fibrinogen might be less favourable for this reaction. It should also be pointed out that a change from isoleucine to leucine at position 8 (compare rabbit and dog with the other species) might also effect the reaction in question.

The present preliminary investigation does not give any information on other possible functional areas in the fibrinogen molecule beyond the arginyl-glycine bond split by thrombin.

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Structure of Thiuret Hydrochloride Hemihydrate

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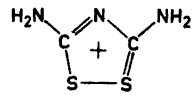
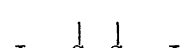
The unsaturated five-membered disulphide ring of the thiuret ion (I) possesses a sextet of π-electrons and is pseudo-aromatic. However, the sulphur-sulphur



(I)

bond length 2.088 ± 0.012 Å, reported by Foss and Tjomsland [1] from a crystal structure analysis of thiuret hydroiodide, indicates that the ring conjugation does not extend over the sulphur-sulphur bond. Support for this idea derives from a structure investigation of 3,5-diamino-1,2-dithiolium iodide.[2] For this compound, which is isomorphous with and analogous to thiuret hydroiodide, a sulphur-sulphur bond length of 2.08 ± 0.02 Å has been found.[2] Molecular orbital calculations [3] show that for the sulphur-sulphur bond in the unsubstituted, 1,2-dithiolium ion a bond length of about 2.00 Å should be expected; this agrees with the found sulphur-sulphur bond in some phenyl-substituted 1,2-dithiolium salts.[4,5] A reason why the sulphur-sulphur bond is longer in thiuret hydroiodide and 3,5-diamino-1,2-dithiolium iodide than in the unsubstituted 1,2-dithiolium ion, may be the effect of the amino groups on the ring conjugation.[2] Attention should, however, also be paid to the environment of the disulphide group. There are in thiuret hydroiodide, and consequently also in the isomorphous 3,5-diamino-1,2-dithiolium iodide, close contacts between the iodide ion and the sulphur atoms. Those of the close contacts which occur in the approximately linear arrangement



may influence the length of the sulphur-sulphur bond, through a transfer of charge from the iodide ions to those p-orbitals on the sulphur atoms which are already engaged in the sulphur-sulphur σ-bond.[4] One may expect the strength of this partial bonding to decrease with increasing electronegativity of the halogen ion, and whether the partial bonding between iodine and sulphur affects the sulphur-sulphur bond in thiuret hydroiodide might therefore be found through structure investigations of thiuret hydrobromide and hydrochloride. Preliminary results of a complete crystal structure determination of thiuret hydrochloride hemihydrate are given here.

The crystals are monoclinic,[6] $a = 19.53$ Å, $b = 5.47$ Å, $c = 14.31$ Å, $\beta = 114\frac{1}{2}°$. Eight formula units per unit cell; space group $C2/c$. The experimental error is estimated to be within 0.2 %.

The structure was solved in the b-axis projection using the same systematic application of Sayre's equation as for xanthan hydride.[7] Three possible sets of signs were derived in this way, and the molecule was recognised in one of the corresponding Fourier maps. This map is shown in Fig. 1, and the position of the

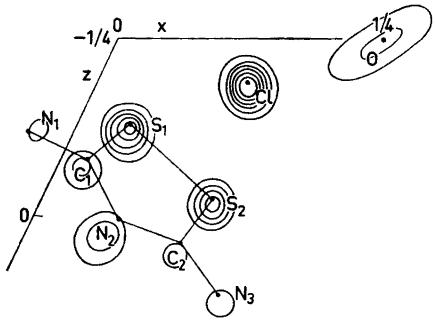


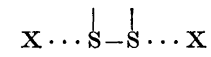
Fig. 1. Electron density projection of thiuret hydrochloride hemihydrate along the b-axis showing one asymmetric unit. Contours at arbitrary but equal intervals.

thiuret ion after finished three-dimensional least squares refinement based on 852 observed reflections is indicated on the map. The final coordinates, without correction for rigid body motion of the thiuret ion, are given in Table 1.

Table 1. Atomic coordinates, in fractions of corresponding cell edges.

	x	y	z
Cl	0.1393	0.9916	−0.1872
S_1	0.0478	0.4327	−0.1280
S_2	0.1590	0.4334	−0.0238
N_1	−0.0423	0.7784	−0.1136
N_2	0.0803	0.8037	0.0077
N_3	0.2074	0.7895	0.1121
C_1	0.0268	0.6955	−0.0736
C_2	0.1484	0.6983	0.0383
O	0.2500	0.3013	−0.2500
H_1	0.044	0.914	−0.093
H_2	−0.073	0.720	−0.178
H_3	0.203	0.892	0.147
H_4	0.253	0.729	0.133
H_5	0.280	0.213	−0.250

The sulphur-sulphur bond length in thiuret hydrochloride is, according to the coordinates in Table 1, 2.063 ± 0.004 Å, and the ring of the ions is planar within experimental error. The close contacts



between halogen and sulphur, which are present in thiuret hydroiodide [1] and hydrobromide,[8] are in thiuret hydrochloride 3.864 ± 0.004 Å and 3.527 ± 0.004 Å and thus reduced to merely van der Waals contacts. The found sulphur-sulphur bond length seems to indicate that there is a weak conjugation across the sulphur-sulphur bond in the thiuret ion and also indicates that if the iodide-sulphur close contacts in thiuret hydroiodide and 3,5-diamino-1,2-dithiolium iodide affects the sulphur-sulphur bond, it does so only to a very small degree.

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