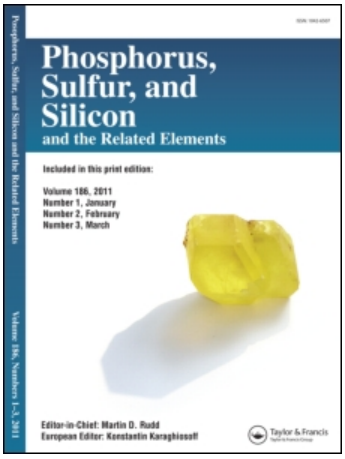

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Solid State Conformation of and the Anomeric Effect in Conformationally Labile and Rigid 2-Thiophosphoryl and 2-Selenophosphoryl Substituted 1,3-Ditianes

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Solid State Conformation of and the Anomeric Effect in Conformationally Labile and Rigid 2-Thiophosphoryl and 2-Selenophosphoryl Substituted 1,3-Ditianes

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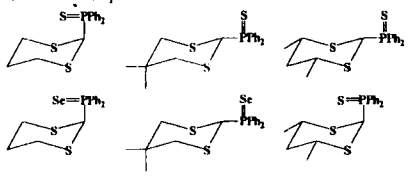
Conformation and geometry of 2-tiophosphoryl and 2-selenophosphoryl 1,3-ditianes is determined by several stereoelectronic and steric efects [1]. The crystal and molecular strustures of the six compouds shown below have been determined by X-ray methods. The differences in the coresponding bond distances and selected structural parameters for all these compounds are discussed in the context of anomeric effect.



The S-C-P anomeric interaction attracted considerable attention recently and their nature is still a matter of debate. Although it is accepted on the basis of accumulated data that n_x-σ^*_{P-C} negative hyperconjugation contributes importantly to the anomeric effect observed in 2-phosphorus substituted 1,3-dithianes [2], their structural parameters, especially the C-S and C-P bond lenghts , are not fully consistent with the operation of this stereoelectronic effect. The C-P bond lenght is generaly longer in the *axial* compounds then in the *equatorial* isomers. In all ditiolane rings the S-C bond distances to anomeric carbon are sligtly shorter then two other ones. Conformation of 4,6-dimetyl substituted compouds is stereochemically determined [3]. The different conformational preferences of tiophosphoryl, and selenophosphoryl group are observed for conformationally labile, unsubstituted and 5,5-dimetyl substituted compounds, and *axial* and *equatorial* conformation of the phosphoryl group is observed, respectively.

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