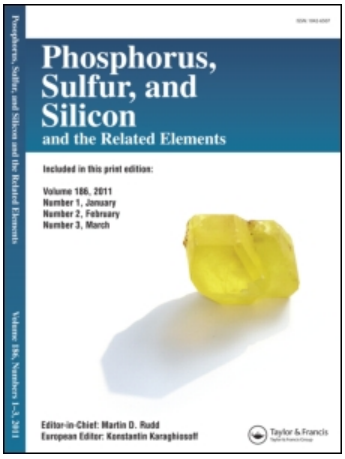

Phosphorus, Sulfur, and Silicon and the Related Elements

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Conformational Studies of a Six-Membered Phostone

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CONFORMATIONAL STUDIES OF A SIX-MEMBERED PHOSTONE

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Although 1,3,2-dioxaphosphorinanes generally assume chair conformations,[1] there are examples in which the ring adopts the boat or twist-boat form.[1] Recent studies on the synthesis, stereochemistry, and reactivity of 2-alkoxy-2-oxo-1,2-oxaphosphorinanes (phostones) have revealed both *cis* and *trans* isomers of 3-(diphenylhydroxymethyl)-2-ethoxy-2-oxo-1,2-oxaphosphorinane[2] to assume a chair conformation in the solid state. In the present work, the conformational properties of *cis* and *trans*-3-methoxycarbonyl-2-methoxy-2-oxo-1,2-oxaphosphorinanes were investigated by X-ray analysis, variable temperature ^{31}P, ^{1}H and $^{1}H\{^{31}P\}$ NMR spectroscopy, molecular mechanics, and semiempirical calculations. The X-ray crystal structure of the *trans* isomer revealed a chair conformation with equatorial phosphoryl and carbomethoxy groups. No changes were observed in the ^{31}P NMR spectra of either isomer in the temperature range of 183-333 K. A complete set of vicinal J_{HH} coupling constants was extracted from the $^{1}H\{^{31}P\}$ spectra of each isomer taken at five temperatures over the range of 213-293 K and refined by simulation of the spectra. The best-fit analysis of this data using a generalized Karplus equation[3] revealed that the conformation of the *trans* isomer in solution was close to that found in the solid state. This conformation corresponded to the global energy minimum calculated by both molecular mechanics and PM3 semiempirical method. A substantial contribution from an inverted chair conformation of the *cis* isomer had to be assumed to achieve a reasonable fit of the coupling constants calculated from the generalized Karplus equation.

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