

The approximately planar $-\text{CH}(\text{NH}_2)\text{COOH}$ groups lie almost perpendicular to the c axis, and are hydrogen-bonded together to form continuous sheets which are almost identical in structure with those found in glycine (Albrecht & Corey, 1939) (see Fig. 2). The structure of

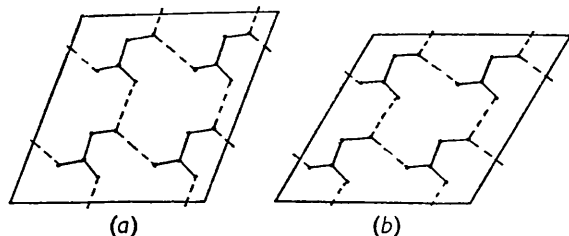


Fig. 2. Diagrammatic representation of (a) one layer of the glycine structure, (b) one layer of $-\text{CH}(\text{NH}_2)\text{COOH}$ groups in the hexagonal L-cystine structure.

hexagonal L-cystine may therefore be thought of as composed of parallel glycine-like sheets with the C-R bonds pointing alternately up and down in successive sheets, linked together in pairs by disulphide bridges. Adjacent sheets which are not linked by disulphide bridges are held together by $\text{N}-\text{H} \cdots \text{O}'_1$ hydrogen bonds.

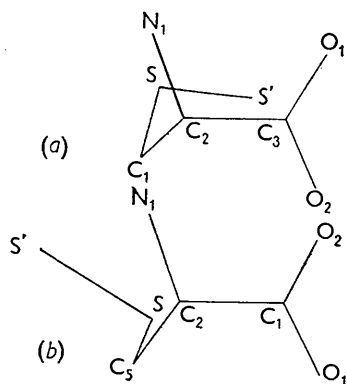


Fig. 3. Projection of one half of the cystine group on to the plane of the planar $-\text{CH}(\text{NH}_2)\text{COOH}$ groups in (a) cystine, (b) $N-N'$ -diglycyl-L-cystine dihydrate.

The conformation of the cystine molecule is different from that found in L-cystine hydrochloride (Cormit, Schuyff & Feil, 1956) and the cystine group in $N-N'$ -diglycyl-L-cystine dihydrate (Yakel & Hughes, 1954) (Fig. 3).

The individual halves of the molecule are very similar in the two types of structure, with only small differences in the orientations of the S-C₁ and C₁-C₂ bonds relative to the planar $-\text{CH}(\text{NH}_2)\text{COOH}$ group. There is, however, rotation about the S-C₁, S-S' and S'-C'₁ bonds, and the disulphide bridge in L-cystine is the mirror image of that in the other two structures. Thus in L-cystine, the S-S' and C₂-C₃ bonds lie on the *same* side of the SC₁C₂ plane, whilst in $N-N'$ -diglycyl-L-cystine dihydrate and L-cystine hydrochloride the equivalent bonds lie on *opposite* sides of this plane.

It appears, therefore, that in the cystine group there is a preferred position of the S-C₁ bond relative to the planar group, with the SC₁C₂ plane approximately bisecting the angle N₁-C₂-C₃. There is also a preferred position of the S-S' bond, which makes an angle of approximately 83° with the SC₁C₂ plane, but the disulphide bridge can take up either of the two possible conformations, related by a mirror plane of symmetry perpendicular to the S-S' bond, which satisfy this condition.

We are much indebted to Dr J. S. Rollett and to members of the staff of the National Physical Laboratory who computed the three-dimensional Fourier synthesis and structure factors on 'Deuce', the N. P. L. electronic computer.

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Further refinement of the crystal structure of cycloserine hydrochloride. By J. W. TURLEY and R. PEPINSKY, *X-Ray and Crystal Analysis Laboratory, The Pennsylvania State University, University Park, Pa., U.S.A.*

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Recent advances in programming large electronic computers for crystallographic calculations have led to extensive refinement of many structures in three dimensions. When these methods of calculation became available to us, it was decided that a least-squares refinement of cycloserine hydrochloride (Turley & Pepinsky, 1956) in three dimensions might yield further information concerning the hydrogen-bond network in this crystal. Accordingly, the calculation was made using the IBM 704 Electronic Data-Processing Machine (Sayre, 1956), and the results are presented in this paper.

All data were placed on an absolute scale by comparing $|F_o|$ with the last set of $|F_c|$. The coordinates and crystal temperature factor resulting from the last IBM 604 calculation were used as beginning parameters. Six least-squares refinement cycles, refining on coordinates and individual temperature factors for all cycles, led to the coordinates and temperature factors shown in Table 1. The agreement factor, $R_1 = \sum ||F_o| - |F_c|| \div \sum |F_o|$, dropped from 15.9% to 14.4% ($F_o \neq 0$). For the last refinement cycle, all indicated shifts were less than 0.001 cell edge.

