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THE CRYSTAL STRUCTURE OF BIS(META-CHLOROBENZOYL)METHANE

By

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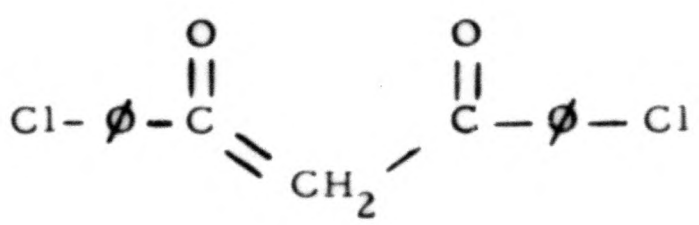
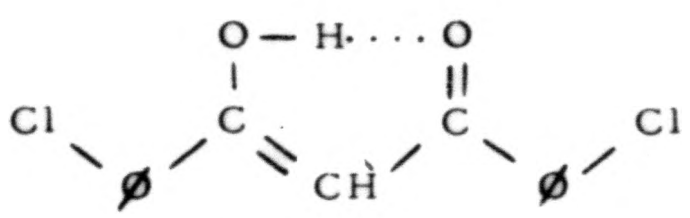
ABSTRACT

The determination of the crystal structure of bis(meta-chlorobenzoyl)-methane was undertaken by x-ray methods in an effort to clarify the ambiguous position of the hydrogen atom in the enolic form of β-diketones and hence in intramolecular hydrogen bonds.

Bis(meta-chlorobenzoyl)methane can be represented by



where one of the hydrogen atoms becomes detached from the methylene group and forms an intramolecular hydrogen bond



The literature is very contradictory as to whether the hydrogen bond is symmetrical or a statistical distribution of the case where the hydrogen is attached to one of the oxygen atoms in part of the molecules and to the other oxygen in the rest of the molecules. In the past one of the great drawbacks was that the two oxygen atoms were always related by some symmetry element and the enolic hydrogen atom always lay on this symmetry element.

Excellent quality intensity data were obtained using a General Electric single crystal orienter. It was found that the compound crystallized in a noncentric space group thereby relieving the symmetry requirement of the two oxygen atoms. Although the enolic hydrogen was not observed directly, a close study of the anisotropic thermal parameters of the two oxygen atoms showed that the intramolecular hydrogen bond was indeed the symmetrical type.

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*This report is based on a Ph. D. thesis by Gordon Roy Engebretson submitted November, 1962, to Iowa State University, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

INTRODUCTION

The importance of the hydrogen bond is demonstrated by its effect on the physical properties of many compounds. The first mention of a hydrogen bond was made in an effort to explain the weakness of trimethylammonium hydroxide as a base (1). Hydrogen bonding was also discovered to be the basic cause of the relatively high degree of association of such liquids as water and hydrogen fluoride (2, 3). Compared to similar "hydrides" of their periodic neighbors this high degree of association of H_2O, HF, and NH_3 resulted in anomalously high boiling points, melting points, and dielectric constants (4). Existence of polymers in the vapor, liquid, and solid states of such compounds as HCN (5, 6) and HF (7, 8, 9) were attributed to hydrogen bonding. A structural investigation of ice showed that it had a more open structure than solid H_2S (10, 11, 12, 13, 14). The structure of ice was found to have each oxygen atom tetrahedrally surrounded by four other oxygen atoms. The oxygen atoms were spaced far enough apart to permit inclusion of a hydrogen atom. Pauling (15) concluded from a comparison of the properties of steam and ice that the hydrogen bond was unsymmetrical with each oxygen atom having two short, strong hydrogen bonds and two long, weak hydrogen bonds.

Pauling *et al*. (16, 17) after an investigation of the structures of amino acids and polypeptides, tried to deduce

stochastically the structure of proteins. They had found that hydrogen bonding and the planarity of the amide group were the determining factors in the simpler molecules, and they used these criteria in obtaining the configuration of proteins. In the α-helix form the protein molecule was found to consist of polypeptide chains coiling about a helical axis. Each planar amide group was bonded by a linear hydrogen bond to the third amide group in either direction from it along the polypeptide chain. The α-helix has been found in several proteins (18, 19). Two stable arrangements of hydrogen bonded extended polypeptide chains were found (20); the identity difference in the direction of the chain was found to differ by 0.05 Å. One form, called the parallel-chain pleated sheet, is thought to be the probable configuration of β-keratin, and there is some evidence that the other form, called the antiparallel-chain pleated sheet, has been shown to be the correct configuration of silk fibroin and synthetic poly-L-alanine (21, 22).

The formerly accepted structure of deoxyribosenucleic acid (DNA), the basic component of the nuclei of living cells and genes, was that proposed by Watson and Crick (23). Their model consisted of two chains forming a helical structure. The chains consisted of sugar groups linked by phosphate groups with planar purine and pyrimidine rings attached to the sugar groups and extending out from the chain. The two chains ran in opposite directions thereby satisfying the dyadic symmetry

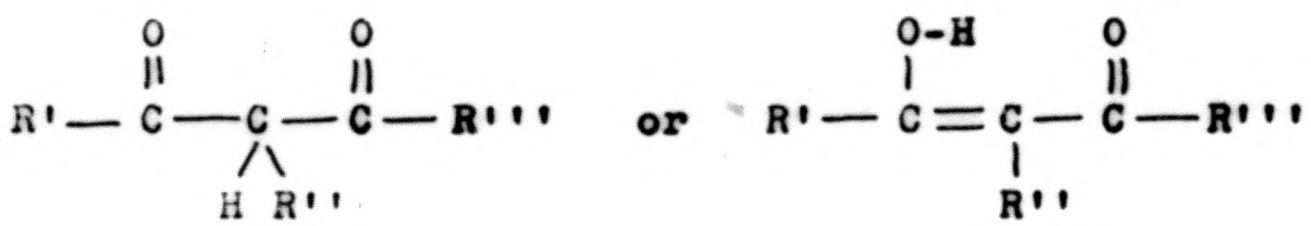
of the fiber axis. The purine and pyrimidine rings pointed inward towards and perpendicular to the fiber axis. The two chains were held together by hydrogen bonds from a purine residue of one chain to a pyrimidine residue of the other chain.

Investigations into the origin of the ferroelectric transition of such compounds as KH_2PO_4, KD_2PO_4, $ND_4D_2PO_4$, and Rochelles Salt (24, 25, 26) indicated that hydrogen bonding was a fundamental determinant of this transition. As an example, Frazer and Pepinsky found (27) that in the structure of KH_2PO_4 as they approached the Curie point from higher temperatures the elongated PO_4 tetrahedron assumed a somewhat more regular shape and the hydrogen bonds shortened. They suggested that the hydrogen bond shortening perpendicular to the dipole axis had the effect of destroying the equidistant arrangement of KO_8. This in turn caused the potassium ion to build up a preferential vibration parallel to the c-axis which induced a similar preferential vibration of the PO_4 ion. At the Curie point the potassium atom remained permanently displaced from its original position and exerted a polarizing influence on the O_4 tetrahedron. This polarizing effect caused the hydrogens to become more ordered and resulted in the observed ferroelectric transition. Thus in a wide variety of phenomena hydrogen bonding plays an important role. This study examines further the nature of very strong hydrogen bonding.

Hydrogen bonds are usually divided into two groups,

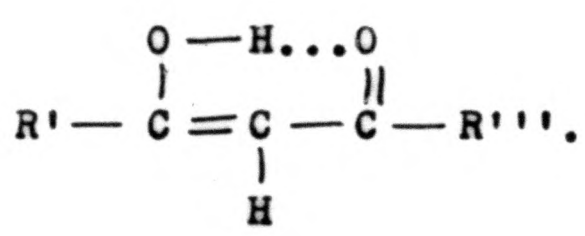
intermolecular hydrogen bonds where the bridging occurs between atoms of two different molecules, and intramolecular hydrogen bonds where the bridging is across atoms within a single molecule. The intramolecular hydrogen bonds are further subdivided into long and short bonds.

A common group of compounds which should form intramolelecular hydrogen bonds are the β-diketones in their enol form. This group of compounds can be represented by



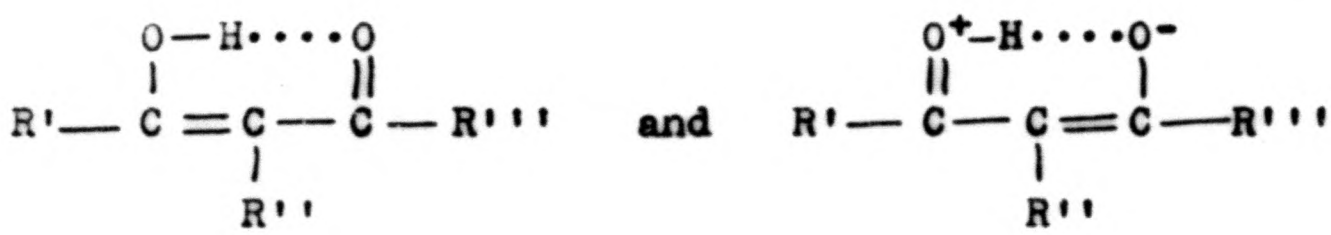
keto-form enol-form

where R', R'', and R''' may or may not be the same group. These compounds have received much attention from the spectroscopists, but their results proved to be conflicting and inconclusive. The simplest group of β-diketones investigated were the diaroylmethanes, where the R'' group is a hydrogen atom. In the enol form hydrogen bonding is expected as shown below:



The simplest diaroylmethane is dibenzoylmethane where R' and R''' are both phenyl groups. In diaroylmethanes the primary

question is whether or not the enol form with an intramolecular hydrogen bond really exists. Gordy (28) concluded in 1939 from chemical evidence that there was an enolic hydrogen bond formed. Kohlrausch (29) in 1934 claimed to show by Raman methods that complete enolization existed in dibenzoylmethane. Later, another investigation was made of dibenzoylmethane by Rasmussen *et al.* (30) and they also concluded that almost complete enolization existed. It was found that no infrared absorption band existed at 3333 cm.$^{-1}$ where the simple OH stretch occurs and that a weak band appeared at 2703 cm.$^{-1}$ No band was observed in the usual conjugated ketone region (1695 - 1672 cm.$^{-1}$), but a very strong band appeared at 1639 - 1538 cm.$^{-1}$ This latter band was attributed to resonance between the forms



where decrease in the CO double bond character accounted for the band shift and the increase in charge accounted for the intensity. Several other interpretations of the infrared spectra of dibenzoylmethane have been made. Bratož, Hadži, and Rossmy (31) assigned several bands as follows:

