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Spectroscopic study of [(C2H5)(C6H5)(S)-(–)CHNH3][(C6H5)(NC5H4NH)P(O)(O)]

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Abstract: A two-step reaction of $(C_6H_5)P(O)Cl_2$ with $NC_5H_4NH_2$ and NH_2-(*S*)-(–)$CH(C_2H_5)(C_6H_5)$ in the presence of an HCl scavenger ($N(C_2H_5)_3$) yielded $[(C_2H_5)(C_6H_5)$(*S*)-(–)$CHNH_3][(C_6H_5)(NC_5H_4NH)P(O)(O)]$. In the $^{13}C\{^1H\}$-NMR spectrum, some phosphorus-carbon couplings were observed ($^nJ_{CP}$, n = 1, 2 and 3 for the phenyl group directly attached to phosphorus and $^2J_{CP}$ for amino-pyridinyl fragment). The main topics related to $^{31}P\{^1H\}$-NMR, ^1H-NMR, $^{13}C\{^1H\}$-NMR and IR were addressed.

Keywords: NMR; phosphorus-carbon coupling constant; IR.

Introduction

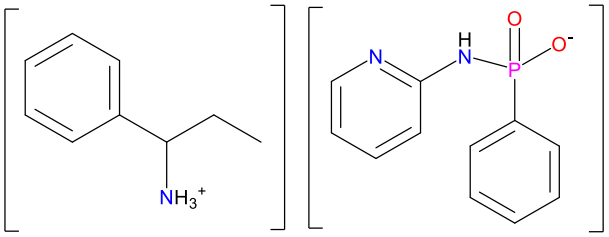
Phosphonamidates are well-known in the field of medicinal chemistry, to form some pro-drugs, and anti-bacterial, anti-infective and anti-viral materials [1–5]. Besides, some phosphonamide compounds were prepared as flame retardants [6]. In the salts including the $[O—P═O]^-$ moiety, the strengths of hydrogen bonds, which assisted from the existing negative charge, were discussed. In order to spectroscopy/structural study, it is possible to use various segments for binding to phosphorus and/or as counter-cation to design the targeted structures [7].

Here, we report on the synthesis and spectroscopic characterization of a new cation-anion compound, $[(C_2H_5)(C_6H_5)$(*S*)-(–)$CHNH_3][(C_6H_5)(NC_5H_4NH)P(O)(O)]$ (Scheme 1).

Experimental Section

The title compound was prepared in two steps, as follows: (step 1) to a solution of $(C_6H_5)P(O)Cl_2$ in chloroform, a solution of ($NC_5H_4NH_2$) and triethylamine (1:1:1 mole ratio) in the same solvent was added at 273 K. After 5 h of stirring, the solution which includes $(NC_5H_4NH)(C_6H_5)ClP(O)/[N(C_2H_5)_3HCl]$ was used for the next step. (Step 2), to the solution noted, a solution of NH_2-(*S*)-(–)$CH(C_2H_5)(C_6H_5)$ and triethylamine (1:1:1 mole ratio) in chloroform was added at 273 K. After 5 h of stirring, the solvent was removed in a vacuum and the obtained solid was washed with distilled water to remove $(C_2H_5)_3NHCl$ salt (and partially hydrolysis of compound). Colorless crystals were obtained from a $CHCl_3$ solution after slow evaporation of solvent at room temperature.

Analytical data: IR (KBr, ν, cm^{-1}): 3337, 3198, 3059, 2964, 2924, 2875, 2665, 2105, 1963, 1899, 1510, 1485, 1446, 1386, 1301, 1186, 1134, 917, 764, 699, 522, 460. ^1H-NMR (400.22 MHz, DMSO-d_6): δ = 8.64 (broad/exchanged, NH), 8.00 (d, *J* = 4.0 Hz, 1H), 7.71 (m, 2H), 7.50 – 7.25 (m, 10H), 6.93 (s, 1H, NH), 6.60 (m, 1H), 4.01 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.98 (m, 1H), 1.79 (m, 1H), 0.71 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$-NMR (100.64 MHz, DMSO-d_6): δ = 157.24 (d, *J* = 5.0 Hz), 147.84 (s), 141.22 (d, *J* = 160.8 Hz), 138.83 (s), 137.34 (s), 131.23 (d, *J* = 9.0 Hz), 129.24 (s), 129.00 (s), 128.66 (s), 127.99 (s), 127.82 (d, *J* = 12.7 Hz), 114.37 (s), 110.55 (s), 56.30 (s), 28.06 (s), 10.53 (s). $^{31}P\{^1H\}$-NMR (162.01 MHz, DMSO-d_6): δ = –0.84 (s).



