

Fig. 3. The O...O hydrogen-bonded distance is rather short ($2.534 \pm 0.009 \text{ \AA}$). This indicates that the bond is strong. So far, crystallographic studies of three other salicylic acid complexes, caffeine-5-chlorosalicylic acid (Shefter, 1968), theophylline-3,5-chlorosalicylic acid (Shefter, 1969) and nicotine-salicylic acid (Kim & Jeffrey, 1971), have been reported. In the last-mentioned, the salicylic acid exists in the ionized form as a salicylate anion. In the other two, complex formation is achieved through a hydrogen bond, one of the carboxyl oxygen atoms in the salicylic acid molecule being the proton donor as in the present structure. The acceptors in these two complexes are nitrogen atoms, and hence their hydrogen-bond parameters are not directly comparable with those in salipyrine where the acceptor is an oxygen.

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A Neutron Diffraction Study of the Structure of L-Cystine. 2HCl

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A neutron diffraction study of L-cystine. 2HCl, $[\text{SCH}_2\text{CH}(\text{NH}_3^+)\text{COOH} \cdot \text{Cl}^-]_2$, has been carried out. The structure is monoclinic, space group $C2$, with two molecules per unit cell. The cell parameters are $a = 18.582$ (7), $b = 5.242$ (2), $c = 7.228$ (3) and $\beta = 103.74$ (1)°. Intensities of 749 independent reflexions have been measured at a wavelength of 1.178 Å, with the diffractometer in the symmetrical setting. The positions of the seven hydrogen atoms in the symmetric unit have been determined from a Fourier map of the nuclear scattering density computed with the phases from the X-ray heavy-atom positions. The structure has been refined by the method of least squares and the final value of the R index (on F^2) is 0.055. The structure is extensively hydrogen bonded. Details of hydrogen bonding and molecular conformation are discussed.

Introduction

The neutron diffraction study of the structure of L-cystine dihydrochloride, $[\text{SCH}_2\text{CH}(\text{NH}_3^+)\text{COOH} \cdot \text{Cl}^-]_2$, was undertaken as a part of the programme of studies currently in progress in our laboratory on the structure and hydrogen bonding in crystalline amino acids. A detailed knowledge of the hydrogen-atom positions and the side-group conformations in amino acids is of considerable interest in the calculation of the configuration of the side groups associated with polypeptide chains. Studies of cystine structures assume added importance since they lead to information about the conformation around the disulphide bond which is one of the important factors stabilizing the conformation of polypeptides.

Preliminary studies of the space group and cell constants of L-cystine. 2HCl were carried out by Steinrauf & Jensen (1956) and Srinivasan (1956). The X-ray study was carried out by Steinrauf, Peterson & Jensen (1958), in which approximate positions of the hydrogen atoms were determined.

Experimental

Large, clear and well formed single crystals of L-cystine dihydrochloride were easily obtained by slow evaporation from a saturated aqueous solution with about 20% excess hydrochloric acid. The crystals were generally needle shaped and elongated along the b axis with $\{201\}$, $\{001\}$ and $\{100\}$ as the principal faces. The density of the crystals measured by flotation in a mix-

ture of chloroform and bromoform was 1.52 g cm^{-3} .

Neutron intensity data were recorded on the four-circle neutron diffractometer, 3D-FAD (Momin, Sequeira & Chidambaram, 1969) at the CIRUS reactor in Trombay. The specimen crystal used was in the shape of a five-sided prism (volume $\approx 42 \text{ mm}^3$) with height = 4.9 mm along **b**; four of its side faces were (001), (100), (201) and (20 $\bar{1}$), and the fifth was cut roughly perpendicular to $[\bar{2}01]$. The widths of these faces were 2.6, 1.8, 1.3, 2.9 and 3.0 mm respectively. The crystal was given a thin coating of an adhesive (brand name: Stickfast) to prevent exposure to air and mounted on the diffractometer with its *b* axis parallel to the φ axis. The cell parameters were refined on the basis of the optimized 2θ , χ and φ values for about 60 strong reflexions with the program *REFINE* (Srikanta & Sequeira, 1968). The resulting values are listed in Table 1 along with other crystal data. The systematic absences were consistent with the space group *C*2.

