

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

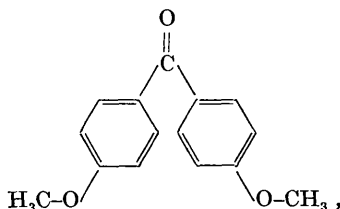
C ₁ -N ₄ -Cl	91.1°	N ₄ -Cl	3.139 Å
C ₁ -N ₄ '-Cl	97.4	N ₄ '-Cl	3.165
C ₁ -N ₄ '-Cl	97.5	N ₄ '-Cl	3.245
C ₃ -N ₅ -O ₆	168.6	O ₆ -N ₅	2.885
O ₇ -N ₅ -O ₆	77.6	O ₆ -O ₇	2.922
C ₃ -O ₆ -O ₇	166.7	N ₄ -O ₇	3.074
C ₁ -N ₄ -O ₆	148.0	N ₄ -O ₆	2.993
C ₁ -N ₄ -O ₆	149.7		

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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)

showed that this circumstance obtains for this crystal. It was therefore necessary to use the phase-determining formulas appropriate to the space group $P\bar{1}$. Owing to limited computing facilities, only the following formulas were used:

$$\Sigma_1: sE_{2h} \sim s(E_h^2 - 1), \quad (1)$$

$$\Sigma_2: sE_h \sim s \sum_{\mathbf{k}} E_{\mathbf{k}} E_{h+\mathbf{k}}, \quad (2)$$

$$\Sigma_3: sE_{2h} \sim s \sum_{\mathbf{k}} E_{2\mathbf{k}} (E_{h+\mathbf{k}}^2 - 1), \quad (3)$$

where s symbolizes 'sign of' and \sim means 'probably is'.

The phase determination was begun by determining the signs of five large positive E_{2h} , using Σ_1 with a probability of 0.85–0.95. Internal consistency was established and additional positive signs were determined by means of Σ_2 and Σ_3 . Once a base of positive signs was obtained, systematic use of Σ_3 yielded the first negative signs. It is to be emphasized that with these phase-determining relationships and a structure of this complexity it is essential to use Σ_3 in order to obtain the first negative signs. Finally, after specifying the origin by choosing arbitrarily the signs of three suitable structure factors, Σ_2 and Σ_3 were used to determine the remaining signs.

This procedure was carried out by hand and 272 of the phases among the largest $|E_h|$'s were determined. A Fourier map was computed using these E_h as coefficients, and the approximate structure of the two molecules in the asymmetric unit (30 carbon and 6 oxygen atoms) was obtained. This structure was refined by means of least squares using ~ 1100 structure-factor magnitudes sampled throughout the copper sphere (every fifth structure factor ordered on $\sin \theta$). At present $R = 0.22$, with accidental zeros included. One temperature factor per atom was used in the refinement procedure and the 28 hydrogen atoms per asymmetric unit were omitted.

The structure of an asymmetric unit is shown in Fig. 1, its projection along the a axis. The eight molecules per

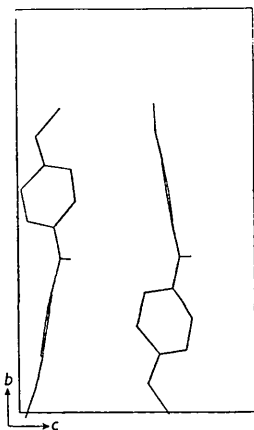


Fig. 1. Projection of an asymmetric unit along the a axis, $\frac{1}{4} \leq x \leq \frac{3}{4}$. The atomic coordinates were obtained from the least-squares refinement.

unit cell are illustrated in Fig. 2, the projection along the c axis. Fig. 2 is characterized by four molecules superimposed upon four other molecules. The molecules in

each superimposed pair are in fact separated by approximately $\frac{1}{2}c$.

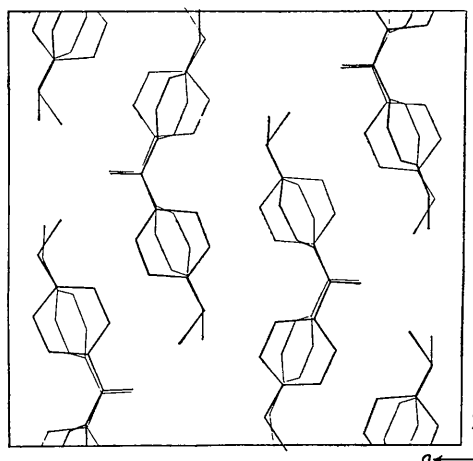


Fig. 2. Projection of the unit cell along the c axis. Molecules with lighter lines are behind the ones with heavier lines, spaced by approximately $\frac{1}{2}c$. The atomic coordinates were obtained from the least-squares refinement.

The average bonded distances, with their average deviations at the present stage of refinement, are listed in Table 1.

Table 1

Bond type	Average distance	Average deviation
C-C (ring)	1.384 Å	0.030 Å
C-C (non-ring)	1.460	0.030
C-O (aromatic)	1.390	0.020
C-O (aliphatic)	1.483	0.038
C=O	1.305	0.005

The smallest intermolecular distances are an O–O distance at 3.41 Å and an O–C distance at 3.45 Å. It can be seen from Figs. 1 and 2 that each methyl carbon lies close to the plane of the adjacent benzene ring. The benzene rings in each molecule are twisted away from each other, the average angle of twist being about 30° from the plane formed by the three oxygen atoms in the molecule.

