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Short-range ^{31}P-X NMR coupling constants (X = ^{1}H and ^{13}C) in two new phosphoramides

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Abstract: The syntheses and spectroscopic characterizations of two new phosphoramides, P(O)(NHCH$_2$C$_6$H$_4$-2-Cl)$_3$ (I) and (4-Cl-C$_6$H$_4$O)P(O)(NHCH$_2$C$_6$H$_4$-2-Cl)$_2$ (II) are investigated. Some topics related to the NMR coupling constants (^{31}P-^{1}H and ^{31}P-^{13}C) and chemical shifts (^{31}P, ^{1}H and ^{13}C) are addressed.

Keywords: Phosphoric Triamide; Diamidophosphoester; Phosphorus-Carbon Coupling Constant; NMR Spectroscopy

Introduction

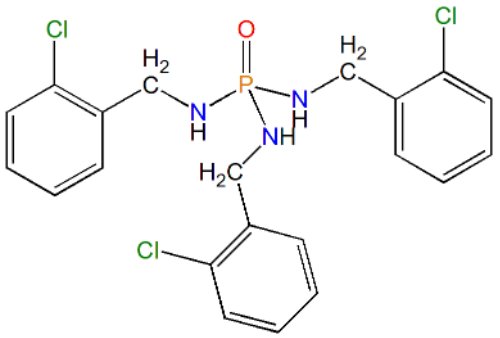
Nuclear magnetic resonance (NMR) is one of the best techniques for the characterization of compounds ranging from small molecules to macromolecules [1–4]. NMR spin-spin coupling constants are interesting for studying, due to the application in conformational analysis and the assignments of some signals [5]. In the phosphorus chemistry (including organic groups), the usual NMR-active nuclei are ^{1}H, ^{13}C and ^{31}P, which are investigated in view point of chemical shifts, coupling constants and the fine structures arisen from couplings [3]. Here, the synthesis and spectroscopic characterization of two new phosphoramides, *i.e.* P(O)(NHCH$_2$C$_6$H$_4$-2-Cl)$_3$ phosphoric triamide (I) and (4-Cl-C$_6$H$_4$O)P(O)(NHCH$_2$C$_6$H$_4$-2-Cl)$_2$ diamidophosphoester (II) are discussed (Schemes 1 and 2).

Experimental Section

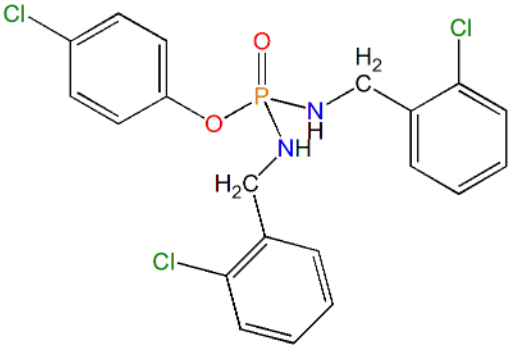
Syntheses

For the preparation of (I), to a solution of POCl$_3$ (6.9 mmol) in dry chloroform (15 ml), a solution of 2-chlorobenzylamine (20.7 mmol) and triethylamine (20.7 mmol) in the same solvent (15 ml) was added at 0 °C under stirring. After 4 hours, the mixture was transferred to a beaker and stood at room temperature (1 week) to evaporate the solvent. The residue (pale brown solid) was washed with distilled water to remove (C$_2$H$_5$)$_3$NHCl salt. ^{1}H NMR (300.81 MHz, DMSO-*d*$_6$): δ = 7.70 – 6.73 (m, 12H), 5.44 (m, 3H), 4.38 (m, 6H). ^{13}C{^{1}H} NMR (75.65 MHz, DMSO-*d*$_6$): δ = 139.18 (d, *J* = 6.1 Hz), 131.98 (s), 129.30 (s), 129.10 (s), 128.44 (s), 127.32 (s), 42.37 (s). ^{31}P{^{1}H} NMR (121.76 MHz, DMSO-*d*$_6$): δ = 17.10 (s). IR (KBr, ν, cm^{-1}): 3399, 3264, 3188, 2925, 1623, 1585, 1471, 1442, 1237, 1183, 1126, 1039, 888, 844, 746, 683.