Table 1. *Crystal data for L-cystine. 2HCl*

| Space group | <i>C</i> 2 |
|----------------------|---------------------------|
| <i>a</i> | 18.582 (7) Å |
| <i>b</i> | 5.242 (2) |
| <i>c</i> | 7.228 (3) |
| β | 103.74 (1)° |
| <i>V</i> | 683.9 Å ³ |
| <i>Z</i> | 2 |
| <i>D_m</i> | 1.52 g cm ⁻³ |
| <i>D_c</i> | 1.5201 g cm ⁻³ |

The integrated intensities of 749 independent reflexions within the limit $\sin \theta/\lambda = 0.60$ ($\lambda = 1.178$ (1) Å) were recorded in the bisecting position with the $\theta-2\theta$ coupled step-scanning technique. The second-order contamination in the beam was avoided by using germanium (115) as the monochromator. The effects of multiple reflexion were checked for the *0k0* reflexions by examining their peak intensities as a function of rotation about the scattering vectors and found to

be negligible. The intensities of three standard reflexions were recorded every 30 reflexions to check on the stability of the crystal and counting equipment. During the course of the experiment, spread over a period of six months, there was some systematic deterioration in the quality of the specimen crystal resulting in a decrease of nearly 30% in the intensities of the standard reflexions. Most of the data, however, were recorded after arresting this crystal deterioration by further enclosing it within a thin Mylar film. The intensities of all the reflexions were normalized based on the standard intensities.

The integrated intensities were then reduced to F_o^2 by applying the standard Lorentz and absorption corrections with our program *DATARED* (Srikanta, 1968) which includes the absorption correction program *ORABS* (Wehe, Busing & Levy, 1962) as a subroutine. An absorption coefficient of 1.685 cm^{-1} (calculated) was used. The transmission factors ranged from 0.610 to 0.654.

Structure refinement

The positions of the seven hydrogen atoms in the asymmetric unit were obtained from a Fourier synthesis of the nuclear scattering density computed with the program *FORDAP* (Zalkin, 1962) with phases calculated from the positions of the non-hydrogen atoms obtained in the X-ray study of Steinrauf, Peterson & Jensen (1958). All the hydrogen atoms excepting H³ were close to those estimated in the X-ray study. The position of H³ however was shifted by about 0.6 Å from the X-ray value. All the structural parameters were then subjected to a series of full-matrix least-squares refinements (on F^2), first with isotropic and then with anisotropic temperature factors, using the program *XFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum \omega(F_o^2 - |F_c|^2)^2$ with initial weights

$$\omega = [\sigma_s^2(F_o^2) + (0.08 F_o^2)^2]^{-1}$$

Table 2. *Final positional and thermal parameters*

All the values are multiplied by 10^4 and their standard deviations (in units of the last digit) are given in parentheses. The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

| | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|----------------------------------|----------|-----------|-----------|--------------|--------------|--------------|--------------|--------------|--------------|
| Cl | 1531 (1) | 890 (0) | 8848 (3) | 25 (1) | 301 (7) | 199 (4) | 17 (2) | 29 (1) | 115 (5) |
| C | 1561 (1) | 4484 (6) | 4426 (4) | 20 (1) | 195 (9) | 143 (6) | 4 (2) | 0 (2) | 40 (7) |
| C ^z | 1452 (1) | 6701 (6) | 3052 (4) | 16 (1) | 153 (9) | 134 (5) | -7 (2) | -3 (1) | 22 (6) |
| C β | 645 (1) | 7530 (7) | 2394 (4) | 19 (1) | 216 (10) | 132 (6) | 11 (2) | 7 (2) | 9 (7) |
| N | 1774 (1) | 6002 (6) | 1423 (3) | 18 (1) | 265 (8) | 214 (5) | 9 (2) | 26 (1) | 98 (8) |
| O ¹ | 1940 (2) | 2667 (8) | 4281 (5) | 27 (1) | 224 (11) | 225 (8) | 21 (3) | 16 (2) | 44 (9) |
| O ² | 1207 (3) | 4795 (11) | 5773 (6) | 61 (2) | 454 (19) | 166 (8) | 66 (5) | 51 (3) | 120 (12) |
| S | 6 (3) | 4995 (13) | 1415 (9) | 16 (2) | 294 (25) | 185 (12) | -1 (5) | 12 (4) | 78 (17) |
| H | 1297 (4) | 3400 (17) | 6671 (11) | 56 (3) | 487 (32) | 206 (14) | 48 (8) | 42 (5) | 69 (22) |
| H ¹ | 1574 (3) | 4312 (15) | 775 (10) | 39 (2) | 378 (31) | 215 (14) | -8 (7) | 32 (4) | 9 (19) |
| H ² | 1667 (3) | 7447 (15) | 407 (10) | 40 (2) | 343 (24) | 312 (17) | 22 (6) | 61 (5) | 141 (20) |
| H ³ | 2333 (3) | 5778 (15) | 1806 (11) | 26 (2) | 468 (29) | 430 (21) | 9 (7) | 36 (5) | 78 (24) |
| H ^z | 1774 (4) | 8368 (11) | 3771 (9) | 31 (2) | 257 (20) | 306 (17) | -30 (5) | -15 (5) | -37 (17) |
| H ^{β1} | 463 (3) | 8235 (14) | 3631 (9) | 39 (2) | 505 (32) | 223 (14) | 33 (6) | 34 (4) | -91 (19) |
| H ^{β2} | 595 (3) | 9086 (12) | 1368 (9) | 33 (2) | 273 (23) | 270 (15) | 7 (5) | 1 (4) | 103 (17) |