ν(OH) ca. 2700 ± 100 cm.$^{-1}$ broad and weak

δ(OH) (in plane) 1435 ± 35 cm.$^{-1}$

ν(CO) 1284 ± 24 cm.$^{-1}$

γ(OH) (out of plane) 948 ± 12 cm.$^{-1}$

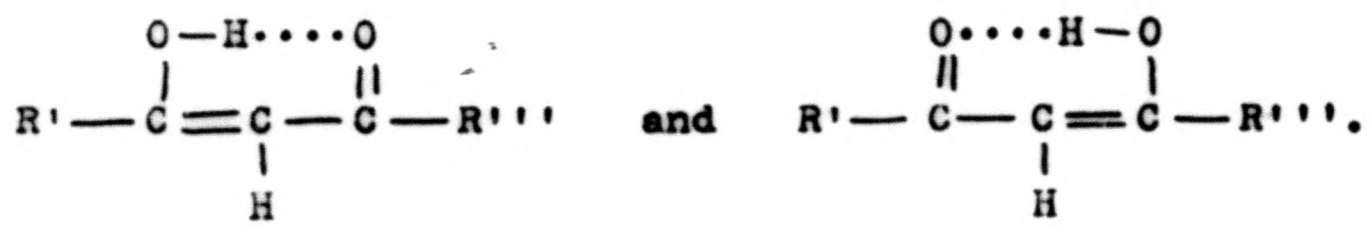
Park et al. (32) found a strong band at 1639 - 1587 cm.$^{-1}$ instead of 1851 - 1639 cm.$^{-1}$ which they attributed to a C=O group attached to an unsaturated methylene group. There are the conflicting reports of others who contend that there is no enolization in the β-diketones. The early work of Morton et al. (33) in 1934 and the work quoted by Barnes (34) in his paper on α- and β-diketones in which no spectroscopic evidence was found for a six membered chelated ring led these authors to believe that no enolization existed. Henecka (35) did not find evidence for either unchelated enols or diketones in his investigations. One of the latest works was that of Delany (36). He investigated eight diaroylmethanes and concluded that these β-diketones were almost completely enolized. He assigned the infrared absorption bands

OH	3521 - 3460 cm.$^{-1}$	(unenolized hydrogen)
OD	2674 - 2659 cm.$^{-1}$	(unenolized deuterium)
OH···O	2604 cm.$^{-1}$	
OD···O	2174 - 2083 cm.$^{-1}$	

So it can be seen that some confusion exists as to the interpretation of the infrared spectrum of β-diketones.

From these reports this author believes that the β-diketones are nearly 100 percent enolized. The question which remains is whether this intramolecular hydrogen bond is a symmetrical bond where the hydrogen atom lies exactly between the two oxygen atoms, or a statistical distribution of the two

forms



One method which has been employed to answer this question is X-ray crystallography. It has been used to study the structure of intramolecular hydrogen bonded compounds in an effort to explain their nature. In 1952 Rundle and Parasol (37) proposed a symmetrical intramolecular hydrogen bond for the dimethylglyoxime complex of nickel. Speakman (38) did a structural investigation of potassium hydrogen bisphenylacetate and found that the hydrogen atom lay on a 2-fold symmetry element. He concluded that the bond must be symmetrical. But Davis and Thomas (39) reported an infrared investigation of the latter compound and found that all the normal OH modes appeared, so they concluded that the bond was not symmetrical.

An interesting facet of this problem is that the hydrogen bond can appear to be symmetrical in two ways. Either the hydrogen atom lies exactly at the center of the bond with a large thermal amplitude in the direction of the line of centers of the bridged atoms, or two "half hydrogens" lay equidistant from the center of the bond in a double potential well (Figure 1) with a lesser thermal amplitude in the O-O direction. Both of these models are equivalent as far as the diffraction of X-rays is concerned. The hydrogen atom need not be at the midpoint of

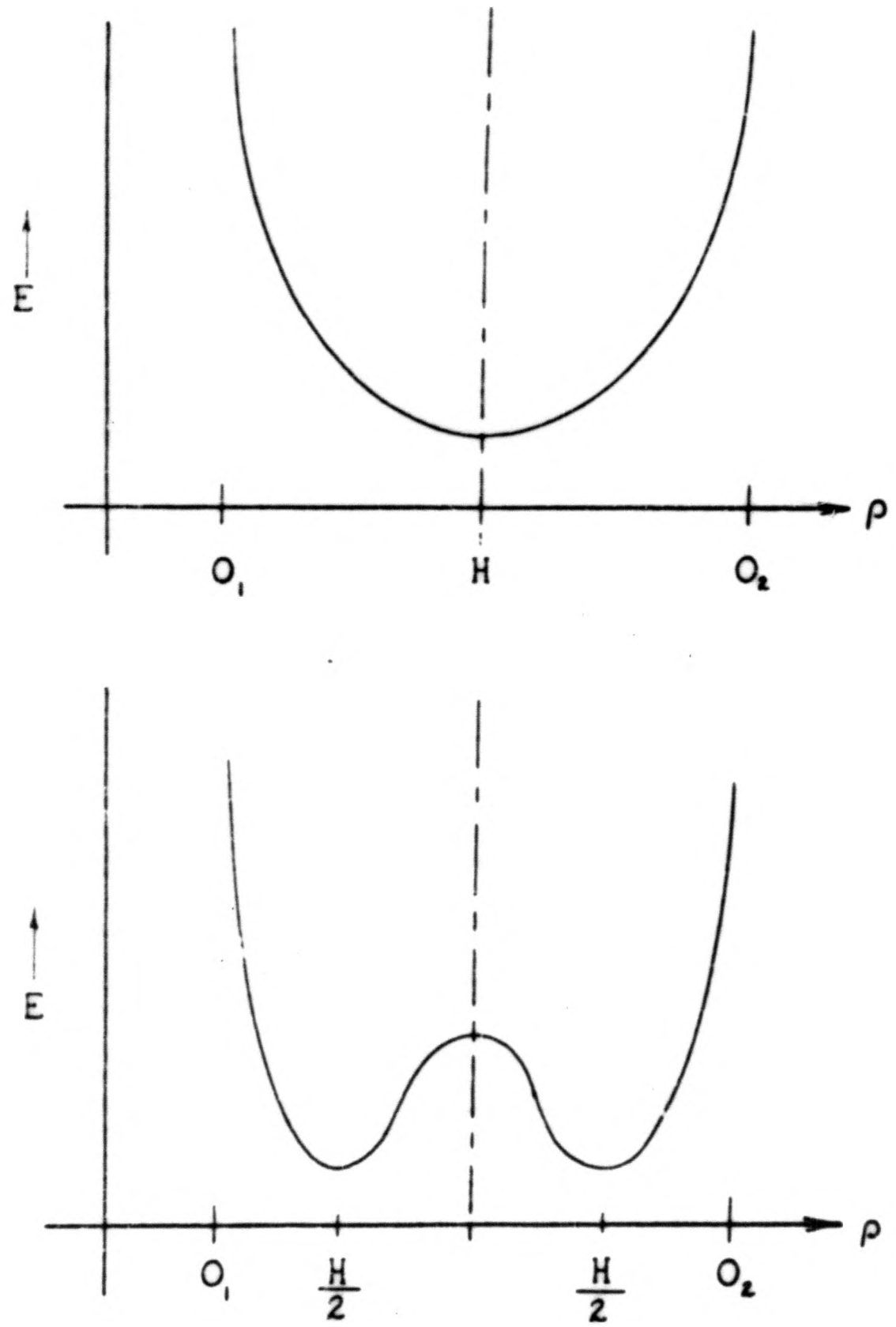


Figure 1. Schematic representation of hydrogen bond between two oxygen atoms a) single potential well b) double potential well

the line of centers of the bridged atoms, but may be above the line of centers. Several structures show this to be the case (40, 41, 42). The problem with an X-ray investigation is that the X-rays are scattered by the electrons surrounding each atom so it is evident that a hydrogen atom's scattering power is one-eighth the scattering power of an oxygen atom. To be able to find the hydrogen atom position one must have a method of "viewing" the hydrogen atom directly. With the advent of large nuclear reactors with a high neutron flux, neutron diffraction is becoming an exceedingly useful tool in this problem. The nucleii of the atoms do the scattering so hydrogen possesses about 80 percent of the scattering power of C, N, O, or F. While only a limited number of structural investigations have been carried out with neutron diffraction, the results so obtained are interesting.

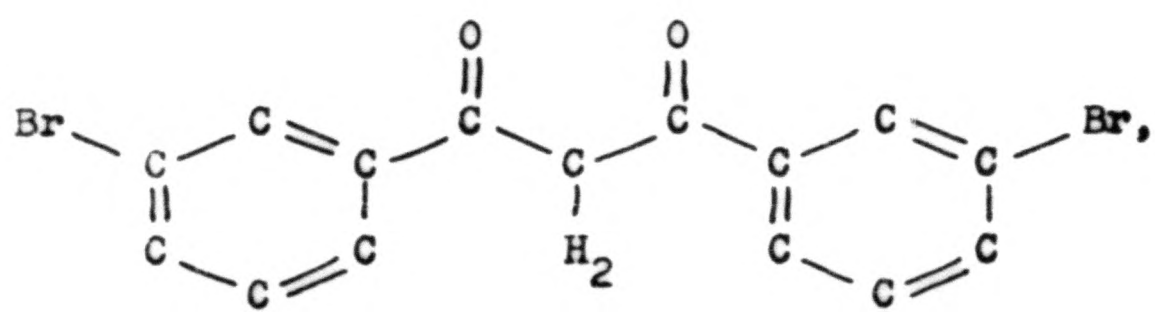
Bacon and Curry (43) redetermined the structure of potassium hydrogen bisphenylacetate in projection by neutron diffraction. They found the O-O distance to be 2.54 Å. If the true situation were the double well model, the OH bond length would have been about 1.07 Å. This left a resulting separation of 0.40 Å. between the two "half hydrogens" so that the hydrogens lay 0.20 Å. to each side of the center of symmetry. But the fourier projection showed a root-mean-square amplitude of 0.30 Å. for the hydrogen atom peak. The centered model seemed to be the likely choice.

A neutron diffraction investigation of potassium hydrogen maleate (44) was made in an effort to locate the true position of the hydrogen atom. A difference fourier showed the hydrogen atom to be directly between the two oxygen atoms. Least squares cycles were run first with the hydrogen atom exactly between the oxygen atoms and then the model in which two half hydrogens were placed 1.05 Å. from each oxygen atom. Both models yielded the same results so the authors could not say where the hydrogen atom lay. However, a study of the anisotropic thermal parameters of the hydrogen atom and the oxygen atoms showed that the displacement of the oxygen atoms was greater than that of the hydrogen. The authors stated that this was a very unusual situation for hydrogen containing crystals. They then concluded that the oxygen atoms were strongly bonded by the hydrogen and that "there exists a mode of correlated motion of considerable amplitude in which the oxygen atoms are displaced but the H is not..... We submit that at least a close approach to actual centering is implied by the foregoing interpretation."