Several articles and reviews have been written in which the attempt has been made to interpret the meaning of the probability formulas in A. C. A. Monograph No. 3 (1953) and to predict the consequences of applying them. In view of the successful determination of the structures of colemanite (Christ, Clark & Evans, 1954), meyerhofferite (Christ & Clark, 1956), and p,p' -dimethoxybenzophenone by probability methods, it is in order to make brief note of some of these predictions and interpretations.

Vand & Pepinsky (1954) have concluded, and others have accepted their argument (e.g. Rogers & Wilson, 1955), that the direct probability method will, with high probability, converge to the Patterson function; and hence will yield the correct solution only when the structure resembles the Patterson. The Patterson function of p,p' -dimethoxybenzophenone has not been computed. However, it is clear upon examination of the structure that the latter does not resemble the Patterson.

Cochran & Woolfson (1954; 1955, p. 8) have concluded

that Σ_3 is of little or no importance. Since Σ_1 is at best useful for determining the signs of positive structure factors (except for extremely simple structures), they further conclude that the procedure used here is of limited usefulness, or will lead to only positive signs (Woolfson, 1954, p. 724). Nevertheless, as pointed out above, Σ_3 played an important role in extending the base of positive signs and the indispensable role of yielding the first negative signs.

It is of interest that, in this instance, using only the simple formulas (1), (2) and (3), the data contained within the copper sphere of reflection were sufficient to solve a complex structure involving 108 independent parameters. We plan to report further on the application of the phase-determining procedure and to describe the results of additional refinements of the structure in a future publication.

We are indebted to many people. Mr C. E. Miller of Bell Telephone Laboratories prepared the single crystals. Dr Seymour Geller of Bell Telephone Laboratories suggested that we apply the probability methods to this crystal and supplied us with some preliminary crystallographic data and diffraction photographs. Mr Peter O'Hara of the National Bureau of Standards computed

the K curve and the E map. Mr Alvin Hatch of the Service Bureau Corporation refined the approximate structure by means of the least-squares program developed by Dr David Sayre. We are grateful to all these people.

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The crystal structure of the ordered alloy Au_4Mn . By DENJIRO WATANABE, *The Research Institute for Iron, Steel and Other Metals, Tôhoku University, Sendai, Japan*

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It was found by Kussmann & Raub (1956) that the alloy Au_4Mn has an ordered face-centred tetragonal lattice ($c/a < 1$) below about 420°C ., but its atomic arrangement has as yet been unknown. According to the said authors, the ordered alloy is ferromagnetic below the Curie temperature at about 100°C . The structure determination of this ordered alloy therefore seemed to be desirable from the crystallographic as well as from the magnetic point of view. The present author studied the superstructure of Au_4Mn by electron diffraction, using

thin oriented films, and was able to determine its complex ordered structure*.

* Raub, Zwicker & Baur (1953) found the alloy Au_3Mn to possess an ordered structure with tetragonal symmetry below 625°C ., but did not report its atomic arrangement. This alloy was studied also by the present author and was found to possess a two-dimensional anti-phase domain structure of a new kind, whose fundamental cell, considered by referring to the original disordered structure, is rhombic. The details will, however, be reported elsewhere.

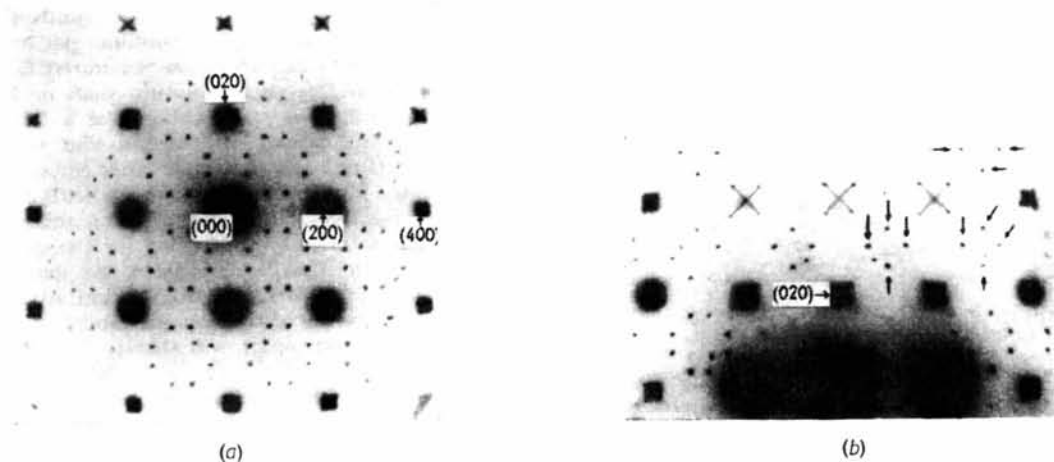


Fig. 1. (a) Electron-diffraction pattern of a thin alloy film containing about 20 atomic % Mn; normal incidence. Indices assigned to normal reflexions are referred to the original cubic system. (b) Electron-diffraction pattern of the same film as in (a); oblique incidence. Angle between the electron beam and the film normal was several degrees.