

Table 5. Intermolecular distances

(i) Hydrogen-bond distances			
O(7) <sub>w</sub> ...O(2)	(-x, ½+y, ½-z)		2.995 Å
O(7) <sub>w</sub> ...O(2)	(1+x, y, z)		2.803
O(7) <sub>w</sub> ...O(8) <sub>w</sub>	(x, y, z)		2.688
O(8) <sub>w</sub> ...O(2)	(-x, -½+y, ½-z)		2.713
O(9) <sub>w</sub> ...O(1)	(-x, ½+y, ½-z)		2.830
O(9) <sub>w</sub> ...O(4)	(x, -1+y, z)		2.746
O(3)...O(5)	(-x, 1-y, -z)		2.662
O(6)...O(5)	(x, -1+y, z)		2.665
(ii) Other important non-bonded distances			
O(1)...O(8) <sub>w</sub>	(-x, ½+y, ½-z)		3.404 Å
O(1)...O(9) <sub>w</sub>	(x, 1+y, z)		3.353
O(4)...O(5)	(x, 1+y, z)		3.505
O(5)...C(5)	(x, 1+y, z)		3.410
O(5)...C(6)	(-x, 1-y, -z)		3.396
O(6)...C(6)	(x, -1+y, z)		3.457
O(7) <sub>w</sub> ...C(2)	(1+x, 1+y, ½-z)		3.358
O(8) <sub>w</sub> ...C(3)	(-x, ½+y, ½-z)		3.364
C(6)...C(6)	(-x, 1-y, -z)		3.308

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## Crystal and Molecular Structure of L-Cystine Dimethyl Ester Dihydrochloride Monohydrate\*

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$C_8H_{16}N_2O_4S_2 \cdot 2HCl \cdot H_2O$  is monoclinic, space group  $P2_1$ , with  $a=14.80$ ,  $b=9.34$ ,  $c=5.85$  Å,  $\beta=91.47^\circ$ ,  $Z=2$ . The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations to a final  $R$  of 0.103 for 1620 observed reflexions. The structure is stabilized by an extensive network of hydrogen bonds. The disulphide dihedral angle is  $84.4^\circ$ . The helical sense of the cystinyl group in the molecule is 'left'.

### Introduction

Cystine and its derivatives form an interesting series of compounds in relation to protein structures. The disulphide bridge constitutes one of the important means by which the polypeptide chains of proteins are held together, and plays an important role in deciding their configuration. Hence a study of the conformation of the cystinyl group under a wide variety of conditions is helpful in the study of protein structures. The ester derivatives of amino acids are also of biochemical importance and undergo enzymatic hydrolysis, one of the most fundamental metabolic transformations.

### Experimental

The compound was crystallized by slow evaporation of its solution in water-ethanol mixture. Only one suitable crystal was obtained and this was cut to obtain

two very small single crystals. Preliminary photographs showed that the crystal is monoclinic. The only systematic absences were  $0k0$ ,  $k$  odd. The space group was uniquely determined to be  $P2_1$ , since it is an L compound. The cell dimensions were measured from precession photographs.

### Crystal data

$C_8H_{16}O_4N_2S_2 \cdot 2HCl \cdot H_2O$ , monoclinic,  $a=14.80$  (1),  $b=9.34$  (1),  $c=5.85$  (1) Å,  $\beta=91.47$  (0.2)°; space group  $P2_1$ ;  $0k0$ ,  $k=2n+1$  absent.  $Z=2$ ,  $M=359.3$ ,  $D_o=1.46$ ,  $D_c=1.475$  g cm<sup>-3</sup>,  $\mu=59.9$  cm<sup>-1</sup>,  $\lambda$  (for Cu  $K\alpha$  radiation)=1.5418 Å.