where $\sigma_s(F_o^2)$ are the standard errors based on counting statistics. In the final stages of the refinement the following weighting scheme based on an error analysis was used:

$$\omega = [0.839 - 3.37 (F_c/10)^2 + 15.5 (F_c/10)^4 - 12.3 (F_c/10)^4 + 3.44 (F_c/10)^8]^{-2}$$

The intensity data showed some moderate extinction effects and a correction for secondary extinction in the form $Y = (1 + 2x)^{-1/2}$ (Zachariasen, 1967) was introduced at the start of the refinement and an isotropic extinction parameter $G (=x/QT)$ was refined (see for

Table 3. Observed and calculated structure factors for L-cystine.2HCl

The five columns in each set contain the Miller indices h and l , $100F_o^2$, $100|F_c|^2$ and $1000Y$. F_o^2 has been divided by the extinction factor Y . Negative F_o^2 values correspond to unobserved reflexions for which the background subtracted signal counts were statistically negative.

| h | l | $100F_o^2$ | $100 F_c ^2$ | $1000Y$ |
|-----|-----|------------|--------------|---------|
| 0 | 0 | 10000 | 10000 | 1000 |
| 1 | 0 | 10000 | 10000 | 1000 |
| 2 | 0 | 10000 | 10000 | 1000 |
| 3 | 0 | 10000 | 10000 | 1000 |
| 4 | 0 | 10000 | 10000 | 1000 |
| 5 | 0 | 10000 | 10000 | 1000 |
| 6 | 0 | 10000 | 10000 | 1000 |
| 7 | 0 | 10000 | 10000 | 1000 |
| 8 | 0 | 10000 | 10000 | 1000 |
| 9 | 0 | 10000 | 10000 | 1000 |
| 10 | 0 | 10000 | 10000 | 1000 |
| 11 | 0 | 10000 | 10000 | 1000 |
| 12 | 0 | 10000 | 10000 | 1000 |
| 13 | 0 | 10000 | 10000 | 1000 |
| 14 | 0 | 10000 | 10000 | 1000 |
| 15 | 0 | 10000 | 10000 | 1000 |
| 16 | 0 | 10000 | 10000 | 1000 |
| 17 | 0 | 10000 | 10000 | 1000 |
| 18 | 0 | 10000 | 10000 | 1000 |
| 19 | 0 | 10000 | 10000 | 1000 |
| 20 | 0 | 10000 | 10000 | 1000 |
| 21 | 0 | 10000 | 10000 | 1000 |
| 22 | 0 | 10000 | 10000 | 1000 |
| 23 | 0 | 10000 | 10000 | 1000 |
| 24 | 0 | 10000 | 10000 | 1000 |
| 25 | 0 | 10000 | 10000 | 1000 |
| 26 | 0 | 10000 | 10000 | 1000 |
| 27 | 0 | 10000 | 10000 | 1000 |
| 28 | 0 | 10000 | 10000 | 1000 |
| 29 | 0 | 10000 | 10000 | 1000 |
| 30 | 0 | 10000 | 10000 | 1000 |
| 31 | 0 | 10000 | 10000 | 1000 |
| 32 | 0 | 10000 | 10000 | 1000 |
| 33 | 0 | 10000 | 10000 | 1000 |
| 34 | 0 | 10000 | 10000 | 1000 |
| 35 | 0 | 10000 | 10000 | 1000 |
| 36 | 0 | 10000 | 10000 | 1000 |
| 37 | 0 | 10000 | 10000 | 1000 |
| 38 | 0 | 10000 | 10000 | 1000 |
| 39 | 0 | 10000 | 10000 | 1000 |