Scheme 1: Chemical structure of $[(C_2H_5)(C_6H_5)$(*S*)-(–)$CHNH_3][(C_6H_5)(NC_5H_4NH)P(O)(O)]$

Results and discussion

The $^{31}P\{^1H\}$-NMR spectrum shows a singlet phosphorus signal at –0.84 ppm in DMSO-d_6. The N—H protons (^1H-NMR spectrum) of the chiral ammonium component and amino-pyridinyl moiety appear at 8.64 and 6.93 ppm as broad peaks.

In the $^{13}C\{^1H\}$-NMR spectrum, the phenyl ring directly bonded to phosphorus appear three well-resolved doublets: the doublet centered at 141.22 ppm ($^1J_{CP}$= 160.8 Hz) is related to the carbon atom attached to phosphorus, and the two doublets at 131.23 ppm (*J* = 9.0 Hz) and

127.82 ppm (J = 12.7 Hz) associate to the *ortho*- and *meta*-carbon atoms of phenyl. The pyridinyl fragment also shows a doublet at 157.24 ppm ($^{2}J_{CP}$= 5.0 Hz), which is assigned to the carbon atom with a two-bond separation from phosphorus (*ipso*-carbon atom) (Figure 1). None of the carbon signal of chiral ammonium cation show coupling with phosphorus.

The broad overlapped band within 3337 to 2665 cm^{-1} (in the IR spectrum) is an evidence to the presence of strong hydrogen bonding between $[(C_2H_5)(C_6H_5)(S)\text{-}(-)CHNH_3]^+$ cation and $[(C_6H_5)(NC_5H_4NH)P(O)(O)]^-$ anion in the prepared salt.

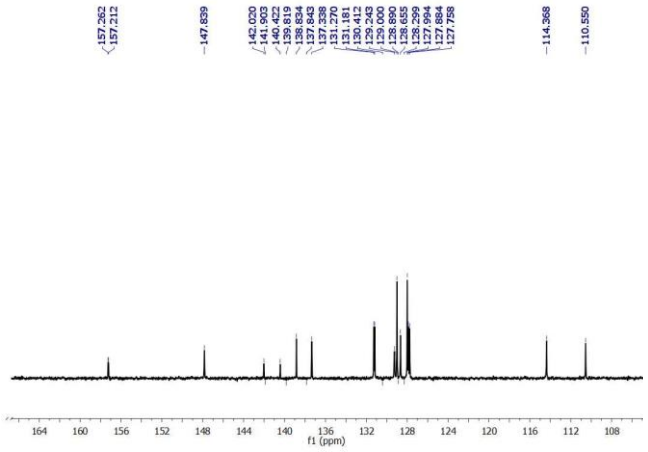


Fig. 1: $^{13}C\{^{1}H\}$-NMR of $[(C_2H_5)(C_6H_5)(S)\text{-}(-)CHNH_3][(C_6H_5)(NC_5H_4NH)P(O)(O)]$ within 108 to 160 ppm (aromatic region)

Conclusion

Spectroscopic features of $[(C_2H_5)(C_6H_5)(S)\text{-}(-)CHNH_3][(C_6H_5)(NC_5H_4NH)P(O)(O)]$ salt were studied. In the $^{13}C\{^{1}H\}$-NMR spectrum, the phenyl group directly attached to phosphorus shows three well-resolved doublets (^{1}J, ^{2}J and ^{3}J), and the pyridinyl moiety shows a doublet for the carbon atom with a two-bond separation from phosphorus. In the ^{1}H-NMR spectrum, the N—H protons of chiral ammonium cation and amino-pyridinyl fragment appear as broad peaks.

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