Intensities were collected photographically by the multiple-film equi-inclination Weissenberg technique with Ni-filtered Cu  $K\alpha$  radiation. Intensities of 1620 independent reflexions ( $hkl$ ,  $l=0-4$  and  $hkl$ ,  $k=0-2$ ) were estimated visually and corrected for Lorentz, polarization and spot-shape factors (Phillips, 1954). The data about the two axes were brought to a single scale (Rollett & Sparks, 1960). An overall temperature factor of 2.8 Å was obtained from a Wilson plot.

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### Determination and refinement of the structure

The two S atoms were located from a sharpened Patterson map. Though there were other peaks of reasonable heights, there were no satisfactory cross-vectors and hence the positions of the two Cl atoms were determined from a sulphur-phased Fourier synthesis. Since the origin along  $y$  in the space group  $P2_1$  is arbitrary, the  $y$  coordinate of S(1) was fixed at 0.25. The remaining 15 atoms were located from a Fourier map.  $R$  after including all the atoms was 0.27.

Initial refinement of the structure was carried out on the CDC-3600 computer at Bombay by full-matrix least-squares calculations with the program written by Gantzel, Sparks & Trueblood (1961). The quantity minimized was  $\sum w(|F_o| - k|F_c|)^2$ . Refinement with isotropic temperature factors and a weighting function of the type  $w = [5.0 + |F_o| + 0.036|F_o|^2]^{-1}$  (Cruickshank, Bujosa, Lovell & Truter, 1961) resulted in an  $R$  of 0.14. A difference map computed at this stage revealed all the hydrogens, except one of the water molecule, at the expected positions, their peak heights ranging from 0.11 to 0.76  $e \text{ \AA}^{-3}$ . These were included in further refinement with isotropic temperature factors of the atoms to which they are bonded. Their positions were not refined.

Further refinement was carried out on the IBM-360 and IBM-1130 computers by the block-diagonal method with the program written by Shiono (1968). Anomalous dispersion corrections were applied: the values of  $\Delta f'$  and  $\Delta f''$  used were 0.348 and 0.702 for  $\text{Cl}^-$  and 0.319 and 0.557 for S (Cromer & Liberman, 1970). Refinement with anisotropic thermal parameters for all the non-hydrogen atoms resulted in an  $R$  of 0.103. During these cycles, the  $y$  coordinates of S(1) and Cl(1) were clamped. It is found that in  $P2_1$ ,

clamping the  $y$  coordinates of more than one atom helps in the refinement (Karle & Karle, 1968). However, after convergence in the last cycle the  $y$  coordinate of Cl(1) was allowed to float keeping that of S(1) clamped. The shift in the  $y$  coordinate of Cl(1) was within the standard deviation. The shifts in the parameters in the last cycle were in the range of one-fifth to one-tenth of the estimated standard deviations. The final positional and thermal parameters of the non-hydrogen atoms are listed in Table 1 and those for hydrogen atoms in Table 2. Table 3 gives the observed and calculated structure factors.

Scattering factors used for S,  $\text{Cl}^-$ , N, O, C and H are those listed in *International Tables for X-ray Crystallography* (1962).

Table 2. *Positional and thermal parameters of the hydrogen atoms*

Atom	Bonded to	$x$	$y$	$z$	$B (\text{\AA}^2)$
H(1)	C(1)	0.236	0.122	0.100	3.21
H(2)	C(1)	0.150	0.006	0.167	3.21
H(3)	C(2)	0.131	0.208	0.800	2.73
H(4)	C(5)	0.319	0.306	0.317	2.55
H(5)	C(5)	0.342	0.483	0.236	2.55
H(6)	C(6)	0.250	0.400	0.650	2.61
H(7)	N(1)	0.003	0.083	-0.042	2.98
H(8)	N(1)	0.021	0.022	-0.306	2.98
H(9)	N(1)	0.042	-0.061	-0.083	2.98
H(10)	N(2)	0.178	0.611	0.506	2.77
H(11)	N(2)	0.242	0.647	0.728	2.77
H(12)	N(2)	0.275	0.683	0.478	2.77
H(13)	C(4)	0.672	0.472	0.611	4.02
H(14)	C(4)	0.411	0.050	0.561	4.02
H(15)	C(4)	0.631	0.394	0.361	4.02
H(16)	C(8)	0.503	0.433	0.967	7.70
H(17)	C(8)	0.489	0.250	0.950	7.70
H(18)	C(8)	0.533	0.350	0.717	7.70
H(19)	O <sub>w</sub>	0.858	0.250	0.824	3.70

