to 7.29 ppm, 7.39 to

7.44 ppm for (II). In the $^{13}C\{^1H\}$ NMR spectra of (I) and (II), eight and ten signals are observed, related to different carbon atoms. The doublet signals at 150.45 ppm ($^2J_{C-P}$ = 6.4 Hz) for (I) and at 150.62 ppm ($^2J_{C-P}$ = 6.2 Hz) for (II) correspond to the *ipso*-carbon atoms of the $C_6H_5O$ moieties. The melting points are 112℃ (I) and 115℃ (II).

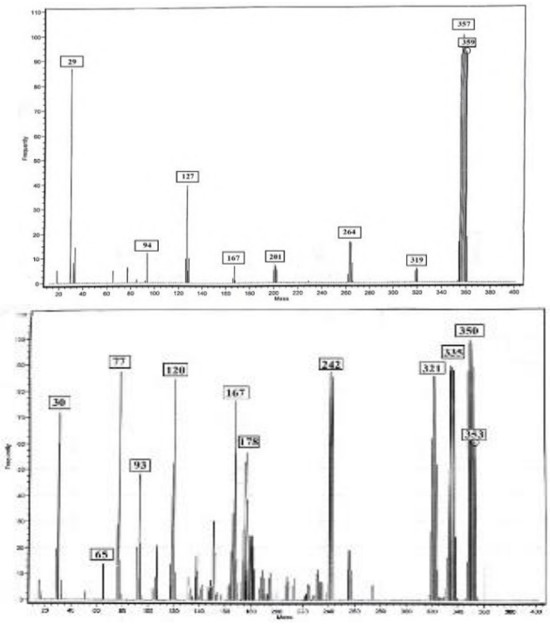

**Fig. 2:** Mass spectra of (I) (top) and (II) (bottom).

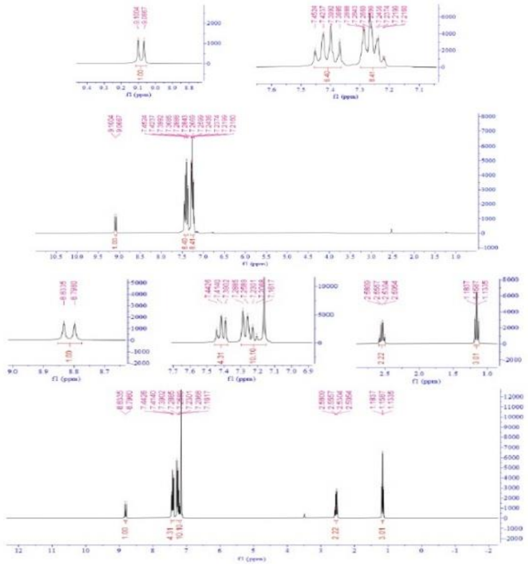

**Fig. 3:** $^1H$ NMR spectra of (I) (top) and (II) (bottom).

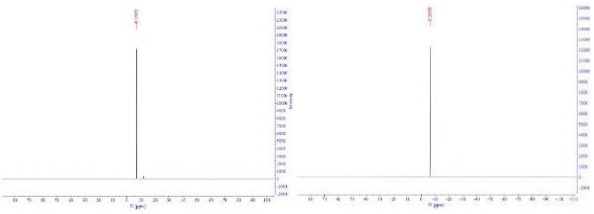

**Fig. 4:** $^{31}P\{^1H\}$ NMR spectra of (I) (left) and (II) (right).

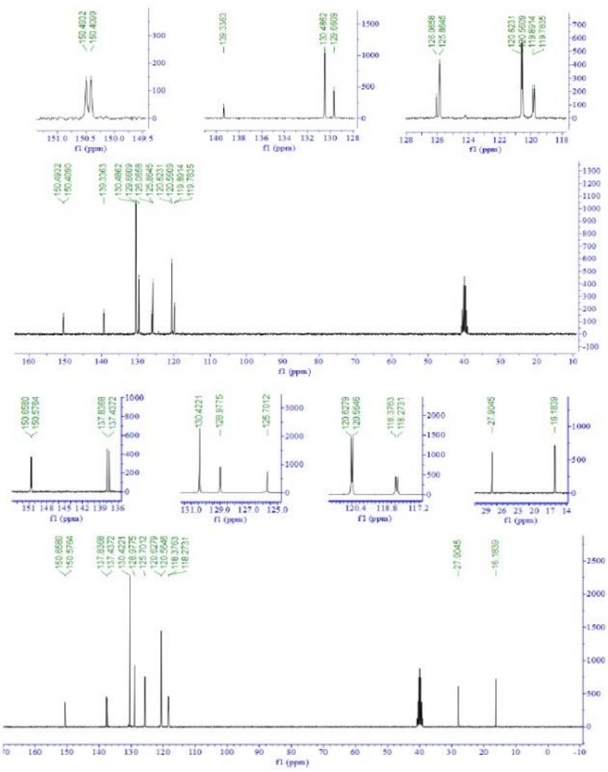

**Fig. 5:** $^{13}C$ NMR spectra of (I) (top) and (II) (bottom).

## Conclusion

Two new diphenyl phosphoramides were synthesized and investigated using infrared spectroscopy, nuclear magnetic resonance, and mass spectrometry. These compounds were prepared with good yield and purity.

## References

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