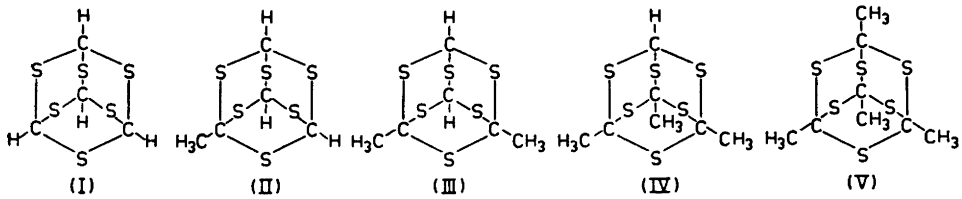

soon starts to form. The mixture is left at room temperature overnight, stirred with 20 ml of conc. hydrochloric acid to dissolve precipitated zinc compounds, and filtered with suction. The precipitate is thoroughly washed with conc. hydrochloric acid, water, methanol and two 25 ml portions of chloroform in that order. The almost colourless product is refluxed for 5 min. with 100 ml of pyridine. The boiling mixture is rapidly filtered through a fluted filter paper. The filtrate is left in the refrigerator overnight. The crystals formed are filtered off, recrystallized from pyridine (95 ml per g of dry substance; a very small amount of insoluble material is removed by rapid filtration of the hot solution) and dried *in vacuo* at 100° for 1 h. Yield about 700 mg of pure dimethyl-hexathia-adamantane (III). (Found: C 26.35; H 2.95; S 70.84. Calc. for $C_6H_8S_6$ (272.5): C 26.44; H 2.96; S 70.60.)

From the chloroform washings, about 200 mg of (IV) is obtained by evaporation to 10 ml, addition of 20 ml of ether, and recrystallization of the precipitate from 5 ml of pyridine. The optimum yield of (IV) (about 600 mg) is obtained, if the amount of formic acid is decreased to 0.35 ml.

From the undissolved residue after the pyridine extraction, about 200 mg of (II) is obtained by recrystallization from 10 ml of dimethyl sulphoxide. The optimum yield of (II) (about 1 g) is obtained, if equal volumes of formic acid and thiol acetic acid are used.

1. Fredga, A. and Olsson, K. *Arkiv Kemi* **9** (1956) 163.
2. Bongartz, J. *Ber.* **19** (1886) 2182.
3. Fredga, A. *Arkiv Kemi, Mineral. Geol.* **25 B** (1947) No. 8.

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The Strain in the 1,2-Dithiolane Ring

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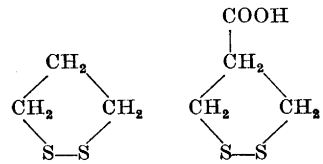
The 1,2-dithiolane ring (I) has been an important unit in modern sulphur chemistry since its presence in 6-thioctic acid was discovered [1]. The hypothesis advanced by Calvin and co-workers [2] about the role of 6-thuoctic acid in the photosynthesis has caused many efforts to determine the steric strain 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.



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 [3]. On the basis of this investigation, we have calculated the strain energy in a classical manner [4], *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

* Both authors contribute equally.

Table 1.

Strain, kcal/mole	Compound	Reference and method
27	1,2-Dithiolane 6-Thioctic acid	Calvin [2]; UV.
min. 11	1,2-Dithiolane	Calvin [2]; Conformation analysis.
6	1,2-Dithiolane	Calvin [2]; Equilibrium measurements.
4—5	1,2-Dithiolane 6-Thioctic acid	Sunner [5]; Thermochemical measurements.
min. 16	1,2-Dithiolane-4-carboxylic acid	This work; Conformation analysis.

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 form 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 pulished in *Arkiv Kemi*.

1. For a review see the article by Reed, L. J. *Advances in Enzymol.* **18** (1957) 319.
2. Calvin, M. and Barltrop, J. A. *J. Am. Chem. Soc.* **74** (1952) 6153; Barltrop, J. A., Hayes, P. M. and Calvin, M. *Ibid.* **76** (1954) 4348.
3. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **11** (1957) 1426 and *Private communication.*
4. Newman, M. S. *Steric Effects in Organic Chemistry.* New York 1956, p. 525 ff.
5. Sunner, S. *Nature* **176** (1955) 217.

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