Table 1. *Positional and thermal parameters of the non-hydrogen atoms with estimated standard deviations in parentheses*

All values are multiplied by  $10^4$ . The temperature factor is of the form  $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ .

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cl(1)	7141 (2)	2525 (6)	9345 (5)	34 (2)	114 (5)	218 (11)	9 (3)	8 (3)	-7 (7)
Cl(2)	9520 (2)	56 (2)	3550 (5)	29 (2)	146 (6)	211 (12)	2 (3)	14 (3)	20 (8)
S(1)	1251 (2)	2500	2616 (5)	32 (2)	85 (4)	172 (10)	-4 (2)	13 (3)	-5 (6)
S(2)	1949 (2)	4231 (4)	1452 (5)	32 (2)	82 (4)	184 (11)	-0 (2)	10 (3)	-4 (6)
C(1)	1735 (9)	1106 (17)	895 (23)	36 (8)	106 (24)	215 (55)	-1 (11)	20 (17)	-31 (30)
C(2)	1367 (8)	1021 (16)	-1492 (23)	25 (7)	103 (22)	225 (53)	-13 (11)	8 (14)	-20 (29)
C(3)	1957 (8)	168 (14)	-3030 (21)	34 (7)	61 (18)	176 (44)	-1 (9)	25 (13)	-6 (23)
C(4)	3458 (11)	-32 (22)	-4321 (26)	44 (9)	171 (35)	248 (59)	15 (16)	24 (19)	-42 (41)
C(5)	2986 (7)	4184 (16)	3154 (21)	19 (6)	90 (20)	221 (49)	-7 (10)	14 (13)	11 (28)
C(6)	2882 (8)	4742 (15)	5588 (21)	21 (6)	97 (21)	188 (45)	9 (9)	13 (13)	-15 (26)
C(7)	3829 (9)	4802 (17)	6757 (24)	31 (7)	119 (26)	243 (54)	3 (12)	24 (16)	-44 (33)
C(8)	4971 (20)	3490 (42)	8716 (47)	59 (16)	376 (93)	565 (132)	-27 (33)	-12 (37)	166 (100)
N(1)	449 (7)	351 (14)	-1577 (19)	26 (6)	122 (21)	195 (43)	1 (9)	13 (12)	-16 (26)
N(2)	2448 (7)	6174 (13)	5679 (18)	27 (6)	101 (19)	167 (41)	5 (9)	22 (12)	-13 (23)
O(1)	2784 (6)	742 (12)	-3058 (18)	31 (6)	115 (19)	316 (48)	-6 (8)	34 (13)	-18 (25)
O(2)	1758 (6)	-913 (13)	-4080 (16)	43 (6)	98 (17)	252 (40)	16 (9)	14 (12)	-50 (22)
O(3)	4306 (9)	5868 (18)	6471 (25)	37 (7)	216 (34)	458 (65)	1 (13)	-19 (18)	63 (42)
O(4)	4017 (9)	3628 (19)	7837 (24)	38 (7)	192 (31)	513 (73)	-7 (13)	1 (18)	32 (41)
O <sub>w</sub>	9265 (8)	2758 (14)	8862 (22)	46 (8)	108 (21)	617 (76)	4 (11)	-4 (19)	-4 (36)