Several other neutron studies of hydrogen-containing crystals have been made with a similar ambiguity as to the position of the hydrogen atom. Peterson and Levy (45) solved the structure of KH_2PO_4 by neutron methods and noticed that the hydrogen peak in the fourier was smeared out between the two oxygen atoms. A difference fourier did not resolve the ambiguity. They tried both the centered model and the double minimum model and found their data to be consistent for both.

Bacon and Pease (46) also did a neutron investigation of KH_2PO_4. They plotted the electron density between the two oxygen atoms and obtained a hydrogen profile which was very smeared out due to the thermal motion. Bacon and Curry (47) also found in the structure of sodium sesquicarbonate that the hydrogen atom from the water of crystallization lies on a center of symmetry. A difference fourier showed a smear in the O-O direction and these authors decided that the double minimum model fitted their data best. All indications are that low temperature neutron studies should make a significant contribution to solving the problem of exactly where the hydrogen atom is in an intramolecular hydrogen bond.

One of the latest contributions was in the area of X-ray crystallography where Williams, Dumke, and Rundle (48) solved the crystal structure of bis(meta-bromobenzoyl)methane. The formula of the compound is



and it was selected for study because its unit cell volume was one half that of dibenzoylmethane. The heavy bromine atom would help in the initial investigation. The intensity data were collected with a General Electric single crystal orienter in order to get the best data obtainable. In this case also it was

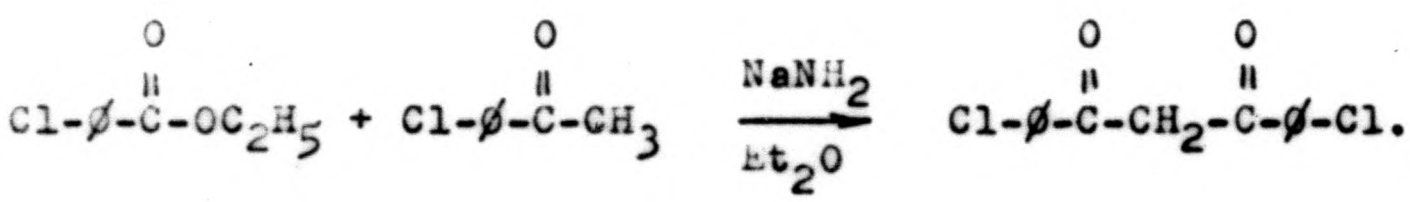
found that the hydrogen atom lay on a two fold symmetry element. But by studying the anisotropic thermal parameters of the oxygen atoms, Williams et al. concluded that because the root-mean-square amplitude parallel to the CO bond was low this indicated that there was no statistical randomness of the hydrogen atom position. The high thermal amplitude of the oxygen atoms out of the molecular plane suggested that they were warped out of the molecular plane. Unfortunately the intensity data were not of sufficient quality to obtain precise results. Also, the heavy bromine atom so dominated the structure that the distances between light atoms were not of the very highest accuracy.

The purpose of this dissertation is to reinvestigate the short intramolecular hydrogen bond in an effort to determine the hydrogen position. A structural investigation of a compound similar to bis(meta-bromobenzoyl)methane in number of atomic and thermal parameters but with a much lighter atom substituted for the bromine atom should give more precise interatomic distances and thermal parameters and hence a better interpretation of the short intramolecular hydrogen bond. The crystal structure of another intramolecular hydrogen bonded compound which does not require the hydrogen atom to be on a symmetry element should also help solve the ambiguity of the hydrogen position in short intramolecular hydrogen bonds. Dr. Rundle suggested solving the crystal structure of bis(meta-chlorobenzoyl)methane in hopes that the lighter chlorine atom would lead to more precise interatomic distances and thermal parameters than was obtained with bis(meta-bromobenzoyl)methane.

EXPERIMENTAL PROCEDURE

Preparation of the Crystal

Crystals of bis(meta-chlorobenzoyl)methane were prepared by a method similar to that used by W. G. Borduin (49) to prepare crystals of bis(meta-bromobenzoyl)methane, in this case a condensation of meta-chloroethylbenzoate and meta-chloroacetophenone in the presence of sodium amide. The reaction is



$$Cl\text{-}\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5 + Cl\text{-}\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightarrow[Et_2O]{NaNH_2} Cl\text{-}\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}\phi\text{-}Cl.$$

An ether suspension of sodium amide was prepared by reacting 1.5 grams of clean, dry sodium with 100 mls. of liquid ammonia. After stirring for 20 minutes the ammonia was allowed to evaporate and enough ether was added to keep the liquid level constant.

6.5 grams of meta-chloroacetophenone in 25 mls. of ether were added to the amide suspension over a period of a few minutes. After not longer than five minutes 10.5 grams of meta-chloroethylbenzoate in 25 mls. of ether were added slowly to the solution and the mixture was refluxed for two hours. The resulting gelatinous mixture was immediately cooled to room temperature in an ice bath. The cool mixture was poured into 150 mls. of water and neutralized with 0.5 N HCl and extracted with ether. The ether layer was separated and the ether then removed leaving white needle crystals and a brown oil. To

remove the oil, the residue was dissolved in 100 mls. of ether, then 200 mls. of two molar hot, filtered cupric acetate solution was added. A light-green, waxy coagulate of the copper complex of the β-diketone precipitated from the solution. The precipitate was washed twice with 100 mls. of petroleum ether and hydrolized in a solution of 250 mls. of 30 percent sulfuric acid and 150 mls. of ether. The hydrolysis did not proceed spontaneously so a few milliliters of concentrated sulfuric acid were added. The hydrolysis then proceeded readily. The ether layer was separated and the water layer extracted twice with 50 ml. portions of ether. The three ether portions were combined and dried over sodium sulfate for two hours. The ether was then allowed to evaporate and white needle crystals (m.p. 154 - 155°C.) remained. These crystals were then recrystallized from chloroform.

X-Ray Investigation

Rotation, zero, and first layer equi-inclination Weissenberg photographs were taken of a crystal rotating about its needle axis. The crystal was found to have orthorhombic symmetry. The axes were arbitrarily assigned and the extinctions were consistent with either of the space groups Pbma or $Pb2_1a$. The axes were permuted in order to obtain a space group listed in the International Tables for X-Ray Crystallography (50); namely, $Pca2_1$. Its centrosymmetric equivalent was Pcam.

Back reflection Weissenberg photographs were taken about

the a- and b-axes with CrK_{α} radiation, and lattice constants consistent with the choice of axes of space group $Pca2_1$ were found to be

$$a = 30.082 \pm 0.002 \text{ Å}.$$
$$b = 3.850 \pm 0.005 \text{ Å}.$$
$$c = 11.123 \pm 0.002 \text{ Å}.$$

The observed density of the crystals determined by the flotation method was 1.50 gms./cc. while the calculated density, assuming four molecules per unit cell and molecular formula $C_{15}H_{10}O_2Cl_2$, was 1.513 gms./cc.

Assuming the molecule to have the configuration represented in Figure 2 it was decided that the molecule lies nearly parallel to the (0,1,0) plane in order for the unit cell to accommodate four molecules. Since no overlap results in this projection it was decided to solve the structure in this projection initially.

It can be seen that the choice of the space group Pcam would not have been correct because this space group has the special four-fold symmetry

$$x,y,1/4; \quad \bar{x},\bar{y},3/4; \quad 1/2 + x,\bar{y},1/4; \quad 1/2 - x,y,3/4.$$

This symmetry demands that the entire molecule lay at z = 1/4 or z = 3/4, but this could not be, because the short axis of 3.850 Å. would have had to accommodate the width of the planar molecule. The width of the planar molecule is essentially that of a benzene ring. Including the Van der Waals radii of the

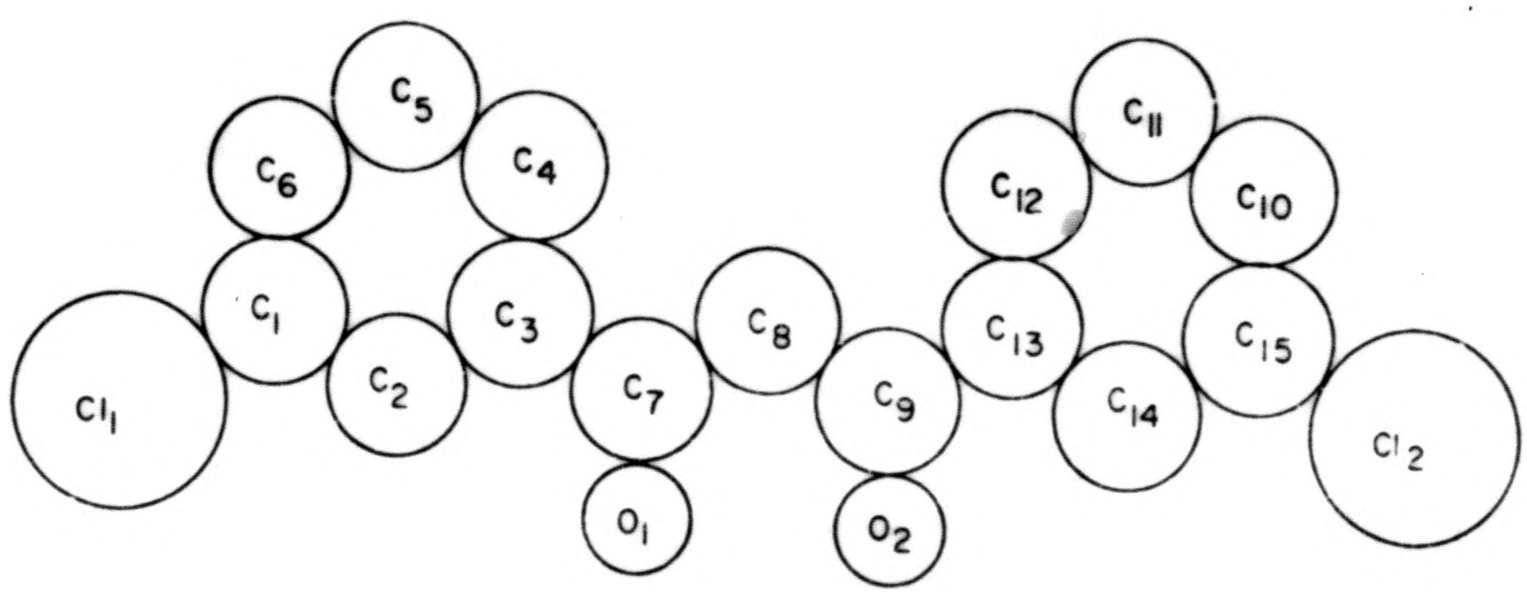


Figure 2. Postulated structure of bis(meta-chlorobenzoyl)methane molecule

terminal hydrogens this width is 5.18 Å. There is clearly not enough room to allow for the Van der Waals interactions of the atoms between unit cells. The choice of $Pca2_1$ as the space group is then seen to be correct.

