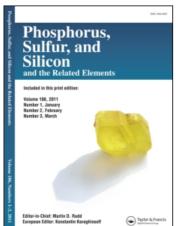
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## Phosphorus, Sulfur, and Silicon and the Related Elements

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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, there are examples in which the ring adopts the boat or twist-boat form. 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<sup>2</sup> 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 <sup>31</sup>P, <sup>1</sup>H and <sup>1</sup>H{<sup>31</sup>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 <sup>31</sup>P NMR spectra of either isomer in the temperature range of 183-333 K. A complete set of vicinal J<sub>HH</sub> coupling constants was extracted from the <sup>1</sup>H{<sup>31</sup>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<sup>3</sup> 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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