**Description of the structure**

*(a) Crystal packing and hydrogen bonding*

The packing of the molecules viewed down *c* is shown in Fig. 1. There is an extensive network of hydrogen bonds. All eight available protons are involved in intermolecular hydrogen bonding. The hydrogen-bond distances and angles are given in Table 4. Each amino nitrogen acts as a donor for three hydrogen bonds. As observed in many amino acids and peptide structures, the amino nitrogen N(1) has a fourth neighbour, O<sub>w</sub>, at 2.866 Å. An examination of the distances and angles involving N(1), H(7), Cl(2)

and O<sub>w</sub> (Table 4, Fig. 2) shows that Cl(2) and O<sub>w</sub> form a bifurcated hydrogen bond with N(1). Such bonds are found to occur, for example in α-glycine (Albrecht & Corey, 1939; Marsh, 1958; Donohue, 1967) and in L-citrulline hydrochloride (Naganathan & Venkatesan, 1971). In view of the large positional errors associated with hydrogen atoms the hydrogen-bond lengths and angles were calculated with the hydrogen atoms of the NH<sub>3</sub><sup>+</sup> group fixed from geometrical considerations and these are given in parentheses in Table 4.

The water molecule donates both its protons, forming hydrogen bonds with Cl(1) and Cl(2). The

Table 3. *Observed and calculated structure factors*

h	k	l	F <sub>o</sub>	F <sub>c</sub>
0	0	0	1000	1000
1	0	0	1000	1000
2	0	0	1000	1000
3	0	0	1000	1000
4	0	0	1000	1000
5	0	0	1000	1000
6	0	0	1000	1000
7	0	0	1000	1000
8	0	0	1000	1000
9	0	0	1000	1000
10	0	0	1000	1000
11	0	0	1000	1000
12	0	0	1000	1000
13	0	0	1000	1000
14	0	0	1000	1000
15	0	0	1000	1000
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22	0	0	1000	1000
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25	0	0	1000	1000
26	0	0	1000	1000
27	0	0	1000	1000
28	0	0	1000	1000
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30	0	0	1000	1000
31	0	0	1000	1000
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35	0	0	1000	1000
36	0	0	1000	1000
37	0	0	1000	1000
38	0	0	1000	1000
39	0	0	1000	1000
40	0	0	1000	1000
41	0	0	1000	1000
42	0	0	1000	1000
43	0	0	1000	1000
44	0	0	1000	1000
45	0	0	1000	1000
46	0	0	1000	1000
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78	0	0	1000	1000
79	0	0	1000	1000
80	0	0	1000	1000
81	0	0	1000	1000
82	0	0	1000	1000
83	0	0	1000	1000
84	0	0	1000	1000
85	0	0	1000	1000
86	0	0	1000	1000
87	0	0	1000	1000
88	0	0	1000	1000
89	0	0	1000	1000
90	0	0	1000	1000
91	0	0	1000	1000
92	0	0	1000	1000
93	0	0	1000	1000
94	0	0	1000	1000
95	0	0	1000	1000
96	0	0	1000	1000
97	0	0	1000	1000
98	0	0	1000	1000
99	0	0	1000	1000
100	0	0	1000	1000

water oxygen is also the acceptor for two hydrogen bonds with N(1), one of them being a bifurcated hydrogen bond with Cl(2). Cl(1) accepts three hydrogen bonds while Cl(2) accepts four. The cations are linked through the Cl atoms and the water molecule into a continuous spiral parallel to **b**. The spirals are held together only by van der Waals forces.

(b) *Bond distances and angles*

The bond lengths and angles are shown in Fig. 3. The average standard deviations in S-C distances are 0.013 Å, while those of the distances and angles involving C, N and O are 0.017 Å and 1.3°.