Infrared Investigation

An infrared spectrum of the bis(meta-chlorobenzoyl)-methane crystals in the form of a KBr pellet (Figure 3) was obtained. The spectrum showed the "breathing" mode of the ring against the chlorine atom at 769 cm.$^{-1}$ and 689 cm.$^{-1}$ The carbonyl stretching mode was also observed at 1516 cm.$^{-1}$ and 1589 cm.$^{-1}$ The interpretation of the rest of the spectrum is more ambiguous as can be seen from pp. 5 - 6.

Collection of the X-Ray Intensity Data

Since it was desired to obtain accurate bond distances it was required that the intensity data be as accurate as possible. Visual judging of photographic film intensity data is generally conceded to be accurate to about 20 percent, while data taken with a scintillation counter is felt to be accurate to about 3 to 5 percent. On this basis it was decided to take scintillation counter data on the bis(meta-chlorobenzoyl)methane compound. A suitable crystal was selected using a polarizing microscope. Almost all of the crystals showed multicolored striae when viewed under polarized light, and at first it was thought that this indicated that the crystals were inferior,

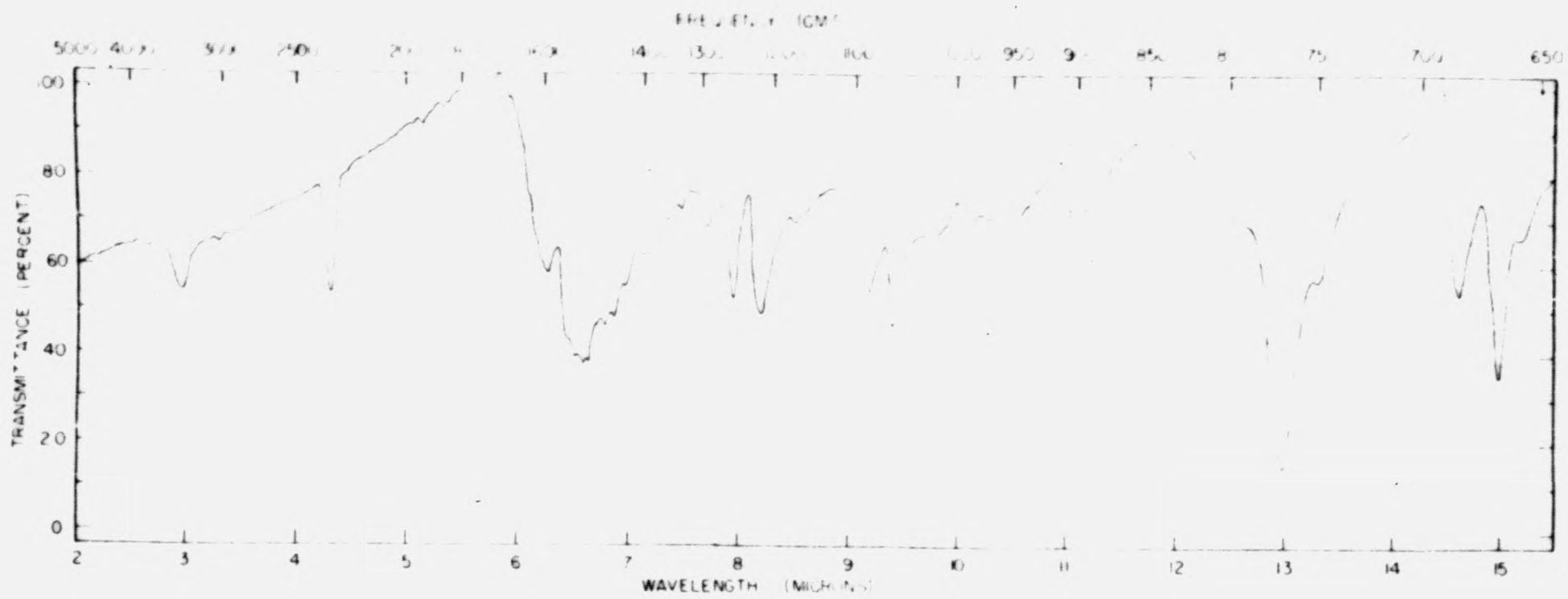


Figure 3. Infrared spectrum of KBr pellet of bis(meta-chlorobenzoyl)methane

but after taking many Weissenberg photographs of crystals with striae and a few without, no difference was found in the quality of the photographs, so it was concluded that the quality of the crystals was not dependent on the striae.

A suitable crystal was finally chosen which measured 115 microns along its needle axis and had an approximate trapezoidal cross section. The base of the trapezoid was 96.7 microns long with angles between the base and sides of 64.5° and 25.5°. The height of the trapezoid was found to be 35.3 microns. The crystal was mounted about its needle axis (b-axis) and aligned on a General Electric XRD-5 X-ray unit equipped with a SPG Spectrogoniometer and scintillation counter.

The Spectrogoniometer measures the intensity of diffracted X-rays in the equatorial plane of the instrument. This equatorial plane is defined (51) as the plane consisting of the center of the counter tube window, the center of the detector slit, the axis of the counter tube collimator system, the center of the specimen to be examined, the axis of the X-ray collimator system, and the center of the X-ray tube target. The "take-off" angle of the instrument is the angle between the plane of the X-ray tube target material and the emitted beam of X-rays. This angle lies in the equatorial plane of the instrument. A "take-off" angle of 0° gives a point source of X-rays, while higher and higher "take-off" angles give wider and wider line sources of X-rays if the hot line on the target is in the horizontal position.

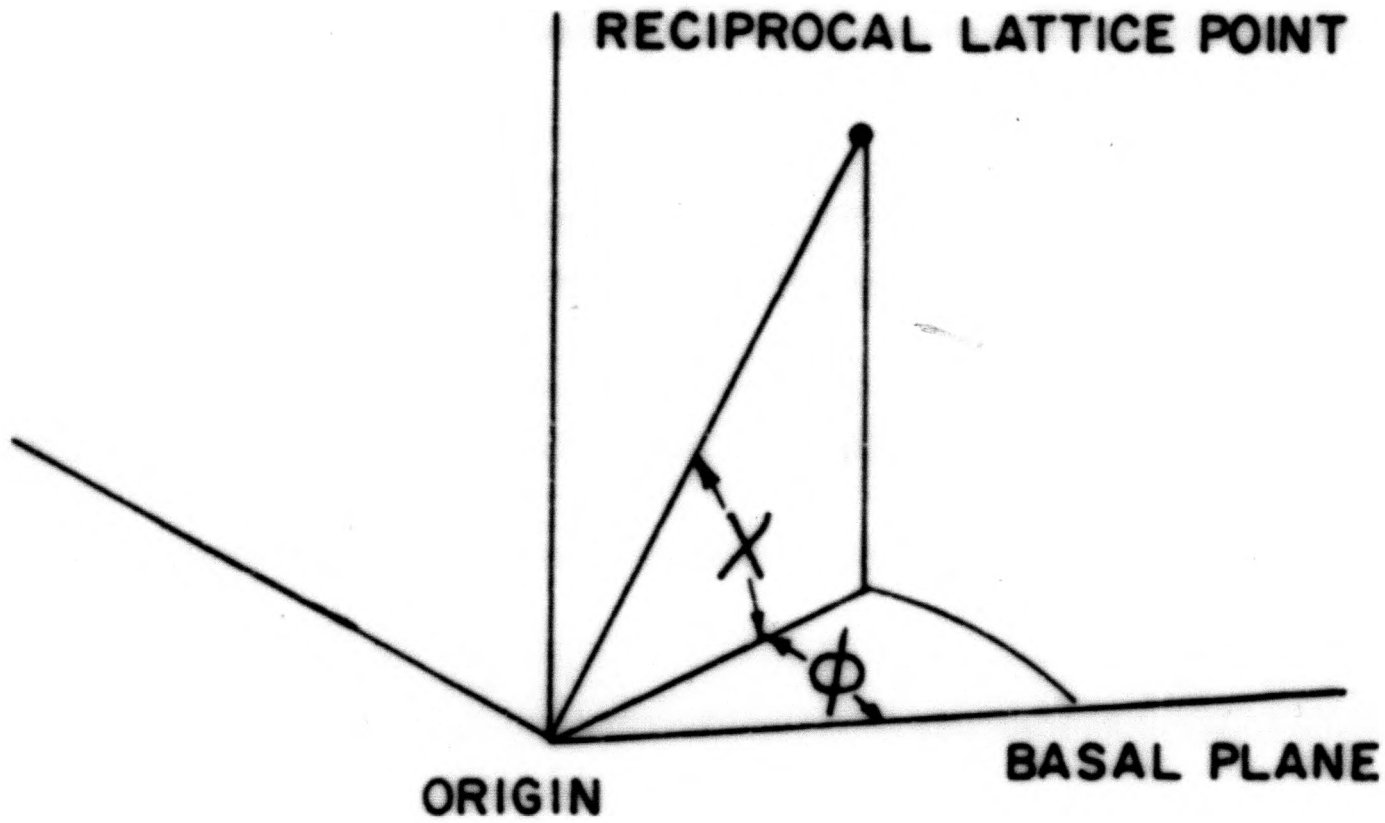
The angle chi (χ) (Figure 4) of the orienter was the angle between the basal plane of the crystal's reciprocal lattice and the equatorial plane of the instrument mentioned above. By adjustment of this angle it is possible to bring a reciprocal lattice point in the vertical plane down into the equatorial plane.