| 40 | 0 | 10000 | 10000 | 1000 |
| 41 | 0 | 10000 | 10000 | 1000 |
| 42 | 0 | 10000 | 10000 | 1000 |
| 43 | 0 | 10000 | 10000 | 1000 |
| 44 | 0 | 10000 | 10000 | 1000 |
| 45 | 0 | 10000 | 10000 | 1000 |
| 46 | 0 | 10000 | 10000 | 1000 |
| 47 | 0 | 10000 | 10000 | 1000 |
| 48 | 0 | 10000 | 10000 | 1000 |
| 49 | 0 | 10000 | 10000 | 1000 |
| 50 | 0 | 10000 | 10000 | 1000 |
| 51 | 0 | 10000 | 10000 | 1000 |
| 52 | 0 | 10000 | 10000 | 1000 |
| 53 | 0 | 10000 | 10000 | 1000 |
| 54 | 0 | 10000 | 10000 | 1000 |
| 55 | 0 | 10000 | 10000 | 1000 |
| 56 | 0 | 10000 | 10000 | 1000 |
| 57 | 0 | 10000 | 10000 | 1000 |
| 58 | 0 | 10000 | 10000 | 1000 |
| 59 | 0 | 10000 | 10000 | 1000 |
| 60 | 0 | 10000 | 10000 | 1000 |
| 61 | 0 | 10000 | 10000 | 1000 |
| 62 | 0 | 10000 | 10000 | 1000 |
| 63 | 0 | 10000 | 10000 | 1000 |
| 64 | 0 | 10000 | 10000 | 1000 |
| 65 | 0 | 10000 | 10000 | 1000 |
| 66 | 0 | 10000 | 10000 | 1000 |
| 67 | 0 | 10000 | 10000 | 1000 |
| 68 | 0 | 10000 | 10000 | 1000 |
| 69 | 0 | 10000 | 10000 | 1000 |
| 70 | 0 | 10000 | 10000 | 1000 |
| 71 | 0 | 10000 | 10000 | 1000 |
| 72 | 0 | 10000 | 10000 | 1000 |
| 73 | 0 | 10000 | 10000 | 1000 |
| 74 | 0 | 10000 | 10000 | 1000 |
| 75 | 0 | 10000 | 10000 | 1000 |
| 76 | 0 | 10000 | 10000 | 1000 |
| 77 | 0 | 10000 | 10000 | 1000 |
| 78 | 0 | 10000 | 10000 | 1000 |
| 79 | 0 | 10000 | 10000 | 1000 |
| 80 | 0 | 10000 | 10000 | 1000 |
| 81 | 0 | 10000 | 10000 | 1000 |
| 82 | 0 | 10000 | 10000 | 1000 |
| 83 | 0 | 10000 | 10000 | 1000 |
| 84 | 0 | 10000 | 10000 | 1000 |
| 85 | 0 | 10000 | 10000 | 1000 |
| 86 | 0 | 10000 | 10000 | 1000 |
| 87 | 0 | 10000 | 10000 | 1000 |
| 88 | 0 | 10000 | 10000 | 1000 |
| 89 | 0 | 10000 | 10000 | 1000 |
| 90 | 0 | 10000 | 10000 | 1000 |
| 91 | 0 | 10000 | 10000 | 1000 |
| 92 | 0 | 10000 | 10000 | 1000 |
| 93 | 0 | 10000 | 10000 | 1000 |
| 94 | 0 | 10000 | 10000 | 1000 |
| 95 | 0 | 10000 | 10000 | 1000 |
| 96 | 0 | 10000 | 10000 | 1000 |
| 97 | 0 | 10000 | 10000 | 1000 |
| 98 | 0 | 10000 | 10000 | 1000 |
| 99 | 0 | 10000 | 10000 | 1000 |
| 100 | 0 | 10000 | 10000 | 1000 |

example; Sequeira, Rajagopal & Chidambaram, 1972) along with other structural parameters. The value of G converged to 0.180×10^4 giving a minimum extinction correction factor of 0.726 for the $\bar{1}\bar{1}\bar{2}$ reflexion. The final discrepancy values were as follows:

