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¹⁵N NMR Study of the P-N Bonding in Phosphoric Amides

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¹⁵N NMR Study of the P-N Bonding in Phosphoric Amides

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A series of phosphoric amidodiester, diamidoesters and triamides was prepared and their ³¹P and ¹⁵N NMR spectra were recorded in order to evaluate the major structural factors that determine the chemical shifts and coupling constants values. Considering the equation expressing the structural effects on shielding^[1]:

$\Delta\delta_p = c \Delta X + k \Delta n_\pi + A \Delta\theta$, where ΔX is the difference in electronegativity in the P-X bond, Δn_π is the change in π electron overlap, $\Delta\theta$ is the change in σ -bond angle, and c, k, A are constants, our results can be summarized as follows.

(i) Shielding of ³¹P nucleus is not sensitive to the atoms at phosphorus (O or N), but strong *deshielding* is observed upon incorporating P atom into a five-membered ring (changes in $\Delta\theta$ values).

(ii) For cyclic systems, substrates with the *exocyclic* N atom show the *deshielding* effect on the ³¹P relative to their analogues with the *endocyclic* location of the amide nitrogen (changes in Δn_π values).

(iii) The ¹⁵N NMR studies indicate^[2] that for the cyclic (five-membered) amidoesters, the *endocyclic* N atoms are *deshielded* relative to *exocyclic* nitrogens (changes in Δn_π values). This implies lower basicity of the *endocyclic* nitrogens, which is in agreement with our earlier results^[3] on the rates of the acid-catalyzed solvolysis of cyclic and non-cyclic phosphoric amidoesters.

(iv) The ¹J_{NP} values were found to be very sensitive to the $\Delta\theta$ (bond angles) component - for the bridgehead nitrogen of 1-oxo-2,8-diphenyl-2,5,8-triaza-1 λ^3 -phosphabicyclo[3.3.0]octane (N close to the 'pure' p hybridization), the lowest value of ¹J_{NP} (5.7 Hz) ever recorded was obtained.

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