Consider a vector $\overline{S}_o$ emerging from the X-ray tube and impinging on a crystal. Let this vector have length $1/\lambda$, where λ is the wave length of the X-rays. The vector sum of the negative of this vector and the vector $\overline{S}$ emerging from the crystal, also of length $1/\lambda$, is a vector of length $\frac{2 \sin \theta}{\lambda}$, called the diffraction vector (Figure 5). These three vectors all lie in the equatorial plane. If this resultant vector is coincident with a reciprocal lattice vector both in direction and magnitude, a maximum X-ray diffraction results, as shown by von Laue. The angle between $\overline{S}_o$ and $\overline{S}$ is the scattering angle, 2θ, for the plane represented by the reciprocal lattice vector above where θ is the same as the Bragg diffraction angle defined by

$$n\lambda = 2d \sin\theta.$$

Adjustment of the angle phi (ϕ) of the instrument allows one to bring a reciprocal lattice point into the vertical plane (Figure 4). The adjustable instrument angle omega (ω) permits alignment of the vertical plane so it contains the diffraction vector $\overline{S} - \overline{S}_o$ (Figure 4).

a



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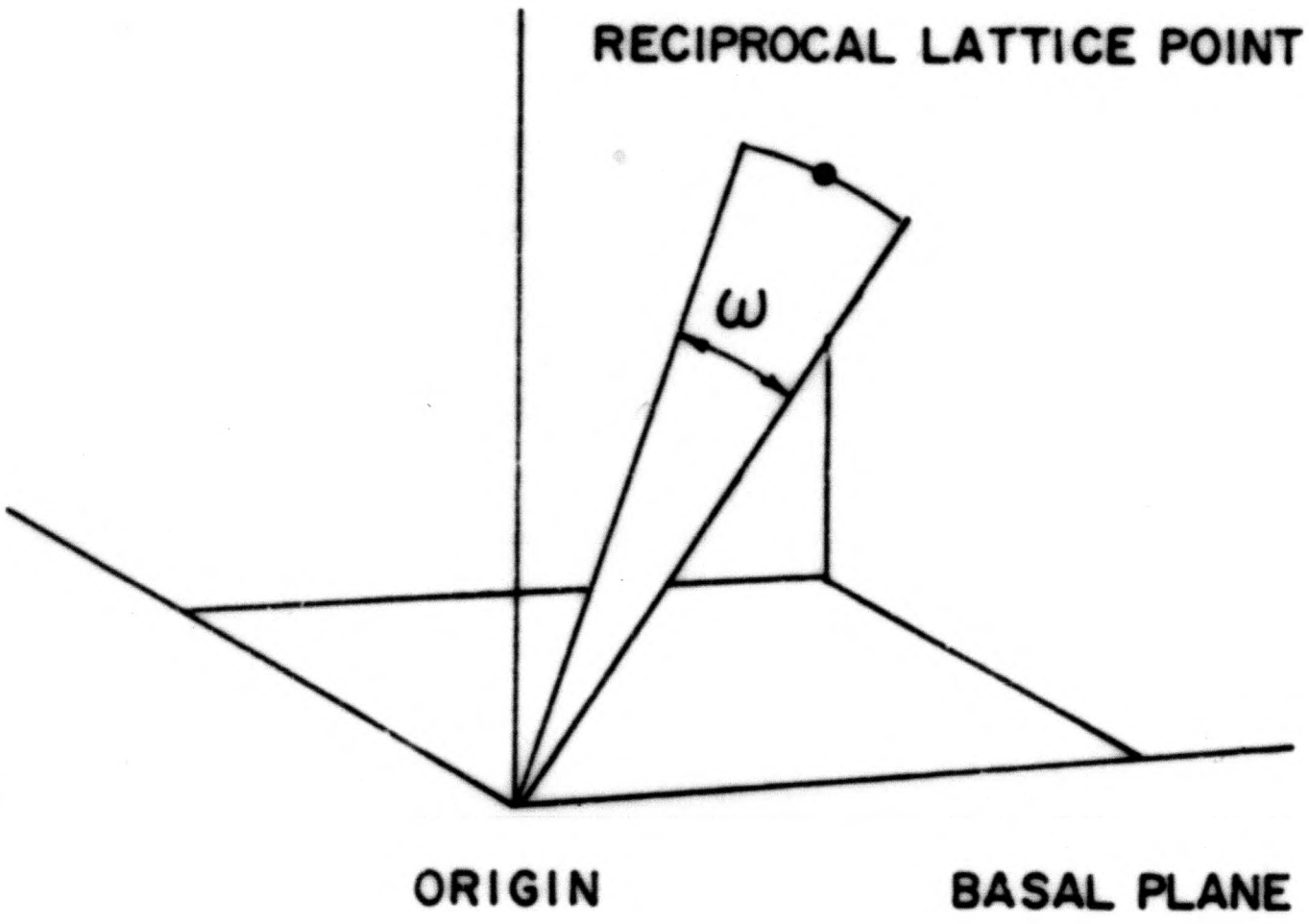

Figure 4. Schematic representation of General Electric single crystal orienter angles a) phi (φ) and chi (χ) b) omega (ω)

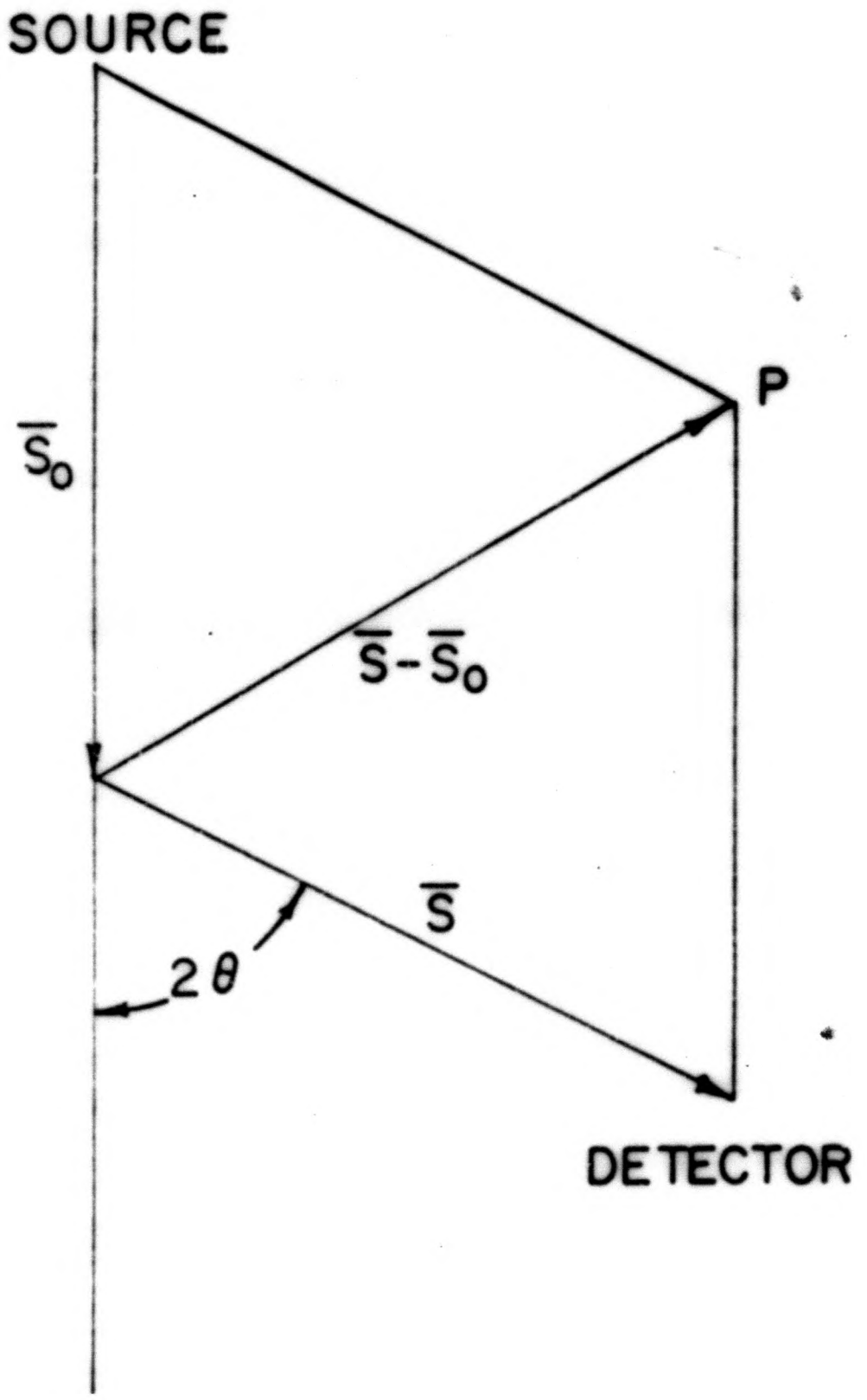

Figure 5. Schematic representation of the diffraction vector, $\overline{S} - \overline{S}_o$, to a reciprocal lattice point P showing its relation to the incident X-ray beam, $\overline{S}$, and the diffracted X-ray beam, $\overline{S}_o$

In the 2θ scan technique ϕ, χ, and 2θ are adjusted such that the conditions for maximum diffraction are satisfied. The 2θ angle is then reduced by 1.66°, so that now the terminus of the diffraction vector, $\overline{S} - \overline{S}_o$, is not coincident with the reciprocal lattice point of interest. 2θ is then allowed to increase slowly while the detector is activated. The increasing 2θ angle serves to move the terminus of the diffraction vector, $\overline{S} - \overline{S}_o$, through, and beyond the reciprocal lattice point of interest. The detector, meanwhile, has been detecting the diffracted X-rays from the reciprocal lattice point and a little to each side of it. The rate-meter chart gives a profile representation of the region scanned, and the scalar contains the integrated X-ray intensity of this region.

The intensity data were collected using a 3.33° 2θ scan with a "take-off" angle of 3.0°. CuK_{α} radiation was used with a Nickel foil filter and a 1.2° beam tunnel apparature. Intensity measurements for 1423 reflections were made in this manner. At the end of the collection of the intensity data, background intensity data were collected by starting at $\chi = 0^{\circ}$ and making a 3.33° 2θ scan every ten degrees in 2θ starting from as near zero as possible and going out to 150° in 2θ. This procedure was repeated every 10° in χ from 0° to 90°. It was found that above values of $\chi = 50^{\circ}$ and $2\theta = 130^{\circ}$ the X-ray beam was being reflected from the goniometer head into the detector thereby giving abnormally high background counts, but

happily no reflections fell into this region. Below those values of χ and 2θ it was found that the background was a function of 2θ only and independent of χ.

Treatment of the Data

Background correction

A program was written for the IBM 650 computer which made a linear interpolation in a table of background counts versus 2θ. Background counts were then calculated for all of the 1423 reflections in this manner.

During the taking of the intensity data if no peak was discernible over two small-scale divisions above the background trace on the rate-meter chart, the reflection was designated as an unobserved reflection.

Absorption correction

Assuming the crystal had the molecular formula $C_{15}H_{10}O_2Cl_2$ and density 1.513 gms./cc. the mass absorption coefficient was calculated to be

$$\mu = 45.05 \text{ cm.}^{-1} \ (52).$$

For the crystal used to obtain the intensity data the maximum and minimum μR values were calculated to be

$$\mu R_{max} = 0.518$$
$$\mu R_{min} = 0.132.$$

By Lambert's Law $\exp(-\mu R)$

is a measure of the transmittance of the crystal to the incident X-ray beam, giving a maximum and minimum transmittance value of 87.6 percent and 59.6 percent respectively. Thus the maximum absorption difference was 28.0 percent, and it was deemed necessary to make absorption corrections.