Table 1. Final coordinates and temperature factors for cycloserine hydrochloride

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C ₁	0.5388	0.4131	0.1284	2.40 Å ²
C ₂	0.3836	0.4381	0.0630	3.84
C ₃	0.5221	0.3136	0.3290	2.76
N ₄	0.6141	0.3520	0.9350	2.36
N ₅	0.3910	0.3030	0.3835	3.11
O ₆	0.6223	0.2625	0.4384	3.87
O ₇	0.3036	0.3678	0.2297	3.78
Cl	0.4147	0.1030	0.8690	2.35

Using the values from Table 1, bond distances and angles as well as all short intermolecular distances were re-calculated. Both the angles and bond distances (see Table 2) are significantly different from those presented in the earlier report; maximum differences of 0.070 Å and 4.5° appear. Short intermolecular distances together

Table 2. Bond angles and lengths in cycloserine hydrochloride

C ₁ -C ₃ -N ₅	109.5°	C ₁ -C ₂ -O ₇	106.2°	C ₁ -C ₂	1.575 Å
C ₁ -C ₃ -O ₆	124.2	C ₂ -O ₇ -N ₅	109.5	C ₂ -O ₇	1.430
O ₆ -C ₃ -N ₅	126.0	O ₇ -N ₅ -C ₃	113.6	O ₇ -N ₅	1.396
C ₃ -C ₁ -C ₂	100.7	N ₄ '-Cl-N ₄	140.7	N ₅ -C ₃	1.316
C ₃ -C ₁ -N ₄	109.0	N ₄ -Cl-N ₄ '	103.6	C ₃ -C ₁	1.549
C ₂ -C ₁ -N ₄	111.6	N ₄ '-Cl-N ₄ '	113.2	C ₃ -O ₆	1.274
				C ₁ -N ₄	1.470

Table 3. Short R-M...N angles and intermolecular distances in cycloserine hydrochloride

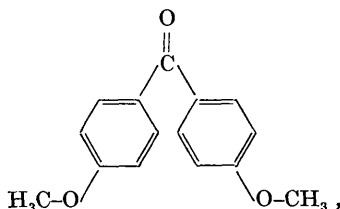
C ₁ -N ₄ -Cl	91.1°	N ₄ -Cl	3.139 Å
C ₁ -N ₄ '-Cl	97.4	N ₄ '-Cl	3.165
C ₁ -N ₄ '-Cl	97.5	N ₄ '-Cl	3.245
C ₃ -N ₅ -O ₆	168.6	O ₆ -N ₅	2.885
O ₇ -N ₅ -O ₆	77.6	O ₆ -O ₇	2.922
C ₃ -O ₆ -O ₇	166.7	N ₄ -O ₇	3.074
C ₁ -N ₄ -O ₆	148.0	N ₄ -O ₆	2.993
C ₁ -N ₄ -O ₆	149.7		

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Crystal and molecular structure of *p,p'*-dimethoxybenzophenone by the direct probability method. By I. L. KARLE, H. HAUPTMAN, J. KARLE and A. B. WING, *U. S. Naval Research Laboratory, Washington 20, D. C., U. S. A.*

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The structure of *p,p'*-dimethoxybenzophenone,



has been found by means of the probability formulas given in A. C. A. Monograph No. 3 (Hauptman & Karle, 1953). The crystallographic data are:

$$a = 16.43, b = 16.03, c = 9.62 \text{ \AA}, \beta = 100^\circ 15',$$

$Z = 8$, ρ (X-ray) = 1.289, ρ (physical) = 1.259, and the space group is $P2_1/a$.

with $R-M \cdots N$ angles are given in Table 3. Applying Donohue's criterion of angle size (Donohue, 1952), only three of the four hydrogen atoms available for hydrogen bonding are used. These are the three which form $N-H \cdots Cl$ bonds. Apparently the H on the ring nitrogen is not involved in any hydrogen bond. In addition to the three $N-H \cdots Cl$ bonds, there are four close approaches which cannot be hydrogen bonds. Three are $N \cdots O$ distances and one is an $O \cdots O$ distance. It seems likely that the large chlorine atoms dominate the packing to produce this result.

Difference maps for the centrosymmetric projections on (001) and (010) have been computed, and indicate reasonable positions for all hydrogen atoms. A three-dimensional $F_o - F_c$ synthesis was calculated in an effort to resolve the hydrogens. However, this is a non-centric space group ($P2_12_12_1$), and the inherent phase error prevented any conclusive interpretation of the three-dimensional difference maps.

$F_o - F_c$ syntheses were computed on X-RAC, as supported by Contract No. N6onr-269, T. O. 16 with the Office of Naval Research. The analysis as a whole was supported by Grant No. A-228 from the National Institutes of Health. IBM 704 computations were kindly accomplished by Prof. V. Vand of this laboratory, at the General Motors Research Center. We are grateful to the latter organization for making the computer available to us.

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Weissenberg photographs were obtained with copper radiation yielding 5527 independent intensity data, almost the entire copper sphere. Of these, 1261 intensities were observed to be zero. The data were corrected for vibrational motion and placed on an absolute scale by means of a K curve (Karle & Hauptman, 1953), thus giving F_h^2 . From these the magnitudes of the normalized structure factors were computed by means of

$$E_h^2 = F_h^2 / \epsilon \sum_{j=1}^N f_{jh}^2,$$

where $\epsilon = 2$ when h is $h0l$ or $0k0$ and $\epsilon = 1$ otherwise.

A simple algebraic argument shows that the circumstance under which the special formulas appropriate to space group $P2_1/a$ may not be used with confidence occurs when a relatively large number of atoms has the same y coordinate. A statistical analysis (Karle, 1956)