

was not available to permit satisfactory analysis of the spots but the presence of the following amino acids were clearly indicated: leucine, valine, alanine and glycine. Spots corresponding to glutamic acid and aspartic acid were also obtained.

The behaviour of CMPX on acid hydrolysis, together with the ultraviolet absorption spectra suggests that the amino acids or peptide are attached to the ribose moiety and not directly to the pyrimidine ring. Complexes between purine nucleotides and amino acids have been detected in alkaline digests of ribonucleic acids prepared from calf pancreas, rabbit liver and yeast; and these authors proposed a phosphoamide linkage³. The amount of CMPX was too small for a more detailed study of the linkage between the two parts of the complex; but in view of the present data the possibility of a phosphoamide linkage is not excluded.

The peaks containing 2'- and 3'-cytidylic acid, which had been eluted with 0.02 M formic acid contained several ninhydrin reacting substances, but we have not found any of them attached to a nucleotide. A substance that shows the same elution position and the same properties as CMPX has been detected in the acid extract of the mycelium of a strain of *Penicillium urticae*⁴.

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1. Pontis, H. G. *Biochim. et Biophys. Acta* **25** (1957) 417.
2. Bergkvist, R. *Acta Chem. Scand.* **10** (1956) 1303.
3. Potter, J. L. and Dounce, A. L. *J. Am. Chem. Soc.* **78** (1956) 3078.
4. Persson, K. *Personal communication*.

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On Different Methyl Derivatives of Hexathia-adamantane

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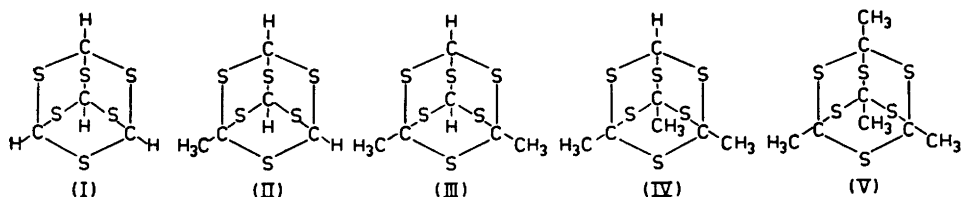
If thiol acetic acid, formic acid and dried zinc chloride are mixed and left at room temperature, a precipitate is gradually formed. This is usually difficultly

soluble in all ordinary solvents and decomposes without melting at approximately 300°. By varying the proportions between the reactants, fractionating the obtained products with the aid of various solvents and recording the infra red spectra of the fractions, five different colourless crystalline compounds were isolated. Two of these were recognized as known compounds, *viz.* hexathia-adamantane (I), recently prepared from formic acid and hydrogen sulphide in strongly acidic media by Fredga and Olsson¹ and its tetramethyl derivative (V), prepared long ago by Bongartz² through the action of dried zinc chloride on thiol acetic acid alone. The structure (V) accepted nowadays was proposed much later by Fredga³.

The analysis and infra red spectra of the remaining three compounds showed these to be mono-, di- and tri-methyl-hexathia-adamantane ((II), (III) and (IV), respectively). The structures (II)–(IV) agree completely with the fact that the properties of the corresponding compounds are intermediate between those of (I) and (V) and vary in a regular manner in the series. Thus the solubility increases rapidly when passing from (I) to (V), but only (IV) and (V) are appreciably soluble in ordinary solvents. The volatility increases in the same direction. All of the compounds can be sublimed *in vacuo*, though (I) requires heating for hours at 225° and 10⁻³ mm Hg. Only (V) melts without decomposition (at 224–225°)², whereas (I)–(IV) decompose without melting at higher temperature. Unsymmetrically substituted hexathia-adamantanes like (II)–(IV) have not been prepared before.

As is to be expected the reaction product gets richer in the highly methylated hexathia-adamantanes with increasing excess of thiol acetic acid and *vice versa*. Since certain details of the procedures for the preparation of (II) and (IV) have not been worked out as yet, only the preparation of (III) will be more closely described here. A more detailed account of this investigation, possibly extended to some more thiol acids, will soon be given elsewhere.

Experimental. 3.2 g of dried zinc chloride is added to a mixture of 6.9 g (6.4 ml) of freshly distilled thiol acetic acid (b.p. 91–96°) and 0.98 g (0.80 ml) of absolute formic acid in a hood. In the beginning, the zinc chloride slowly dissolves, hydrogen sulphide is evolved, and gentle heat is generated. A precipitate



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.

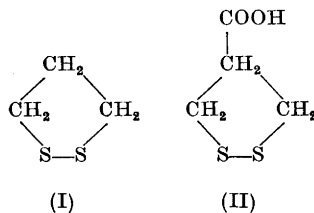
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The Strain in the 1,2-Dithiolane Ring

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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 discovered¹. The hypothesis advanced by Calvin and co-workers² 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 Foss³. On the basis of this investigation, we have calculated the strain energy in a classical manner⁴, *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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