For the preparation of (II), to a solution of 4-chlorophenyl dichlorophosphate (5.8 mmol) in dry chloroform (15 ml), a solution of 2-chlorobenzylamine (23.2 mmol) in the same solvent (15 ml) was added at 0 °C under stirring. After 4 hours, the mixture was transferred to a beaker and stood at room temperature (1 week) to evaporate the solvent. The resulting white precipitate was washed with distilled water to remove [2-Cl-C$_6$H$_4$CH$_2$NH$_3$]Cl salt. ^{1}H NMR (300.81 MHz, DMSO-*d*$_6$): δ = 7.56 – 7.15 (m, 12H), 5.66 (dt, *J* = 11.4 Hz, 7.4 Hz, 2H), 4.13 (dd, *J* = 12.0 Hz, 7.5 Hz, 4H). ^{13}C{^{1}H} NMR (75.65 MHz, DMSO-*d*$_6$): δ = 150.76 (d, *J* = 6.6 Hz), 138.17 (d, *J* = 5.8 Hz), 132.00 (s), 129.73 (s), 129.27 (s), 128.78 (s), 128.36 (s), 127.42 (s), 122.77 (d, *J* = 4.8 Hz), 42.23 (s). ^{31}P{^{1}H} NMR (121.76 MHz, DMSO-*d*$_6$): δ = 13.25 (s). IR (KBr, ν, cm^{-1}): 3600, 3457, 3409, 3263, 3170, 2917, 2847, 1592, 1484, 1440, 1358, 1232, 1196, 1117, 1094, 1040, 1010, 928, 828, 756, 736, 644, 600.



Scheme 1: Chemical structure of (I)



Scheme 2: Chemical structure of (II)

Results and Discussion

Spectroscopic measurements

In the $^{31}P\{^{1}H\}$ NMR spectra, the signlets are observed at 17.10 ppm for (I) and at 13.25 ppm for (II).

The NH protons (in the ^{1}H NMR spectra) appear a multiplet at 5.44 ppm for (I), and a well-resolved doublet of triplets at 5.66 ppm for (II), due to geminal phosphorus-hydrogen (^{2}J = 11.4 Hz) and vicinal hydrogen-hydrogen couplings (^{3}J = 7.4 Hz).

For two compounds, the *ipso*-carbon atom of the 2-Cl-$C_6H_4CH_2NH$ moiety appears as a doublet, at 139.18 ppm (J = 6.1 Hz) for (I) (Figure 1) and at 138.17 ppm (J = 5.8 Hz) for (II) (Figure 2), due to a phosphorus-carbon coupling with a three-bond separation between nuclei.

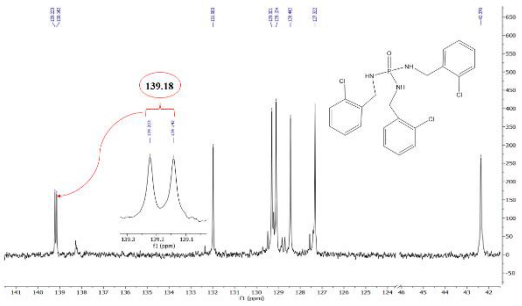


Fig. 1: $^{13}C\{^{1}H\}$ NMR spectrum of $P(O)(NHCH_2C_6H_4\text{-}2\text{-}Cl)_3$

The two doublets at 150.76 ppm (J = 6.6 Hz) and 122.77 ppm (J = 4.8 Hz) in the $^{13}C\{^{1}H\}$ NMR spectrum of (II) associate to the *ipso*- and *ortho*-carbon atoms of the 4-Cl-C_6H_4O moiety. In the IR spectrum of (I), the bands centered at 3264/3188 and 1237 cm^{-1} are assigned to the NH and P=O stretching vibrations. Similar bands for II are revelad at 3263/3170 and 1232 cm^{-1}.

Conclusions

Two new phosphoramides belonging to the phosphoric triamide and diamidophosphoester families were synthesized and characterized by spectroscopic methods. These compounds are $P(O)(NHCH_2C_6H_4\text{-}2\text{-}Cl)_3$ (I) and $(4\text{-}Cl\text{-}C_6H_4O)P(O)(NHCH_2C_6H_4\text{-}2\text{-}Cl)_2$ (II). Both two compounds show a doublet signal for the *ipso*-carbon atom of the $NHCH_2C_6H_5$-2-Cl moiety with the three-bond separation phosphorus-carbon coupling constants of 6.1 Hz for (I) and 5.8 Hz for (II). The *ipso*- and *ortho*-carbon atoms of the 4-Cl-C_6H_4O moiety are revealed as doublets with $^{2}J_{PC}$ = 6.6 Hz > $^{3}J_{PC}$ =4.8 Hz.

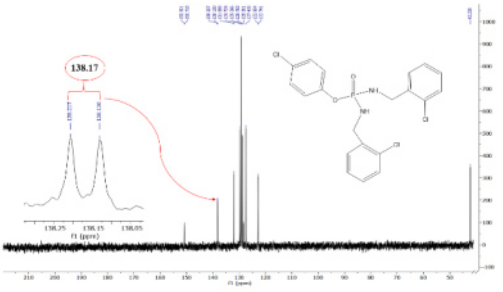


Fig. 2: $^{13}C\{^{1}H\}$-NMR spectrum of $(4\text{-}Cl\text{-}C_6H_4O)P(O)(NHCH_2C_6H_4\text{-}2\text{-}Cl)_2$

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