σ-Push-Pull Substitution in Iminophosphanes, a Theoretical Study

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A combination of α-electron-withdrawing/-releasing substituents (push-pull substitution) at iminophosphanes considerably lengthen (shorten) the central PN bond as revealed by ab initio calculations on model geometries; they also stress the importance of the energy barrier to inversion at nitrogen.
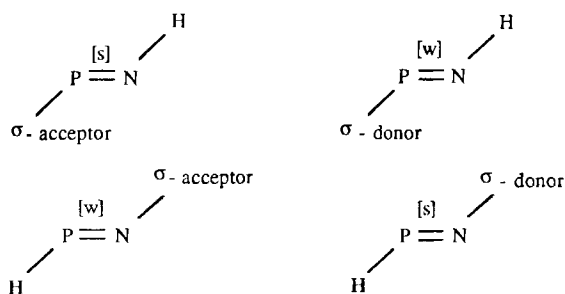
Hitherto a plethora of structures of iminophosphanes **1** have been reported. They range from extremely short PN double bonds [R^1 = $AlCl_4$, R^2 = Mes* (2,4,6-tri-*tert*-butylphenyl); PN = 147.5 pm[1]; R^1 = Cl, R^2 = Mes*: PN = 149.5 pm[1]) to extremely long double bonds [R^1 = (2,2′,6,6′-tetramethylpiperidyl, R^2 = $N(SiMe_3)_2$: PN = 159.8 pm[2]; R^1 = tBu_2P, R^2 = $N(SiMe_3)_2$: PN = 161.9 pm[3]]. Hence, a variation in substituents R^1 and R^2 causes considerable changes in geometries. The fact that iminophosphanes are one of the best structurally characterized class of double bond system[4] among higher main group elements prompted us to develop on the basis of quantum-chemical calculation a model of substituent effects of R^1 and R^2 on the central PN bond in **1**.

$$R^1 \diagup P = N \diagdown R^2$$

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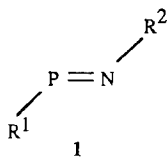
On the basis of the calculations on the double-ξ quality*[*] we will show in detail that σ-push-pull substituents R^1 and R^2 at iminophosphanes considerably effect (a) the central PN bond and (b) the energy barrier to inversion at nitrogen.

The rules for PN bond length variation are as follows:

(1) At phosphorus a σ-acceptor (e.g. F) shortens (s) while a σ-donor (e.g. SiH_3) weakens (w) the PN bond.

At nitrogen the substituents exert the opposite effect. Consequently, the PN σ-bond is maximally shortened (weakened) by a suitable combination of σ-electron-withdrawing (-releasing) substituents R^1 (R^2).

(2) At phosphorus and/or nitrogen π-donors (e.g. NH_2) weaken (w) the central π-bond. Overall σ- and π-effects superimpose each other, being either additive or counteractive.

The various substituent effects have been probed by energy-optimized ab initio calculations at a double-ξ level-ξ[5] on model-substituted iminophosphanes (Figure 1).

The results are in full accord with the model, with the shortest PN bond length for PNH⊕ and the longest one for PNH⊖. [At the given RHF-SCF level the latter structure prefers a triplet ground state]. An intermediate case is R = NH_2; at nitrogen it lengthens (additive σ- and π-effects) while at phosphorus it only slightly effects (counteractive σ- and π-effects) the PN bond. In accord with the PN bond in *trans*-$H_2NP = NH$ it is 157.4 pm, i.e. slightly longer than in the parent HPNH. A detailed study of the electronic hypersurface of PNH⊕ indicates that this species is the only energy minimum, and at the SCF level HPN⊕ rearranges without any energy barrier to HNP⊕. Thus, HNP⊕ is an energy minimum and HPN⊖ a saddle point on the electronic hypersurface of this species[6].

Electronegative substituents at phosphorus bear some additional important consequences. Due to large differences in electronegativity between P and R^1 the bond between these atoms tends to become ionic, promoting the formation of a close ion pair $R^{1⊖}$ PNH⊕. As a consequence, electronegative substituents R^1 considerably reduce the energy barrier to inversion at nitrogen (Table 1).

(The transition states for inversion at nitrogen have been determined by saddle-point search[5c] at the SCF level and energy-corrected at the CEPA-1 level[5d,7]). On this basis the energy barrier to inversion at nitrogen becomes almost negligible with a σ-electron-withdrawing substituent at phosphorus and a σ-electron-donating substituent at nitrogen. In addition, the σ-electron-withdrawing substituents at phosphorus (F, Cl) promote a *cis* rather than a *trans* conformation. On this basis it is not surprising that FP=NSiH₃ (see Figure 1) is most stable in a *cis* rather than in a *trans* orientation of substituents. In practice, however, the π-systems are substituted in general by bulky substituents such as the Mes* group which induces more steric hindrance in the *cis* conformation than in the *trans* conformation. Thus, the preference of a *cis* over a *trans* geometry may well be superseded by steric hindrance.