The program of Donald E. Williams[1] of this laboratory was used to make absorption corrections on the crystal. This program, titled ABCOR-I, was written for the Iowa State Cyclone computer. The program was restricted to the case in which the crystal was made up of n planes either parallel or perpendicular to the goniometer rotation axis. The equations of the planes forming the faces of the crystal were found by setting $\phi = \chi = 2\theta = 0^{\circ}$ on the single crystal orienter and referring the crystal to the dextral coordinate system (xyz) in which x points directly at the observer, y points into the X-ray beam collimator, and z points upward. It was found that the b-axis of the crystal coincided with the z-axis of this dextral coordinate system, and that the (1,0,1) face of the crystal made an angle of 142° with the x-axis. The equations of the planes making up the crystal faces were then expressed in the form

$$a_s x + b_s y + c_s z \pm d_s \geqq 0; \quad s = 1,2,\ldots\ldots,n$$

where a_s, b_s, c_s, and d_s are in millimeters and the sign of d_s

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[1]Williams, D. E. Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Private communication. 1960.

is chosen so as to make the indicated inequality valid.

The derivation of the following is due to Donald E. Williams[1]. The transmission factor is given by the expression

$$A(\phi,\chi,2\theta) = \frac{1}{V} \int_a^b \int_c^d \int_e^f \exp\left[-\mu(R_p + R_d)\right] dz\,dy\,dx$$

where ϕ, χ, 2θ are the instrument angles defined above, V is the volume of the crystal defined by the inequalities

$$a \leqq x \leqq b;\ c(x) \leqq y \leqq d(x);\ e(x,y) \leqq z \leqq f(x,y),$$

μ is the mass absorption coefficient, R_p is the distance traveled by the primary beam, and R_d is the distance traveled by the diffracted beam within the crystal. This integral may be approximated numerically by Gauss' method

$$A \cong \frac{1}{V} \sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{k=1}^{m} (b - a)\left[d(x_i) - c(x_i)\right]$$
$$\left[f(x_i,y_{ij}) - e(x_i,y_{ij})\right] P_i P_j P_k \exp\left\{-\mu\left[R_p(x_i,y_{ij},z_{ijk}) - R_d(x_i,y_{ij},z_{ijk})\right]\right\}$$

where $x_i = a + (b - a)g_i$

$$y_{ij} = c(x_i) + \left[d(x_i) - c(x_i)\right]g_j$$

$$z_{ijk} = e(x_i,y_{ij}) + \left[f(x_i,y_{ij}) - e(x_i,y_{ij})\right]g_k.$$

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[1]This information is given in D. E. Williams' private communication on the ABCOR-I program.

The constants g_i and P_i (53, 54) are functions of m only (Table 1).

Table 1. Values of g_i and P_i for selected values of m in Gauss' method of approximation of a triple integral

m	g_i	P_i
4	.0694 3184	.1739 2742
	.3300 0948	.3260 7258
	.6699 9052	.3260 7258
	.9305 6815	.1739 2742
5	.0469 1008	.1184 6344
	.2307 6534	.2393 1434
	.5000 0000	.2844 4444
	.7692 3466	.2393 2434
	.9530 8992	.1184 6344
7	.0254 4605	.0647 4249
	.1292 3441	.1398 5270
	.2970 7743	.1909 1503
	.5000 0000	.2089 7959
	.7029 2258	.1909 1503
	.8707 6560	.1398 5270
	.9745 5396	.0647 4249

Thus the $m + m^2 + m^3$ coordinates of the points at which the integrand is to be evaluated are easily obtained. These coordinates and the m^3 weights $(b - a)(d - c)(e - f)P_iP_jP_k$ depend only on m and the shape of the crystal.

The directed distance from a point (x_i, y_{ij}, z_{ijk}) inside the crystal to the $s^{\underline{th}}$ bounding plane of the crystal is

$$R_{ps} = \frac{d_s - a_s x_i - b_s y_{ij} - c_s z_{ijk}}{a_s \gamma_{px} + b_s \gamma_{py} + c_s \gamma_{pz}}$$

where γ_{px}, γ_{py}, and γ_{pz} are the direction cosines of the reverse primary beam vector. Similarly we have an expression for the diffracted beam vector where γ_{dx}, γ_{dy}, and γ_{dz} are direction cosines of the diffracted beam vector. The correct values of R_p and R_d are the smallest positive values in each n-fold set.

If the crystal space, (xyz), mentioned above is defined to coincide with the tabletop space, (uvw), when $\phi = \chi = 2\theta = 0^\circ$, the direction cosines of the tabletop space may be transformed to the direction cosines of the crystal space by the following matrix equation:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\chi & 0 & -\sin\chi \\ 0 & 1 & 0 \\ \sin\chi & 0 & \cos\chi \end{pmatrix} \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix}.$$

If the direction cosines of the reverse primary beam vector are (0,1,0), then the direction cosines of the diffracted beam vector are (sin 2θ, -cos 2θ, 0) in (uvw) space. Substituting into the matrix equation yields the following equations for the direction cosines:

$$\gamma_{px} = \cos\phi \cos\chi \sin\theta - \sin\phi \cos\theta$$
$$\gamma_{py} = \sin\phi \cos\chi \sin\theta + \cos\phi \cos\theta$$
$$\gamma_{pz} = \gamma_{dz} = \sin\chi \sin\theta$$
$$\gamma_{dx} = \cos\phi \cos\chi \sin\theta + \sin\phi \cos\theta$$
$$\gamma_{dz} = \sin\phi \cos\chi \sin\theta - \cos\phi \cos\theta.$$

The distances R_p and R_d may now be found; the value of the

integrand may then be found and substituted into Gauss' formula to obtain the transmission factor $A(\phi,\chi,2\theta)$.

The greater the value of m, the better Gauss' approximation to the triple integral. But as m gets large the calculation time of the approximation becomes prohibitive.

The program was run for several calculated settings of ϕ, χ, and 2θ which gave maximum and minimum path lengths for the primary and diffracted beams to travel in the crystal. The calculation was run for values of m = 7 and m = 4. For the same set of orienter angles the difference in calculated absorption coefficients ran between 3 and 6 percent. A comparison was then made between the calculations when the values of m were 7 and 5; it was then found that the difference in absorption coefficients was less than 3 percent. Absorption coefficients were then calculated for all observed reflections with a value of m = 5 in Gauss' approximation.

In order to obtain transmission factors for unobserved reflections a plot of transmission factor versus $(\chi + 2\theta)$ was made for the observed reflections. A best fit curve through these points was used to make up a table of transmission factor versus $(\chi + 2\theta)$ for every degree in $(\chi + 2\theta)$. This table was then used to obtain a transmission factor for each unobserved reflection using a linear interpolation program on an IBM 650 computer. The entire intensity data were then divided by their respective transmission factors to give the absorption

corrected intensity for each reflection.

Treatment of unobserved reflections

The demanded requirement that a reflection be significant, i.e., observed, was that the observed intensity be three times greater than its standard deviation

$$\text{Intensity} = [C_t - C_b] \geqq 3\sigma(C_t - C_b)$$

where C_t was the total counts of the scalar due to the integrated intensity of the reflection, C_b was the scalar counts due to the background of the reflection and $\sigma(C_t - C_b)$ was the standard deviation of the intensity. Substituting the expression for the standard deviation of the intensity

$$(C_t - C_b) \geqq 3\sqrt{\sigma^2(C_t) + \sigma^2(C_b)}$$

or

$$\geqq 3\sqrt{C_t + C_b}.$$

If $[C_t - C_b]$ is to be significant, we must have the condition that

$$[C_t - C_b] \geqq I_{min}$$

where I_{min} is the minimum number of counts over and above the background counts which one is able to detect. In the limit

$$3\sqrt{C_t + C_b} = I_{min},$$

but C_t approaches C_b in the limit, therefore, since

$$I_{min} = k\ C_b$$

where k is some experimental constant

$$k\ C_b = 3\sqrt{2C_b}$$

therefore, $$k = 3\sqrt{2} / \sqrt{C_b}.$$

The constant k was calculated for each reflection and if

$$I_{obs} > k\ C_b,$$

the reflection was treated as an observed reflection, unobserved otherwise.

All the unobserved reflections were treated using Hamilton's method (55). Hamilton stated that the most probable intensity of an unobserved reflection, μ, was

$$I_{min} / 2 \quad \text{and} \quad I_{min} / 3$$

for the noncentrosymmetric and centrosymmetric cases respectively. Hamilton also stated that the standard deviations of the intensities for these two cases were

$$\sigma^2(I) = 4\ I^2_{min} / 45$$

and $$\sigma^2(I) = I^2_{min} / 12$$

respectively. The formula for the standard deviation of the structure factors for the unobserved reflections was given by

$$\sigma(F) = \frac{\sigma(I)}{2\mu}\ (F).$$

Substituting the proper values for μ and $\sigma(I)$ given above, the respective formulas for the centrosymmetric and noncentrosymmetric cases were

$$\sigma(F) = \frac{\sigma(I)}{2\mu} (F) = .4472 (F)$$

$$\sigma(F) = \frac{\sigma(I)}{2\mu} (F) = .2886 (F)$$

where now

$$F = \sqrt{\frac{k\ C_b}{LP}}$$

where LP is the equatorial Lorentz-Polarization correction

$$LP = \frac{1 + \cos^2 2\theta.}{4 \sin\theta \cos\theta}$$

A subroutine was written for the IBM 650 computer which was incorporated into a modified version of the Lorentz-Polarization correction program, INCOR-I, of Zalkin and Jones[1]. This subroutine calculated the value of k for each reflection, then determined whether the reflection was to be treated as an observed or unobserved reflection.

For the case in which the reflections were observed the formula used to calculate the standard deviation of the structure factor was

$$\sigma(F) = \frac{\sigma(I)}{2\ I} (F)$$

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[1]Zalkin, A., and Jones, R. E. Department of Chemistry, University of California, Berkeley, California. Private communication. ca.1958.

where I was the intensity corrected for LP and absorption, and $\sigma(I)$ was defined by

$$\sigma^2(I) = C_t + C_b + (.xx\ C_b)^2 + (.yy\ I)^2$$

where C_t, C_b, and I were defined above, and .xx and .yy were confidence values placed on the individual quantities, i.e., if it was felt that the background data were good to 5 percent, .xx = .05, etc. A value of .05 was used in the calculation for .xx and .yy.

