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STUDY OF THE P-N BOND IN PHOSPHORIMIDATES BY ^{15}N AND ^{31}P SPECTROSCOPY

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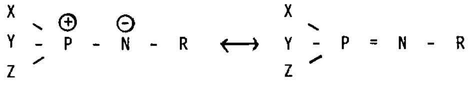
The P-N double bond character in phosphorimidates is discussed in terms of ^{1}JP-N coupling and $\delta^{15}N$ or $\delta^{31}P$ chemical shifts.

Cyclic phosphazene derivatives have been studied by ^{15}N spectroscopy (1) and the ^{15}N spectra of acyclic compounds containing the P-N bond were reviewed recently (2). In phosphorimidates the tetracoordinated phosphorus atom behaves as an electrophilic center and the nitrogen-phosphorus bond is anticipated to have some double bond character. The reactivity of such compounds was studied recently (3) but no direct spectral data concerning the P-N bond are available. We have investigated the ^{15}N and ^{31}P spectra of a series of derivatives corresponding to the formula (I) :



$$\begin{array}{c}X\\Y\\Z\end{array}\!\!>\!\overset{\oplus}{P}-\overset{\ominus}{N}-R \longleftrightarrow \begin{array}{c}X\\Y\\Z\end{array}\!\!>\!P=N-R \qquad (I)$$

(A) (B)

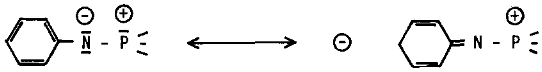
in which X = Y = Z = CH_3O- (Ia, b) or $(CH_3)_2N$- (Ic, d, e)
and X = $(CH_3)_2N$- Y, Z = $CH_2-N(CH_3)$-
$CH_2-N(CH_3)$-
X = CH_3O- Y, Z = $(CH_3)_2C-O$-
$(CH_3)_2C-O$-
and R = C_2H_5, C_6H_5, tosyl

We have shown by a correlation analysis of ^{15}N, ^{31}P and J P-N values determined in amino -P(III) compounds (4) that the steric hindrance of phosphorus substituents and the X-P bond polarizability are important factors which govern the change of NMR parameters. In phosphorimidates I the ^{15}N and ^{31}P chemical shifts and the $^{1}J^{15}N-^{31}P$ coupling constants are affected significantly by the change in hybridization of the P and N atoms induced by the substituents X, Y, Z and R (Table).

The phosphorimidate ^{15}N atom in I is characterized with chemical shift values ranging from -290 to -340 ppm on the CH_3NO_2 scale (2), which are rather unusual for bicoordinated nitrogen. In fact, these values are observed at a lower frequency than for all other Z=N-X molecules (2), excepted for azides, where the α nitrogen atom is strongly shielded.

$$R-\overset{\ominus}{\underline{\bar{N}}}-\bar{N}=\overset{\oplus}{\bar{N}} \longleftrightarrow R-\bar{N}=\overset{\oplus}{N}-\overset{\ominus}{\bar{N}}|$$

Thus phosphorimidates should be represented by a mesomeric equilibrium I(A) ⟷ I(B) displaced towards I(A). When R is an electron-accepting group such as C_6H_5, the extra electronic density of the nitrogen atom is delocalized on the aromatic ring and the ^{15}N chemical shift increases significantly (paramagnetic contribution).

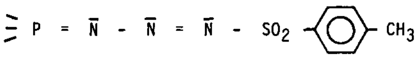


as it appears in the table for compounds 1b, 1d compared to compounds 1a, 1c.

In the same way, the coupling constant ^1J P-N shows drastic changes in the series.The observed values of the ^1J P-N coupling constant are higher for phosphorimidates substituted with N-alkyl groups than they are for O-alkyl derivatives. This behaviour can be compared with the change in ^1J P-N measured in cyclophosphazene $Cl_5P_3N_3$ (NHAr) (Ib) : the cyclic phosphorous atom exhibits a coupling constant ^1J P-N = 31 Hz when substituted with two chlorine atoms whereas ^1J P=N = 5.8 or 18 Hz for a $P(NHAr)_2$ or P(Cl, NHAr) fragment respectively.