| | | |
|---|--------|--------------------------|
| Number of observations: | 749 | 665 ($F_o^2 > \sigma$) |
| $R(F) = \frac{\sum F_o - F_c }{\sum F_o}$ | - | 0.0461 |
| $R(F^2) = \frac{\sum F_o^2 - F_c ^2 }{\sum F_o^2}$ | 0.0552 | 0.0515 |
| $R_w(F^2) = \left[\frac{\sum \omega F_o^2 - F_c ^2 ^2}{\sum \omega F_o^4} \right]^{1/2}$ | 0.0598 | 0.0572 |

The values of scattering amplitudes (in units of 10^{-12} cm) used were: H = -0.3723, C = 0.6626, N = 0.94, O = 0.575, S = 0.2847 and Cl = 0.9584 (Shull, 1971). The final positional and thermal parameters are listed in Table 2, and the observed and calculated structure factors are compared in Table 3.

Discussion of the structure

A stereoscopic picture of the molecule drawn using the program *ORTEP* (Johnson, 1965) is shown in Fig. 1. The non-hydrogen atom backbone structure found in the earlier X-ray study (Steinrauf, Peterson & Jensen, 1958) is basically correct. The distances and angles within the molecule computed using the program *ORFFE* (Busing, Martin & Levy, 1964) are given in Table 4. The distances and angles involving the amino acid residue are compared in Table 5 with the weighted average X-ray values (Sundaralingam & Putkey, 1970) and the weighted average neutron values for 'unionized' amino acids. The latter are based on the neutron diffraction studies of L-tyrosine.HCl (Frey,

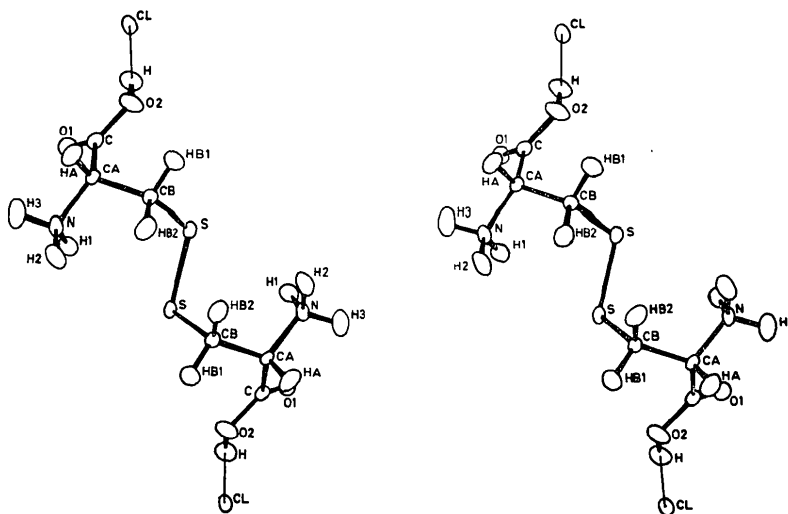


Fig. 1. A stereoscopic drawing of the molecule.

Koetzle, Lehmann & Hamilton, 1973) and L-glutamic acid.HCl (Sequeira, Rajagopal & Chidambaram, 1972). The mutual agreement between the three sets in Table 5 is very good except for the angles $C-C^\alpha-C^\beta$ and $C^\beta-C^\alpha-H^\alpha$. Interestingly, a large spread in the values of $C-C^\alpha-C^\beta$ has also been observed (Ramana-dham, Sikka & Chidambaram, 1973) in a similar comparison based on the neutron diffraction studies of a number of 'ionized' amino-acid residues.

Table 4. Bond distances (Å) and angles (°) within the molecule

The standard deviations are given in parentheses.