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*[*] Huzinaga bases sets[5] P, Si [4, 6 × 1/3, 3 × 1/1 d (ξ = 0.5, 0.4)]; F, O, N [5, 3 × 1/3, 1/1 d (ξ = 1.4, 1.25, 0.95)]; H [3, 1] have been used. Geometry optimizations have been performed with the Karlsruhe version of set of programs[5b,c]. The accuracy of optimization[5c] is ≤ 10⁻⁸ au in energy. Concomitantly, the accuracy of bond lengths is ≤ 10⁻⁴ Å.
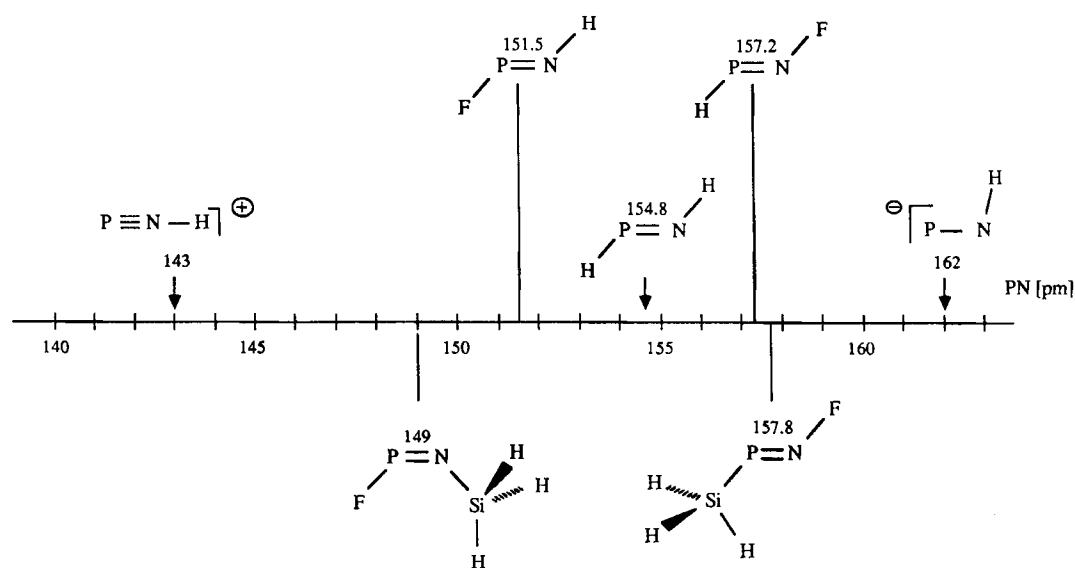
Figure 1. PN bond lengths [pm] of substituted iminophosphanes, determined at the ab initio level[5]

Table 1. Barriers to inversion at nitrogen in 1; energies [kcal/mol] at the SCF/CEPA-1 level

R[1]	R[2]	$E_{inv.}$[a]	E_{ct}[b]
H	H	16.4 (14.0)[c]	0.86
F	H	4.3 (3.6)	−3.66
Cl	H	4.8 (3.9)	−5.02
OH	H	6.9 (5.9)	−1.72
NH₂	H	11.3 (9.9)	1.23
H	CH₃	14.6 (11.6)	−1.44
H	SiH₃	2.6 (1.4)	−0.75

[a] $E_{inv.} = E_{TS} − E_{trans.}$ — [b] $E_{ct} = E_{cis} − E_{trans.}$ — [c] Values in parentheses at the SCF level.

While it should be clear that at the SCF level the absolute PN bond distances for the various model geometries are too short by about 2−3 ppm, the corresponding relative changes in bond lengths are correctly reproduced. Their variance by approximately 10% (at the maximum) is indicative of rather considerable substituent effects acting on the PN double bond.

CAS Registry Numbers

HPNH: 61559-67-9 / FPNH: 127332-96-1 / ClPNH: 14616-35-4 / HOPNH: 54499-95-3 / H₂NPNH: 27629-58-9 / HPNCH₃: 127332-97-2 / HPNSiH₃: 127332-98-3

[1] E. Niecke, M. Nieger, F. Reichert, *Angew. Chem.* **100** (1988) 1781; *Angew. Chem. Int. Ed. Engl.* **37** (1988) 1715.

[2] U. Dressler, E. Niecke, S. Pohl, W. Sachs, W. W. Schoeller, H.-G. Schäfer, *J. Chem. Soc., Chem. Commun.* **1986**, 1086.

[3] O. Altmeyer, E. Niecke, M. Nieger, T. Busch, W. W. Schoeller, D. Stahlke, *Heteroatom Chem.* **1** (1990) 191.

[4] E. Niecke, in *Multiple Bonding in Low Coordinated Phosphorus Chemistry* (O. Scherer, M. Regitz, Eds.), Thieme Verlag, Stuttgart (in preparation).

[5] [5a] S. Huzinaga, *Approximate Atomic Functions, II*, Technical Report, The University of Alberta, Edmonton, Alberta, Canada, 1971. — [5b] R. Ahlrichs, H. J. Böhm, C. Ehrhardt, P. Scharf, H. Schiffer, H. Lischka, M. Schindler, *J. Comput. Chem.* **6** (1985) 200. — [5c] The geometry-search program was written by one of us (T. B.). — [5d] The correlation calculations were carried out with the MOLPRO program system of H. J. Werner and P. J. Knowles: W. Meyer, *J. Chem. Phys.* **58** (1973) 1017; H. J. Werner, P. J. Knowles, *J. Chem. Phys.* **82** (1985) 5053.

[6] See also: R. J. Buenker, P. J. Bruna, S. D. Peyerimhoff, *Isr. J. Chem.* **19** (1980) 309.

[7] For the parent iminophosphane inversion at nitrogen has already been investigated [7a], the results are in agreement with our findings. For a general discussion of *cis/trans* isomerization by inversion or rotation in diimines and diphosphenes see: W. W. Schoeller, in *Multiple Bonding in Low Coordinated Phosphorus Chemistry* (O. Scherer, M. Regitz, Eds.), Thieme Verlag, Stuttgart (in preparation). — [7a] G. Trinquier, *J. Am. Chem. Soc.* **104** (1982) 6969; M. T. Nguyen, M. A. McGlinn, A. F. Hegarty, *J. Am. Chem. Soc.* **107** (1985) 8029.

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