between the temperature factor and the occupational parameter, and it was found that a positive value for the temperature factor was obtained in a refinement, where the occupational parameter was held fixed at a value exceeding that given in Table 1 by one standard deviation.

With the fractional occupation of the 4b nickel position as obtained from the refinement, the composition of the crystal is calculated to be $\text{Ni}_4\text{Si}_2\text{B}$. While the phase relationships in the Ni—Si—B system still remain to be clarified in detail, the result of the present structure analysis is taken as a strong indication that the ternary $W_{\text{Si}}\text{Si}_2\text{Si}_2$-type phase in this system exhibits a similar nonstoichiometric behaviour as the corresponding phases in the Co—Si—B and Fe—Si—B systems.

Acknowledgements. The work has been financially supported by the Swedish Natural Science Research Council. One of the authors (A.A.U.) is indebted to The International Seminar in Physics, Uppsala, and the Swedish International Development Authority (SIDA) for financial support.


Received May 20, 1970.

Equilibration of cis and trans 6-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinane

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The conformational energies of substituents on cyclohexane rings have been widely studied, both because of the wide occurrence and importance of this ring system, and also because of the simplicity of the theoretical treatment of the data so obtained. In contrast to the abundance of information in the cyclohexane area, there has been, until very recently, a paucity of data concerned with conformational preferences in heterocyclic systems, with the result that relatively little is known regarding the conformational consequences of introducing one or more heteroatoms into a six-membered ring. This paper reports the conformational equilibria of the cis and trans isomers of 6-methyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane (II). The preparation of the geometric isomers has been reported in a previous paper.

In analogy with cyclohexanes it has been found by X-ray diffraction method, and proton magnetic resonance studies that the 1,3,2-dioxaphosphorinane (I) ring exists in a chair-like structure where the phosphoryl oxygen atom occupies the equatorial position.

Proton magnetic resonance and infrared spectra of cis and trans isomers of 6-methyl-2-oxo-2-alkoxy-1,2-oxaphosphorinanes indicate difference in the configuration around the phosphorus atom. The 6-methyl group is found to occupy the equatorial position in both isomers.

Table 1. Equilibration data for 6-methyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane (cis⇒trans).

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>% cis</th>
<th>Equilibrium constant, K</th>
<th>$\Delta G^\circ$ kcal/mole</th>
<th>$\Delta H^\circ$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.5</td>
<td>36.2</td>
<td>1.76</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>200.0</td>
<td>37.8</td>
<td>1.65</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>218.6</td>
<td>38.4</td>
<td>1.61</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>239.0</td>
<td>39.9</td>
<td>1.51</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>262.0</td>
<td>42.2</td>
<td>1.37</td>
<td>0.33</td>
<td>1.50 ± 0.15</td>
</tr>
<tr>
<td>276.0</td>
<td>43.9</td>
<td>1.28</td>
<td>0.28</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrations of the isomers were carried out in sealed tubes catalysed by trifluoroacetic acid at elevated temperatures. Care was taken to fill the tubes sufficiently so that when they reached the equilibrium temperature, the volume not occupied by liquid, was essentially zero. This avoids the problem of presence of a gas phase in which the equilibrium constant differs from that in the liquid. Equilibrium was usually approached from both sides, and the equilibrium mixture was analysed by gas liquid chromatography. The equilibrations were carried out at six different temperatures over a range of ca. 100°C, and each sample was analyzed several times. From the slope of a plot log K against 1/T, the enthalpy of isomerization was found. The results are summarized in Table 1.

Equilibration of the isomers of I shows that the trans isomer is more stable than the cis isomer. The calculated enthalpy, $\Delta H^\circ$, is very similar to values found for 1,3-disubstituted cyclohexanes. Enthalpies of similar magnitude are reasonable since it is found by X-ray analysis that the length of the P–O bond in the ring of 2-phenoxy-2-oxo-1,3,2-dioxaphosphorinane, and the C–C bond length in cyclo-hexane are very similar, 1.56 and 1.54 Å, respectively. The flattening of the 1,3,2-dioxaphosphorinane ring is found exclusively in the phosphate part, all other angles have values normally occurring in six-membered rings.

Further detailed studies of compound II and other methyl-substituted 1,2-oxaphosphorinanes are in progress in this institute.


Received March 20, 1970.