Bond distances

| | | | |
|--------------------------------|------------|---------------------------------|------------|
| C—O ¹ | 1.205 (5) | O ² —H | 0.965 (10) |
| C—O ² | 1.308 (6) | N—H ¹ | 1.029 (8) |
| C—C ^α | 1.511 (4) | N—H ² | 1.041 (8) |
| C ^α —N | 1.487 (4) | N—H ³ | 1.017 (6) |
| C ^α —C ^β | 1.525 (3) | C ^α —H ^α | 1.115 (6) |
| C ^β —S | 1.810 (7) | C ^β —H ^{β1} | 1.093 (8) |
| S—S ¹ | 2.041 (14) | C ^β —H ^{β2} | 1.091 (7) |

Bond angles

| | | | |
|--|-----------|--|-----------|
| C—O ² —H | 111.6 (7) | C ^α —N—H ³ | 113.0 (5) |
| O ¹ —C—O ² | 124.9 (4) | H ¹ —N—H ² | 108.5 (6) |
| O ¹ —C—C ^α | 122.7 (3) | H ² —N—H ³ | 106.7 (6) |
| O ² —C—C ^α | 112.4 (3) | H ³ —N—H ¹ | 105.0 (6) |
| C—C ^α —C ^β | 113.1 (2) | C ^α —C ^β —H ^{β1} | 108.3 (4) |
| C—C ^α —H ^α | 108.8 (4) | C ^α —C ^β —H ^{β2} | 110.1 (4) |
| C—C ^α —N | 108.4 (2) | S—C ^β —C ^α | 114.7 (3) |
| N—C ^α —C ^β | 112.0 (2) | S—C ^β —H ^{β1} | 105.4 (5) |
| N—C ^α —H ^α | 106.9 (4) | S—C ^β —H ^{β2} | 109.9 (4) |
| C ^β —C ^α —H ^α | 107.5 (4) | H ^{β1} —C ^β —H ^{β2} | 108.1 (6) |
| C ^α —N—H ¹ | 113.8 (5) | C ^β —S—S ¹ | 104.0 (4) |
| C ^α —N—H ² | 109.5 (5) | | |

Table 5. Comparison of bond distances and angles

| Distance (Å) | Present value | Weighted average for un-ionized amino-acid residues | |
|--|---------------|---|------------|
| | | Neutron | X-ray |
| C—O ¹ | 1.205 (5) | 1.207 (3) | 1.203 (9) |
| C—O ² | 1.308 (6) | 1.303 (3) | 1.306 (11) |
| C ^α —C | 1.511 (4) | 1.522 (3) | 1.524 (7) |
| C ^α —N | 1.487 (4) | 1.492 (2) | 1.482 (4) |
| C ^α —C ^β | 1.525 (3) | 1.536 (3) | 1.523 (13) |
| C ^α —H ^α | 1.115 (6) | 1.097 (5) | — |
| Angle (°) | | | |
| O ¹ —C—O ² | 124.9 (4) | 126.3 (2) | 126.1 (9) |
| C ^α —C—O ¹ | 122.7 (3) | 122.0 (2) | 122.8 (15) |
| C ^α —C—O ² | 112.4 (3) | 111.7 (2) | 111.1 (10) |
| C—C ^α —N | 108.4 (2) | 108.2 (1) | 108.4 (12) |
| C—C ^α —C ^β | 113.1 (2) | 110.3 (2) | 110.2 (21) |
| N—C ^α —C ^β | 112.0 (2) | 110.2 (2) | 110.4 (6) |
| C—C ^α —H ^α | 108.8 (4) | 109.9 (3) | — |
| N—C ^α —H ^α | 106.9 (4) | 107.6 (2) | — |
| C ^β —C ^α —H ^α | 107.5 (4) | 110.8 (3) | — |
| $\langle C^\alpha-N-H^i \rangle_{i=1,2,3}$ | 112.1 (3) | 110.9 (2) | — |
| $\langle H^i-N-H^j \rangle_{i,j=1,3}$ | 106.7 (4) | 107.8 (3) | — |
| C—O ² —H | 111.6 (7) | 110.6 (3) | — |

Molecular conformation

The molecular conformation and the torsion angles about various bonds are shown in Fig. 2, following the nomenclature of IUPAC-IUB Commission (1970). The α -carbon atom (C^α) is planar with the carboxyl group—CO¹O², and the best plane through these

$$12.69x + 2.39y + 2.83z = 4.31$$

passes within 0.003 Å of all the four atoms. The carboxyl hydrogen (H) is within 0.038 Å from this plane.