The S-S length is 2.045 (4) Å. As in other compounds with disulphide bridges, the central part of the mole-

cule C(1)-S(1)-S(2)-C(5) adopts a skewed non-planar configuration. The angle between the planes containing C(1), S(1), S(2) and S(1), S(2), C(5) is 84.4°. The bond angles C(1)-S(1)-S(2) and S(1)-S(2)-C(5) are 100.0 and 103.1° respectively. A value of about 103° has been observed in other cystine compounds: *N,N'*-diglycyl-L-cystine dihydrate (Yakel & Hughes, 1954), L-cystine dihydrochloride (Steinrauf, Peterson & Jensen, 1958), L-cystine dihydrobromide (Peterson, Steinrauf & Jensen, 1960), L-cystinediamide dihydrochloride (Chaney & Steinrauf, 1968) and tetragonal L-cystine (Chaney & Steinrauf, 1974). But the value (114°) observed in the case of hexagonal L-cystine (Oughton & Harrison, 1959) differs from these.

The C-O lengths of 1.292 and 1.337 Å in the carboxyl

Table 4. *Hydrogen-bond lengths (Å) and angles (°)*

Symmetry code							
i	$x-1$	$y$	$z$	vii	$2-x$	$y+\frac{1}{2}$	$1-z$
ii	$x-1$	$y$	$z-1$	viii	$1+x$	$y$	$z$
iii	$1-x$	$y-\frac{1}{2}$	$1-z$	ix	$x$	$y$	$1+z$
iv	$1-x$	$y+\frac{1}{2}$	$1-z$	x	$1+x$	$y$	$1+z$
v	$1-x$	$y+\frac{1}{2}$	$2-z$	xi	$1-x$	$y-\frac{1}{2}$	$2-z$
vi	$x$	$y+1$	$z+1$				

Donor	Acceptor	$D\cdots A$	$H\cdots A$	$D-H\cdots A$	$C-D\cdots A$	$H-D\cdots A$
C(2)-N(1)-H(7)	Cl(2 <sup>i</sup> )	3.342	2.56 (2.70)	131.7 (122.6)	113.5	34.9 (42.9)
C(2)-N(1)-H(7)	O <sub>w</sub> <sup>ii</sup>	2.866	2.16 (2.07)	123.7 (135.0)	103.0	38.8 (30.8)
C(2)-N(1)-H(8)	Cl(2 <sup>iii</sup> )	3.145	2.21 (2.16)	174.1 (171.5)	116.3	4.1 (5.8)
C(2)-N(1)-H(9)	O <sub>w</sub> <sup>iii</sup>	2.921	1.96 (1.94)	160.2 (161.1)	102.1	13.1 (12.5)
C(6)-N(2)-H(10)	Cl(2 <sup>iv</sup> )	3.140	2.33	133.2	96.3	32.7
C(6)-N(2)-H(11)	Cl(1 <sup>v</sup> )	3.216	2.29	158.1	108.3	15.4
C(6)-N(2)-H(12)	Cl(1 <sup>iv</sup> )	3.269	2.51	139.3	103.0	30.0
O <sub>w</sub> -H(19)	Cl(1)	3.171	2.25	141.4		26.2
O <sub>w</sub>	Cl(2 <sup>vii</sup> )	3.156				

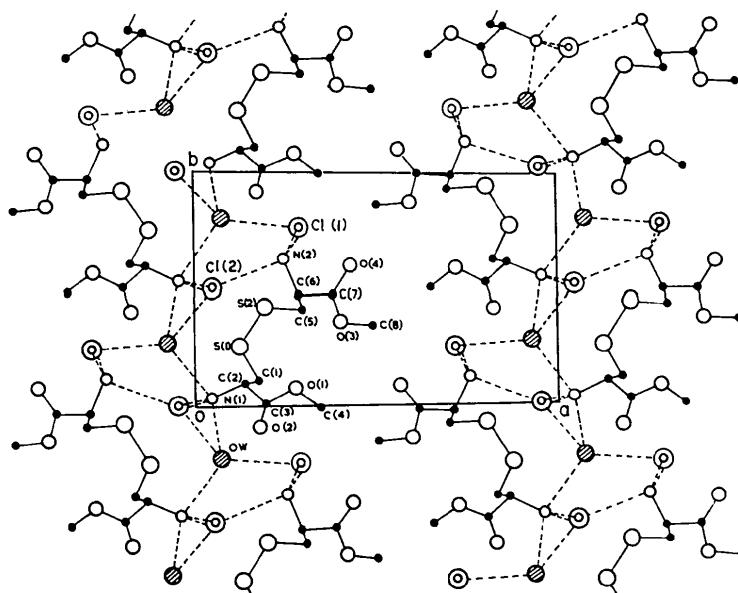


Fig. 1. Packing of the molecules viewed down the *c* axis.

