The N–H Link as a 'Probe' for the Electronic Structure of the Phosphorus–Nitrogen Bond in Aminophosphines. An Infrared Spectroscopic Study

By RAYMONDE MATHIS* and FERDINAND MATHIS
(Laboratoire des Hétérocycles du Phosphore et de l'Azote, Université Paul Sabatier, 118, route de Narbonne, 31077 Toulouse Cédex, France)

and NACEUR AYED, ALI EL BORGI, and BEL-GACEM BACCAR
(Department de chimie, Faculté des Sciences de Tunis, Tunisie)

Summary Mechanical anharmonicity and hydrogen bond donor ability of the NH group in 26 aminophosphines X_2P–NHR have been measured; large variations have been observed, which are related to the effect of substituents X on the *s* character of the nitrogen part of the NH bond orbital.

THE spectral properties of a secondary amino group NH linked to three-co-ordinate phosphorus in aminophosphines X_2PNHR provide valuable information on the so-called 'hybridization state' of the nitrogen atom and therefore on the electronic structure of the P–N bond. It has been demonstrated from i.r. spectra that some of these compounds are mixtures of two rotational isomers[1] and there is a correlation between the spectral characteristics of the NH group and the nucleophilicity of the nitrogen atom, a correlation which can be interpreted by a variable bond order of the P–N bond.[2]

The NH bond orbital can be approximated by a normalized hybrid orbital of nitrogen $a(2s\mathrm{N}) + b(2p\mathrm{N})$ $(a^2 + b^2 = 1)$. A large amount of experimental data on compounds in which *a* could be reasonably estimated (from geometrical considerations for instance) leads to the following conclusions: when the *s* character of the nitrogen part of the NH bond orbital (a^2) increases, the anharmonicity of the NH stretching motion $2\Delta\nu_{1-2}$ ($= 2\nu_{0-1} - \nu_{0-2}$; ν_{0-1} and ν_{0-2} are the frequencies of the fundamental and harmonic bands in a non polar solvent) decreases, and the solvent shift between a non-polar solvent (*e.g.* hexane or carbon tetrachloride) and a polar solvent (*e.g.* dioxan, pyridine, *etc.*)

TABLE. Correlation between $2\Delta\nu_{1-2}$, $\nu(\mathrm{CCl_4}) - \nu(\text{dioxan})$, and Taft constants σ^* (X_2) for the aminophosphines X_2PNHR.[a]

X_2	R	$\sigma^*(X_2)$	$2\Delta\nu_{1-2}$	$\nu(\mathrm{CCl_4}) -$ ν(dioxan)
$\mathrm{Bu^t_2}$	$\mathrm{Pr^i}$	−0·6	—	21
$\mathrm{Ph_2}$	$\mathrm{Bu^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^s}$, $\mathrm{Bu^t}$	+1·2	161—170	44—48
$\mathrm{(MeO)_2}$	Me, $\mathrm{Bu^n}$, $\mathrm{Bu^t}$	+3	154—165	66—69
$\mathrm{(EtO)_2}$	$\mathrm{Bu^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$, $\mathrm{C_6H_{11}}$	+3	148—150	67—75
$\mathrm{-OCH_2CH_2O-}$	Me, $\mathrm{Bu^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$	*ca.* +3	149—156	65—70
$\mathrm{-OCH_2CH_2S-}$	Me, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$	—	165—169	71—74
$\mathrm{-OC_6H_4O-}$(*ortho*)	Me, $\mathrm{Bu^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^s}$, $\mathrm{Bu^t}$, $\mathrm{CH_2Ph}$	—	144—153	87—106
$\mathrm{Cl_2}$	$\mathrm{Pr^i}$	+5·9	140	150

[a] For preparation of the compounds see: N. Ayed, Thèse de spécialité, Toulouse, 1974; A. El Borgi, Thèse de spécialité, Tunis, 1976. A Perkin-Elmer 125 spectrometer was used.

becomes greater. *E.g.*, for Et_2NH: $2\Delta\nu_{1-2} = 164\ cm^{-1}$; ν_{0-1} (CCl_4) − ν_{0-1} (dioxan) = $13\ cm^{-1}$; for pyrrole: $2\Delta\nu_{1-2} = 138\ cm^{-1}$; ν_{0-1} (CCl_4) − ν_{0-1} (dioxan) = $139\ cm^{-1}$.

In the present work, we have tried to vary the nature of the substituents X widely enough to ensure a large variation of the multiplicity of the P–N bond and therefore the hybridization state of the nitrogen atom. Our results (Table) suggest that the hybridization state of the nitrogen atom varies widely between X = Bu^t and X = Cl. When the substituents X are electron-releasing, this hybridization state resembles that of amines, in which the valence bonds of the N atom are in a pyramidal configuration; when the substituents X are strongly electron-attracting, such as Cl, this hybridization resembles that of compounds with trigonal nitrogen such as pyrrole. Intermediate situations are observed with alkoxy or aryloxy substituents on P.

The results can be interpreted as follows: electron-attracting substituents lower the energy of phosphorus *d* orbitals, and facilitate the N to P back co-ordination; the *p* character of the nitrogen lone pair orbital is raised, and so is the *s* character of the orbital by which N is linked to hydrogen. There is a significant difference between dioxaphospholan and benzodioxaphospholan derivatives: O to P back co-ordination partially compensates for the electron-attracting effect of oxygen atoms; this back co-ordination should be less (and the whole electron-attracting effect greater) in benzodioxaphospholan derivatives, in which the oxygen lone-pair electrons are presumably partially delocalized over the aromatic system.

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[1] R. Mathis, N. Ayed, Y. Charbonnel, and R. Burgada, *Compt. rend.*, 1973, **277**C, 493.

[2] N. Ayed, R. Mathis, R. Burgada, and F. Mathis, *Compt. rend.*, 1974, **278**C, 1085.