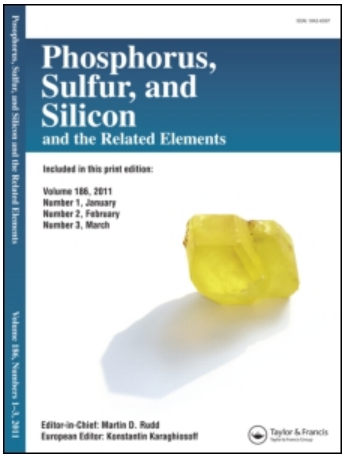

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NMR Spectroscopic and X-Ray Structural Studies of Two Diazadiphosphetidines

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NMR Spectroscopic and X-Ray Structural Studies of Two Diazadiphosphetidines

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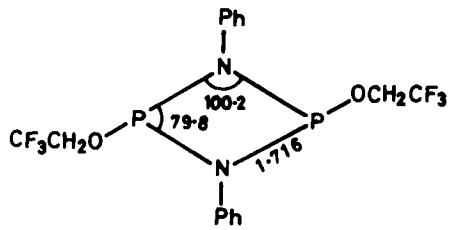
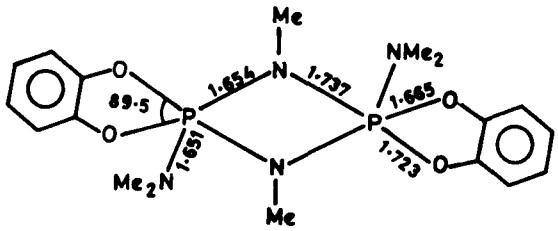
The crystal structures of the two diazadiphosphetidines, $[PhNP(OCH_2CF_3)]_2$ (1) and $[MeNP(NMe_2)(O_2C_6H_4)]_2$ (2) have been determined. The trifluoroethoxy groups in (1) have a trans orientation. The phosphorus chemical shift for (1) is at 189.8 δ. On standing in solution, (1) transforms slowly (~ 10 days) and almost completely into its 'high-field' (cis) isomer (142.2δ).



(1)



(2)

The $-NMe_2$ groups in (2) are trans to each other; the geometry around each phosphorus is slightly distorted trigonal bipyramidal. The ^1H NMR spectrum of (2) shows only one triplet (δ 2.64, J_{PH} = 12 Hz) for the ring 'NMe' protons at ambient temperatures; this signal does not split into two sets of doublets (as would be anticipated owing to coupling with two different phosphorus nuclei) even at −50°C. However, another triplet (δ 2.61, J_{PH} ≈ 12 Hz) with a lower intensity appears for the ring 'NMe' protons after 24 hours at ambient temperature.

Similar results are observed for the alkoxy derivatives, $[RNP(OR')(O_2C_6H_4)]_2$ except that in these cases two sets of signals are observed for NR(R=Me) and OR' protons immediately upon dissolution of the compounds in $CDCl_3$ at ambient temperatures. Possible reasons for this behaviour are discussed.