moieties in the ester groups indicate considerable double-bond character, which is a common feature in all carboxylic esters. A comparative study of the di-

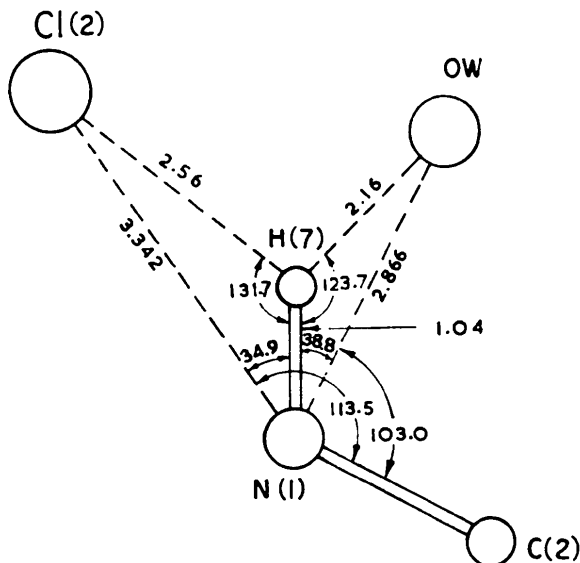


Fig. 2. Surroundings of amino nitrogen N(1) in the structure.

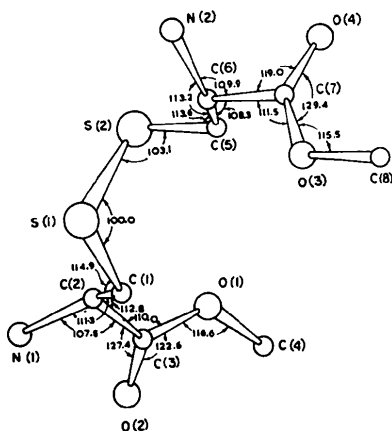
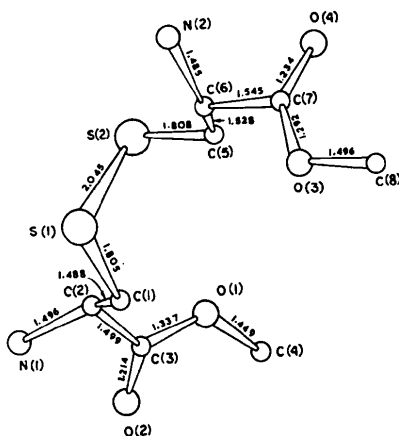


Fig. 3. Bond lengths and angles in the molecule.

mensions of the ester group in various compounds has recently been made by Kroon & Kanters (1973), and reflects a sharper distinction between single and double bonds of the carboxyl group moiety in the ester compared with free acids in general. While the two distances C(3)-O(1) (1.337) and C(3)-O(2) (1.214 Å) corroborate this finding, the other pair C(7)-O(3) (1.292) and C(7)-O(4) (1.234 Å) are closer to each other. The average C-O and C=O distances in carboxylic acids are 1.31 and 1.23 Å (Kanters, Kroon, Peerdeman & Schoone, 1967). The other bond lengths in the side chain agree well with the average values found in amino acids (Marsh & Donohue, 1967).

