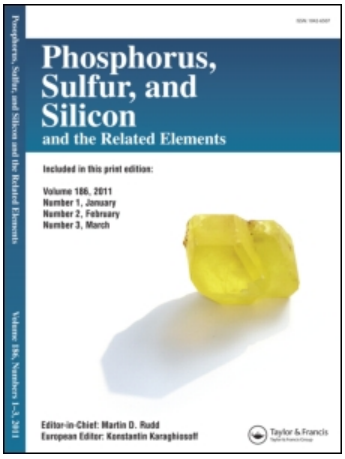

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^{15}N NMR Study of the P-N Bonding in Phosphoric Amides

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A series of phosphoric amidodiesters, diamidoesters and triamides was prepared and their ^{31}P and ^{15} N NMR spectra were recorded in order to evaluate the major structural factors that determine the chemical shifts and coupling contants 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 ^{31}P 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 ^{31}P relative to their analogues with the *endocyclic* location of the amide nitrogen (changes in Δn_π values).

(iii) The ^{15}N 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-1λ^5-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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