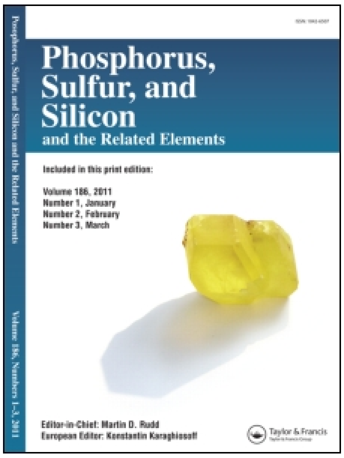

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Substituent Effect on ^{31}P Chemical Shifts and Conformation of some Cyclic Phosphonates

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Substituent Effect on ^{31}P Chemical Shifts and Conformation of some Cyclic Phosphonates

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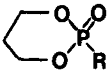
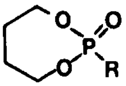
A series of 2-alkyl-2-oxo-1,2,3-dioxaphosphorinane (I) and some 2-alkyl-2-oxo-1,2,3-dioxaphosphepane (II) were synthesized and their NMR, IR as well as MS were reported. The substituent effect on ^{31}P chemical shifts and conformations of these compounds were investigated by the molecular mechanics calculations using Allinger's MM2 program.


I


II

The substituent effect of alkyl groups on the chemical shifts was proved to be governed by the Local Van der Waals interaction(Evdw.l) of phosphorus atom. It is not only for compounds I but also for other alkylphosphates, phosphonates and phosphine oxides. A linear correlation existed between Evdw.l and ^{31}P for each group. The attractive VDW interaction is associated with the shielding effect and the repulsive VDW interaction is related to the deshielding phenomenon.

The MS data indicated that the relative stability of cyclic ring and P-C bond was determined chiefly by the ring size and the structures of alkyl groups.

As demonstrated by ^{31}P NMR and MM calculation the conformation of I is chair form with equatorial alkyl group while compounds II possess twist chair conformation.