Structural Investigations

The observed reflections were used to calculate a Patterson projection onto the (0,1,0) plane (Figure 6) and a three dimensional Patterson map. The chlorine Harker peaks were found to have coordinates

$$(\pm 2x, -2y, 1/2);\ (1/2 \pm 2x, 0, 1/2);\ (1/2, \pm 2y, 0).$$

The Patterson peak between the two chlorine atoms at the opposite ends of the molecule was not evident from the Patterson projection onto (0,1,0).

It was decided to calculate a fourier transform in an effort to find the angular orientation of the molecule in the unit cell. First a weighted reciprocal lattice was constructed (Figure 7). This was done (56) by dividing the absolute magnitude of each (h,0,ℓ) observed structure factor by the absolute magnitude of the largest observed structure factor in

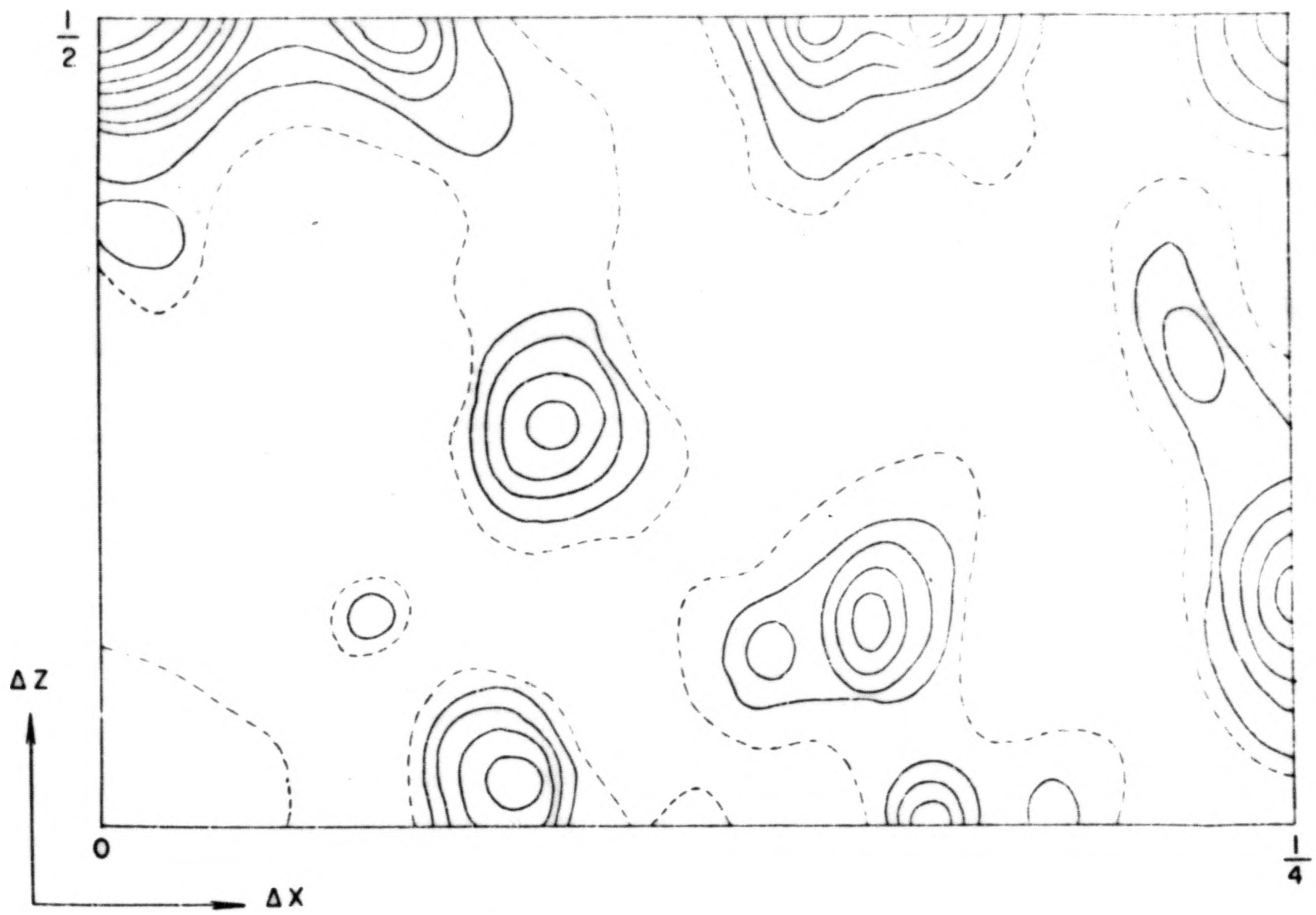


Figure 6. Asymmetric unit of the Patterson projection onto the (0,1,0) plane of bis(meta-chlorobenzoyl)methane. Dashed lines are the arbitrary zero contours

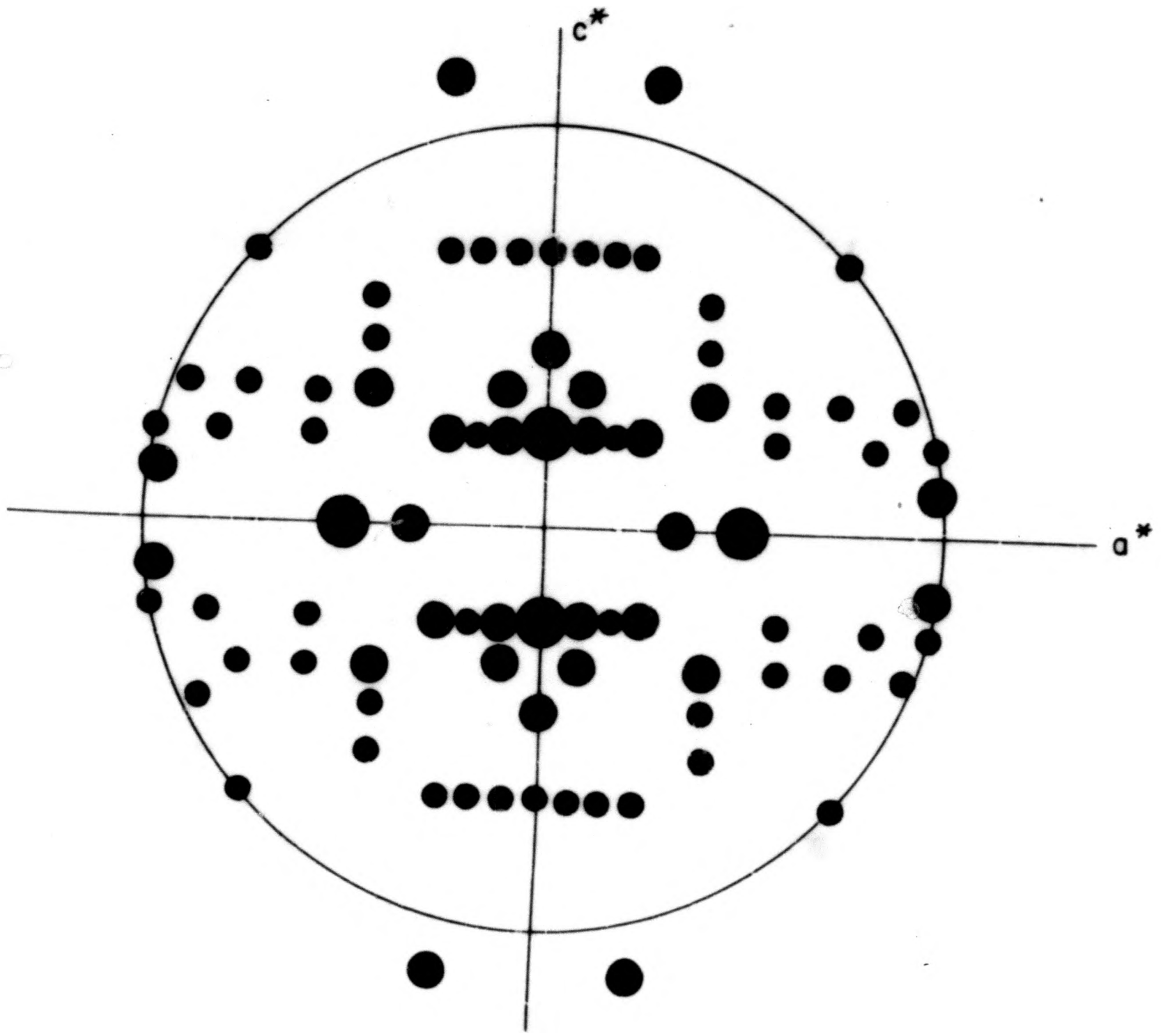


Figure 7. Weighted reciprocal lattice of the [h, o, ℓ] zone of bis (meta-chlorobenzoyl) methane.

that zone. The reflections were then divided into groups according to the value of the ratio of their structure factor to the largest valued structure factor

0.0-0.1; 0.1-0.3; 0.3-0.5; 0.5-0.7; 0.7-0.9; 0.9-1.0.

The first two groups were omitted for clarity. Each reflection was then represented by a spot on a reciprocal space coordinate system; the area of the spot was proportional to the value of the indicated structure factor ratio. The "benzene circle" was defined as the locus to which a benzene ring would transform if the plane of the benzene ring was exactly parallel to the plane of the "benzene circle"; the radius of this circle was 0.8 $\mathring{A}^{-1}$. A benzene ring would then show six prominant peaks on the "benzene circle" if the planes of both were parallel. If the plane of the benzene ring was tilted at an angle to the plane of the "benzene circle," the projection of the benzene ring would contract perpendicular to the axis of rotation and, therefore, the benzene ring transform would expand in this direction an amount equal to the secant of the angle of tilt.

