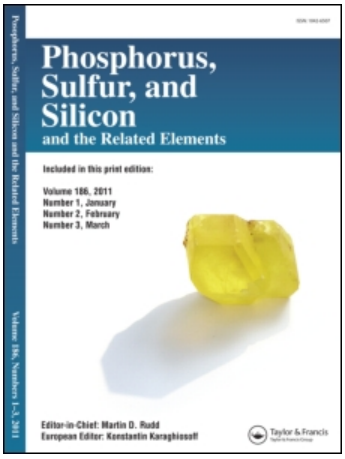

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NMR Studies of the Structures of Cyclic Phosphorus Compounds

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NMR STUDIES OF THE STRUCTURES OF CYCLIC PHOSPHORUS COMPOUNDS

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Abstract [RNPOCl]$_3$ (R = Ph, p-Tol, p-MeOC$_6$H$_4$) has been shown by ^{31}P n.m.r. to consist mainly of the 2α,4α,6β(C_2) isomer (AB_2 spin system), along with small amounts of the symmetric (C_3) isomer (2α,4α,6α). The ^{31}P shifts are almost independent of the nature of the group R. Confirmation of the ring structure requires the determination of J_{BB} which is achieved by second-order analysis of ^{13}C or ^{1}H spectra. Similar techniques have been applied to the phosphorus-oxygen ring system [$PhPO_2$]$_3$. We have discovered a relationship between the orientation of N-phenyl substituents on cyclophosphazane ring systems and the ^{13}C n.m.r. shifts of the ring carbons. In cyclodiphosphazanes the phenyl rings are coplanar with the P-N ring, whereas in cyclotriphosphazanes the phenyl rings are perpendicular to the P-N-P plane; the ^{13}C shifts of the ortho and para carbons are quite different in these two situations, and we have used these shifts to obtain structural information on a number of cyclophosphazanes. Rotation of the ring about the C-N bond has also been studied by low-temperature n.m.r.