The Strain in the 1,2-Dithiolane Ring

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The 1,2-dithiolane ring (I) has been an important unit in modern sulphur chemistry since its presence in 6-thioctic acid was discovered. The hypothesis advanced by Calvin and co-workers about the role of 6-thioctic acid in the photosynthesis has caused many efforts to determine the steric strain in the 1,2-dithiolane ring. A necessary condition for Calvin's hypothesis to be true is that the strain is at least 20-25 kcal/mole. The estimates of the steric strain reported in the literature are widely scattered as can be seen from Table 1.

\[ \text{COOH} \]

\[ \begin{array}{c}
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{S} \text{S} \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{array} \]

(I)

\[ \begin{array}{c}
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{S} \text{S} \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{array} \]

(II)

The exact structure of the 1,2-dithiolane ring in 1,2-dithiolane-4-carboxylic acid (II) is now known thanks to an X-ray investigation performed by Professor Olav Foss. On the basis of this investigation, we have calculated the strain energy in a classical manner, i.e. with the assumptions that the strain is composed of three terms: stretching, bending and torsion. This method gives a strain of 16-30

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2. Bongartz, J. Ber. 19 (1886) 2182.

Received February 22, 1958.
Table 1.

<table>
<thead>
<tr>
<th>Strain, kcal/mole</th>
<th>Compound</th>
<th>Reference and method</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>1,2-Dithiolane</td>
<td>Calvin (^2); UV.</td>
</tr>
<tr>
<td>min.</td>
<td>6-Thioctic acid</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1,2-Dithiolane</td>
<td>Calvin (^2); Conformation analysis.</td>
</tr>
<tr>
<td>6</td>
<td>1,2-Dithiolane</td>
<td>Calvin (^2); Equilibrium measurements.</td>
</tr>
<tr>
<td>4—5</td>
<td>6-Thioctic acid</td>
<td>Sunner (^2); Thermochemical measurements.</td>
</tr>
<tr>
<td>min.</td>
<td>1,2-Dithiolane-4-carboxylic acid</td>
<td>This work; Conformation analysis.</td>
</tr>
</tbody>
</table>

Kcal/mole, when uncertainties in structural parameters and assignments of normal valence angles are taken into account. We believe that our smallest value (16 kcal/mole) is too far from the values found in the thermochemical measurements to be explained as due to differences in the structural parameters for 1,2-dithiolane-4-carboxylic acid on the one hand and 6-thioctic acid and the unsubstituted 1,2-dithiolane ring on the other. As far as steric strain is concerned it is therefore our opinion that Calvin’s hypothesis about the rôle of 6-thioctic acid in photosynthesis cannot be disregarded.

A detailed report of our calculations will soon be published in *Arkiv Kemi*.

1. For a review see the article by Reed, L. J. *Advances in Enzymol.* **18** (1957) 319.

Received February 26, 1958.

*Acta Chem. Scand.* **12** (1958) No. 2