This fact can be understood in terms of rehybridization of the nitrogen atom, (and, consequently of the phosphorus atom), passing from a pseudo pyramidal arrangement in I(A) for R = C_2H_5 to a pseudo planar structure in I(B) for R = C_6H_5. It should also be noted that in compounds I c, d, e, f the chemical shift of the tricoordinated nitrogen atom does not change very much whereas the coupling constant ^1J P-N is significantly affected by the change in angular parameters. Given the above considerations, the values of the ^1J P-N coupling constant reported for analogous compounds (6, 7, 8, 9 in ref. 5) are surprising. However a spectrum of Ib recorded at 40.56 MHz gives chemical shift and coupling constant values which are consistent with those measured at 25.18 MHz (δ=-304.7 ppm, ^1J P-N = 11.0 Hz).

We have also studied a triazo derivative IIe which is a precursor of Ie. The nitrogen atom linked to the phosphorus (^1J P-N = 6 Hz) is strongly deshielded compared to the same atoms in the phosphorimidates I



This assignment is in agreement with data concerning toluene-sulfonylazide (6) and phosphorus azides (7).

The phosphorimidates I were prepared from the reaction of P(III) derivatives on azides using the Staudinger reaction (3).

COMPOUND	X	Y	Z	R	N $\delta^{15}N$(a)	N ^1J P-N	P $\delta^{31}P$(b)	X $\delta^{15}N$	X ^1J P-N	Y $\delta^{15}N$	Y ^1J P-N	Z $\delta^{15}N$	Z ^1J P-N
I a	CH_3O	CH_3O	CH_3O	C_2H_5	- 337.9	6.8	- 1.3	-	-	-	-	-	-
I b	CH_3O	CH_3O	CH_3O	C_6H_5	- 306.3	11.4	- 2.6	-	-	-	-	-	-
I c	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	C_2H_5	-336.8_5	29.0_5	21.5	- 360.9	32.7	- 360.0	32.7	- 360.9	32.7
I d	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	C_6H_5	- 293.3	24.5	16.6	- 356.2	24.4	- 356.2	24.4	- 356.2	24.4
I e	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	tosyl	-307.8_5	(c)	25.3	- 357.6	30.2	- 357.6	30.1	- 357.6	30.1
I f	$(CH_3)_2N$	$CH_3-N\backslash$ $(CH_2)_2$	$/N-CH_3$	C_6H_5	- 301.0	11.0	19.6	- 359.3	34.8	- 354.1	15.9	- 354.1	15.9
I g	CH_3O	$O\backslash$ $(C(CH_3)_2)_2$	$/O$	C_6H_5	-300.5_5	4.5	5.3	-	-	-	-	-	-
II e	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	tosyl	- 148.9 - 284.0 (c)	0 ~ 6	36.2	- 357.6	29.8	- 357.6	29.8	- 357.6	29.8

TABLE : ^{15}N and ^{31}P parameters of phosphorimidates (I) $\begin{matrix}X\\Y\\Z\end{matrix}\!>\!P=N-R$ and (II) $\begin{matrix}X\\Y\\Z\end{matrix}\!>\!P-N_3-R$.

The NMR spectra were measured at 25.18 MHz (^{15}N) using a 15 mm OD cell (Pulse width PW = 60 10^{-6} s, acquisition time At = 3.4 s, sweep width SW = 3000 Hz) in the broad band ^1H decoupling mode. 10 to 20% solutions in $CHCl_3$, containing 0.05 M $Cr(acac)_3$ were used.

The ^{31}P spectra were obtained at 36.4 MHz using a 10 mm OD cell (PW = 8 10^{-6}s, At = 1.2 s, SW = 4000 Hz)

(a) in $CHCl_3$ (b) in toluene (c) not observable

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