Table 5. Intermolecular non-bonded contacts (Å) less than 3.5 Å

Cl(1)····S(2 <sup>III</sup> )	3.395
Cl(1)····C(5 <sup>III</sup> )	3.449
Cl(2)····S(1 <sup>III</sup> )	3.488
C(1)····O <sup>III</sup>	3.464
Cl(1)····O(2 <sup>IV</sup> )	3.497
O(2 <sup>V</sup> )····O <sup>IV</sup>	3.382
Cl(2)····S(1 <sup>VIII</sup> )	3.485
S(1)····C(3 <sup>IX</sup> )	3.492
C(1)····O(2 <sup>IX</sup> )	3.492
O(4)····O(1 <sup>IX</sup> )	3.289

Intermolecular distances less than 3.5 Å are listed in Table 5. An interesting feature is the close van der Waals contacts between each S and its non-bonded neighbours. There are four such contacts Cl(2)-S(1) = 3.485, S(1)-C(3) = 3.492, Cl(1)-S(2) = 3.395 and Cl(2)-S(1) = 3.488 Å. Assuming Pauling's (1960) values (S 1.85, C 1.70, Cl 1.80 Å), these distances are all shorter than the sum of the van der Waals radii. This supports the suggestion made by Donohue (1950) that the van der Waals radius for S should be about 1.65, which is 0.2 Å less than Pauling's value.

The equations to the two carboxylate planes and the deviations of the atoms from these planes are given in Table 6. The amino nitrogen N(2) is very significantly deviated (0.834 Å) from the plane through the atoms C(6), C(7), O(3) and O(4).

### (c) Conformation of the molecule

The conformation of the amino acid is described by a sequence of partial conformations starting from the C-terminal towards the disulphide bridge. The notation followed is that of Edsall *et al.* (1966). The torsion angle N(1)-C(2)-C(3)-O(2) is small (-3.4°) as found in other amino acids (Marsh & Donohue, 1967), while the other angle, N(2)-C(6)-C(7)-O(4), is significantly larger (-39.3°). The side-group conformation is described by a set of dihedral angles which are close to 60, 180 and 300° (positions I, II & III, Lakshminarayanan, Sasisekharan & Ramachandran, 1967). The S<sup>γ</sup> atom occupies position III with  $\chi' \approx 300^\circ$ , while in all other cystine structures it occurs in position I with  $\chi' \approx 60^\circ$ . The torsional angles  $\chi^2$  [S(2)-S(1)-C(1)-C(2) and S(1)-S(2)-C(5)-C(6)] are 280.8 (-79.2°) and

Table 6. *Least-squares planes*

Equation of the plane  $Ax + BY + CZ = D$  with respect to the crystallographic axes  $a$ ,  $b$  and  $c^*$  where  $X$ ,  $Y$ ,  $Z$  and  $D$  are in Å.

Plane	Atom	Deviation (Å)	Equation of the plane
Plane I			
Carboxyl group C(2), C(3), O(1), O(2)	C(2)	-0.003	$-0.2680X + 0.5636Y$
	C(3)	0.010	$-0.7814Z = 0.6744$
	O(1)	-0.003	
	O(2)	-0.004	
	N(1)*	0.047	
	C(4)*	-0.106	
Plane II			
Carboxyl group C(6), C(7), O(3), O(4)	C(6)	-0.006	$-0.4045X + 0.4005Y$
	C(7)	0.019	$+0.8222Z = 2.7747$
	O(3)	-0.007	
	O(4)	-0.007	
	N(2)*	0.834	
		C(8)*	-0.202

\* Excluded from the least-squares calculations.

282.6 ( $-77.4^\circ$ ). The configuration of the cystinyl group is given by the angle  $\chi^3$  [C(1)-S(1)-S(2)-C(5)], equal to  $-84.4^\circ$ , which indicates that the helical sense of the disulphide group in the molecule is 'left'. A similar configuration has been observed in other cystine derivatives, while the hexagonal and tetragonal modifications of cystine in pure form have the opposite helical sense with dihedral angles of  $+73.8^\circ$  and  $+69.3^\circ$  respectively. The occurrence of a twist of either sense has been observed in lysozyme (Blake, Johnson, Mair, North, Phillips & Sarma, 1967).

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