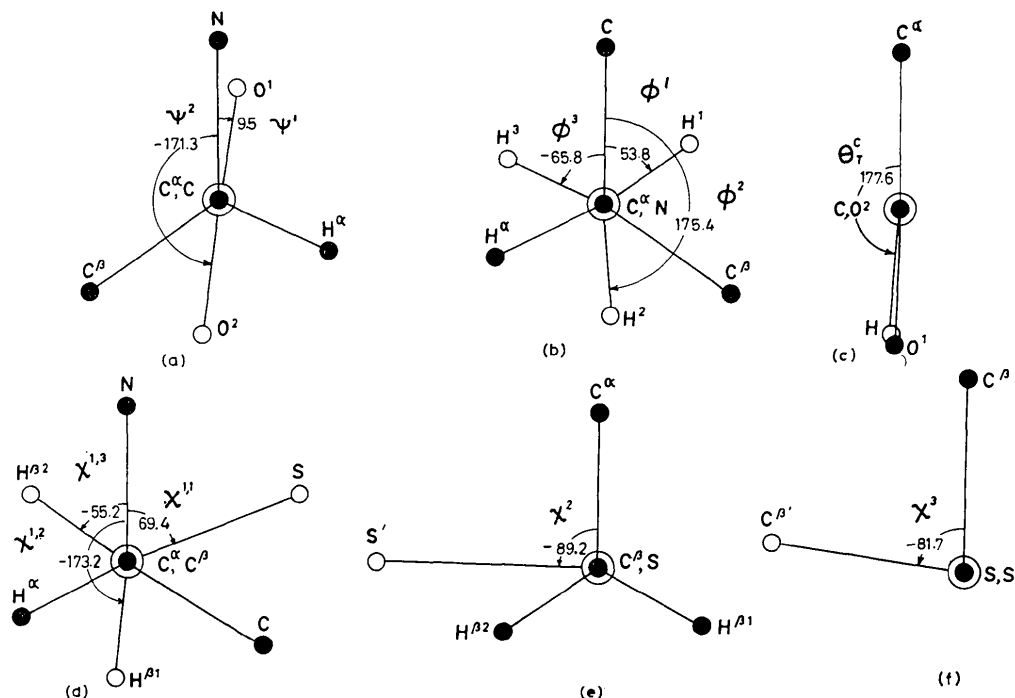


Fig. 2. Torsional conformations looking down bonds: (a) C^α—C; (b) C^α—N; (c) C—O²; (d) C^α—C^β; (e) C^β—S; (f) S—S¹.

The amino nitrogen is displaced from it by 0.22 Å such that the torsion angle ψ^1 is $+9.5^\circ$. The α -NH₃⁺ group is staggered relative to the substituents on C^α as shown in Fig. 2(b).

The side-group conformation is normal, the torsion angle $\psi^{1,1}$ ($=69.4^\circ$) being close to the generally expected value of 60° in L-cystine groups (Lakshminarayanan, Sasisekharan & Ramachandran, 1967). The values of torsion angles χ^2 and χ^3 are close to those observed in L-cystine.2HBr (Peterson, Steinrauf & Jensen, 1960), *N,N'*-diglycyl-L-cystine dihydrate (Yakel & Hughes, 1954) and L-cystinediamide.2HCl (Chaney & Steinrauf, 1968) but opposite to those in hexagonal L-cystine (Oughton & Harrison, 1959) as can be seen from Table 6. As suggested by Oughton & Harrison (1959), there are two preferred types of conformation about the disulphide bond in cystine groups. In the first type (type 1), the disulphide bond and the C^α-C bond are on opposite or antiparallel sides of the C^αC^βS plane, resulting in an extended conformation for the molecular backbone (C-C^α-C^β-S-S'-C^{β'}-C^{α'}-C'). In the second type (type 2), the disulphide bond is almost parallel to the C^α-C bond resulting in a coiled S type of conformation for the backbone.

Hydrogen bonding

The structure is extensively hydrogen-bonded. Each molecule is hydrogen-bonded to eight chlorines and each chlorine links four neighbouring molecules. The distances and angles characterizing these hydrogen bonds are given in Table 7. The structure consists of columns of cystine molecules stacked along the *b* axis and held together by a three-dimensional network of

hydrogen bonds. The adjacent molecules within the column are linked by N-H¹...Cl and N-H²...Cl hydrogen bonds, while the N-H³...Cl and O²-H...Cl hydrogen bonds cross-link the molecules in neighbouring columns as shown in Fig. 3.

