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Spectroscopic characterization and *Ab initio* calculations of new diazaphosphole and diazaphosphorinane

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Abstract

Phosphoryl chloride is used as a starting material to synthesize new diazaphosphole, $4\text{-}OCH_3\text{-}C_6H_4NHP(O)[4\text{-}CH_3\text{-}NH\text{-}C_6H_3\text{-}NH]$ (**1**) and diazaphosphorinane, $4\text{-}OCH_3\text{-}C_6H_4NHP(O)[NH\text{-}C_{10}H_6\text{-}NH]$ (**2**).

The products are characterized by ^{1}H, ^{13}C, ^{31}P NMR, and IR spectroscopy. A high value $^{2}J(PNH)$ = 17.0 Hz, 17.2 Hz is measured for two non-equivalent NH protons of endocyclic nitrogen atoms in compound **1**, while it greatly decreases to 4.5 Hz in **2**. Also, great amounts are obtained for two $^{2}J(P,C)$ as well as two $^{3}J(P,C)$ in the ^{13}C NMR spectrum of **1**, but they are zero in **2**. Here, the effect of ring strain and ring size on the structural and spectroscopic parameters is observed. The ^{31}P NMR spectra reveal that $\delta(^{31}P)$ of compound **1** is far much more downfield (12.63 ppm) relative to that of compound **2** (−10.39 ppm). Furthermore, *ab initio* quantum chemical calculations are performed to optimize the structures of these molecules by density functional theory (B3LYP) and Hartree-Fock (HF) methods, using the standard 6−31+G** basis set. The stabilization energies are calculated by the equation $\Delta E_{\text{stabilization}} = E_{\text{molecule}} - \Sigma E_i$, where i = atom. To obtain the atomic hybridizations, NBO computations are made at the B3LYP/6−31+G** level. Also, by NMR calculations the ^{1}H, ^{13}C, ^{31}P chemical shifts are obtained and compared with the experimental ones.

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