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Table 6. Torsion angles about the C^β-S(χ^2) and S-S(χ^3) bonds in various cystine crystals

| Crystal | Type 1 | | Type 2 | |
|--|----------|----------|----------|----------|
| | χ^2 | χ^3 | χ^2 | χ^3 |
| 1. L-Cystine.2HCl | -89.2° | -81.7° | | |
| 2. L-Cystine.2HBr | -88.9 | -81.3 | | |
| 3. <i>N,N'</i> -Diglycyl-L-cystine dihydrate | -97.0 | -78.6 | | |
| 4. L-Cystinediamide.2HCl | -94.3 | -81.4 | | |
| 5. Hexagonal L-cystine | | | 81.6° | 73.7° |
| Average | -92.3° | -80.8° | | |

Table 7. Hydrogen bonds in L-cystine.2HCl

| Bond description | d_{X-H} | $d_{H...Y}$ | $d_{X...Y}$ | $\angle H-X...Y$ |
|---------------------------------------|--------------|-------------|-------------|------------------|
| X-H...Y | | | | |
| O ² -H...Cl ^I | 0.965 (10) Å | 2.018 (8) Å | 2.976 (5) Å | 5.8 (5)° |
| N-H ¹ ...Cl ^{II} | 1.029 (8) | 2.261 (8) | 3.233 (3) | 16.0 (4) |
| N-H ² ...Cl ^{III} | 1.041 (8) | 2.111 (8) | 3.136 (3) | 8.2 (4) |
| N-H ³ ...Cl ^{IV} | 1.017 (6) | 2.270 (7) | 3.202 (3) | 19.6 (5) |

Key for symmetry-related atoms

| | | | |
|-----|--------------------------|--------------------------|-------------|
| I | <i>x</i> | <i>y</i> | <i>z</i> |
| II | <i>x</i> | <i>y</i> | <i>z</i> -1 |
| III | <i>x</i> | <i>y</i> +1 | <i>z</i> -1 |
| IV | $\frac{1}{2}$ - <i>x</i> | $\frac{1}{2}$ + <i>y</i> | 1- <i>z</i> |

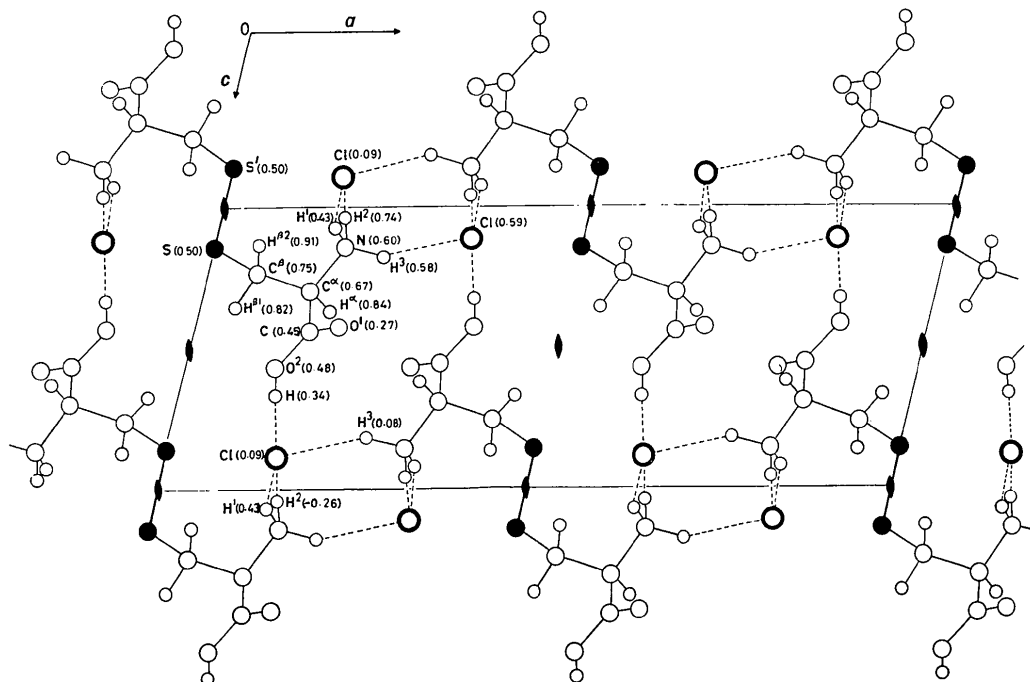


Fig. 3. The projection of the unit cell structure on the (010) plane; y coordinates are in parentheses.

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