To obtain an accurate fourier transform one should have considered all the molecules in the unit cell, but it was decided to attempt an interpretation of the weighted reciprocal lattice using only one molecule instead of four. Since the molecule possesses mirror symmetry only half of the molecule had to be specified. Half of the molecule was drawn to scale in the xz-plane parallel to the x-axis, and the x- and z-coordinates in $\mathring{A}$ of each atom were obtained. For mirror symmetry

perpendicular to the x-axis at x = 0 the derivation of the fourier transform expression was as follows:

$$G_j = f_j \exp\{2\pi i \left[a^* x_j + c^* z_j\right]\} + f_j \exp\{2\pi i \left[a^*(-x_j) + c^* z_j\right]\}$$

where G_j was the contribution of the jth atom to the total fourier transform, f_j was the scattering factor of the jth atom, a^* and c^* were the coordinates of the point in reciprocal space at which the fourier transform was to be calculated, and x_j and z_j were the real space coordinates of the jth atom in Å. The expression for the total transform was

$$G = \sum_{j=1}^{N/2} f_j \exp(2\pi i c^* z_j)\left[\exp(2\pi i a^* x_j) + \exp(-2\pi i a^* x_j)\right]$$

$$G = \sum_{j=1}^{N/2} f_j \exp(2\pi i c^* z_j)\left[\cos 2\pi a^* x_j + i \sin 2\pi a^* x_j + \cos 2\pi a^* x_j - i \sin 2\pi a^* x_j\right]$$

$$G = \sum_{j=1}^{N/2} f_j \exp(2\pi i c^* z_j)\left[2 \cos 2\pi a^* x_j\right]$$

$$G = \sum_{j=1}^{N/2} f_j \left[\cos 2\pi c^* z_j + i \sin 2\pi c^* z_j\right]\left[2 \cos 2\pi a^* x_j\right]$$

$$G = \sum_{j=1}^{N/2} 2f_j \left[\cos 2\pi a^* x_j \cos 2\pi c^* z_j + i \cos 2\pi a^* x_j \sin 2\pi c^* z_j\right].$$

This function G was then calculated for 200 reciprocal lattice points in the first quadrant of the [0,1,0] zone in reciprocal space, and the results were plotted on the same scale as the

weighted reciprocal lattice (Figure 8). For an indication of the angular orientation of the benzene ring, peaks were sought on the "benzene circle." Comparing peaks on the "benzene circles" of the weighted reciprocal lattice and the fourier transform it was seen that if the fourier transform was rotated 13° about an axis perpendicular to the plane of the paper, better agreement of peaks both near the "benzene circle" and in the interior would result. Also, if the molecule was tilted about 24° out of the plane of the paper, the peaks would move off of the "benzene circle." The results of this calculation are shown in Figure 9. Most of the features of the weighted reciprocal lattice were in agreement with those of the fourier transform, hence it was concluded that these angles must approximate the actual angular orientation of the molecule in the unit cell. This rotation of 13° leads one to conclude that the peak on the [0,1,0] Patterson projection at $\Delta x = .25$, $\Delta z = .14$ was the peak due to parallel carbon-carbon vectors between the two benzene rings of the molecule. These peaks were 24-fold degenerate due to the four molecules per unit cell and six carbon-carbon interactions per molecule. This peak, the strongest on the Patterson map, then, was not due to the heavy atom interaction.

To check on the value of 24° for the tilt of the molecule out of the xz-plane, a section of the three dimensional Patterson was studied at $\Delta x = .25$ (Figure 10). Taking the Δx coordinate from the [0,1,0] Patterson map and looking at this

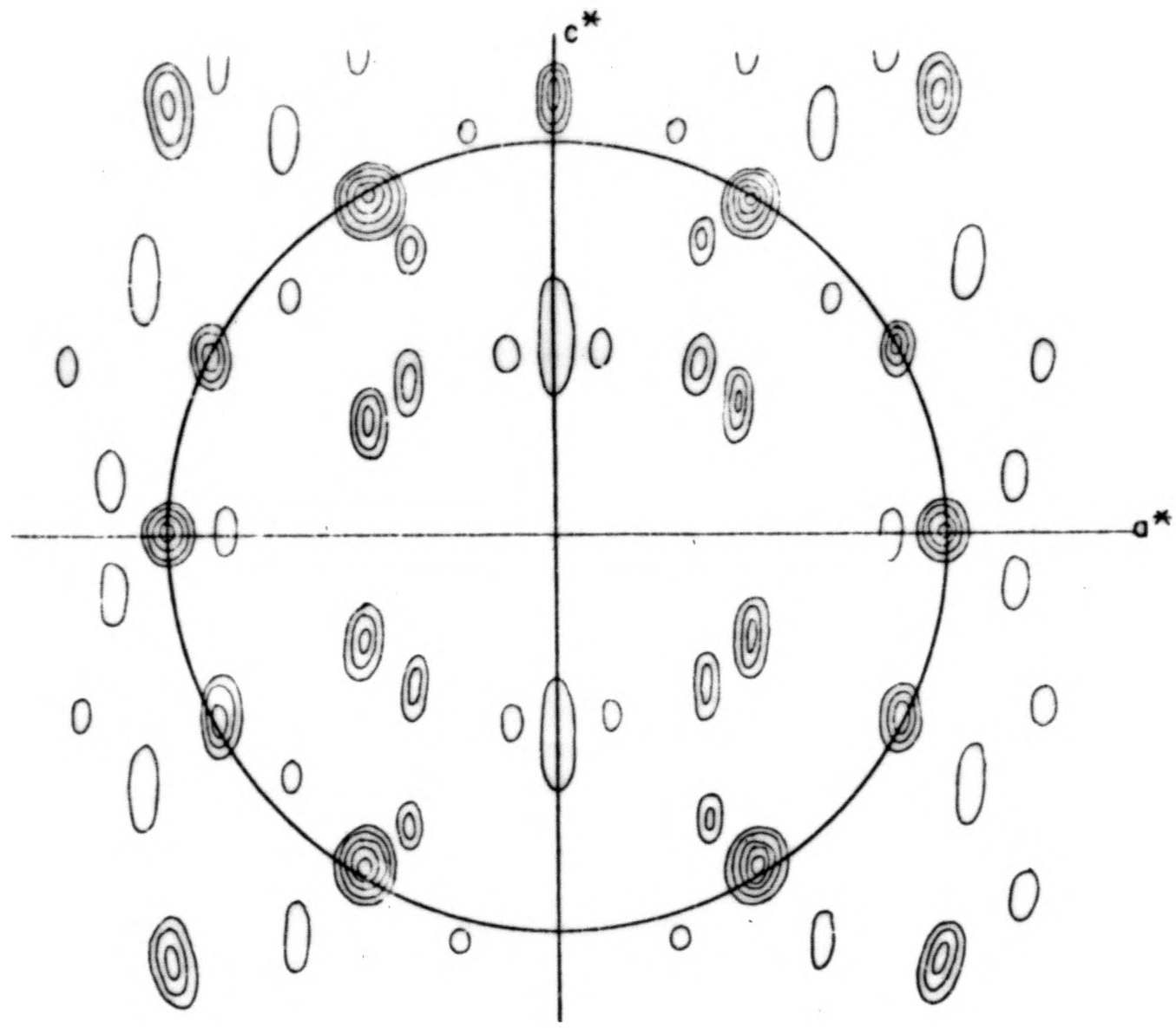


Figure 8. Fourier transform of the (h,0,ℓ) data for bis(meta-chlorobenzoyl)-methane with the length of the molecule parallel to the real space x-axis and the molecule lying in the (0,1,0) plane. Circle is the "benzene circle"

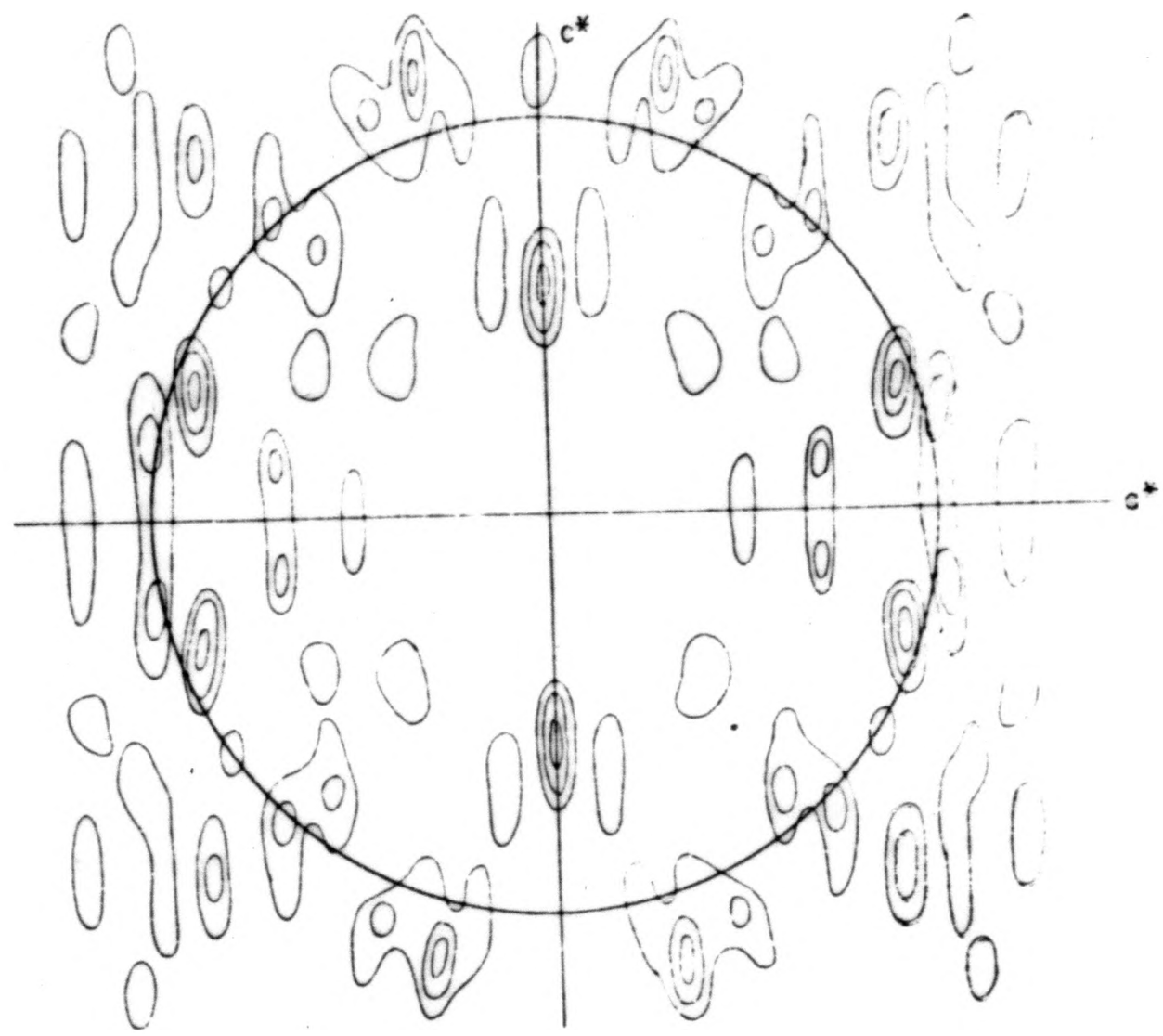


Figure 9. Fourier transform of the (h,0,ℓ) data for bis(meta-chlorobenzoyl)-methane with the length of the molecule tilted 13° to the real space x-axis and the molecule tilted 24° out of the (0,1,0) plane. Circle is the "benzene circle"

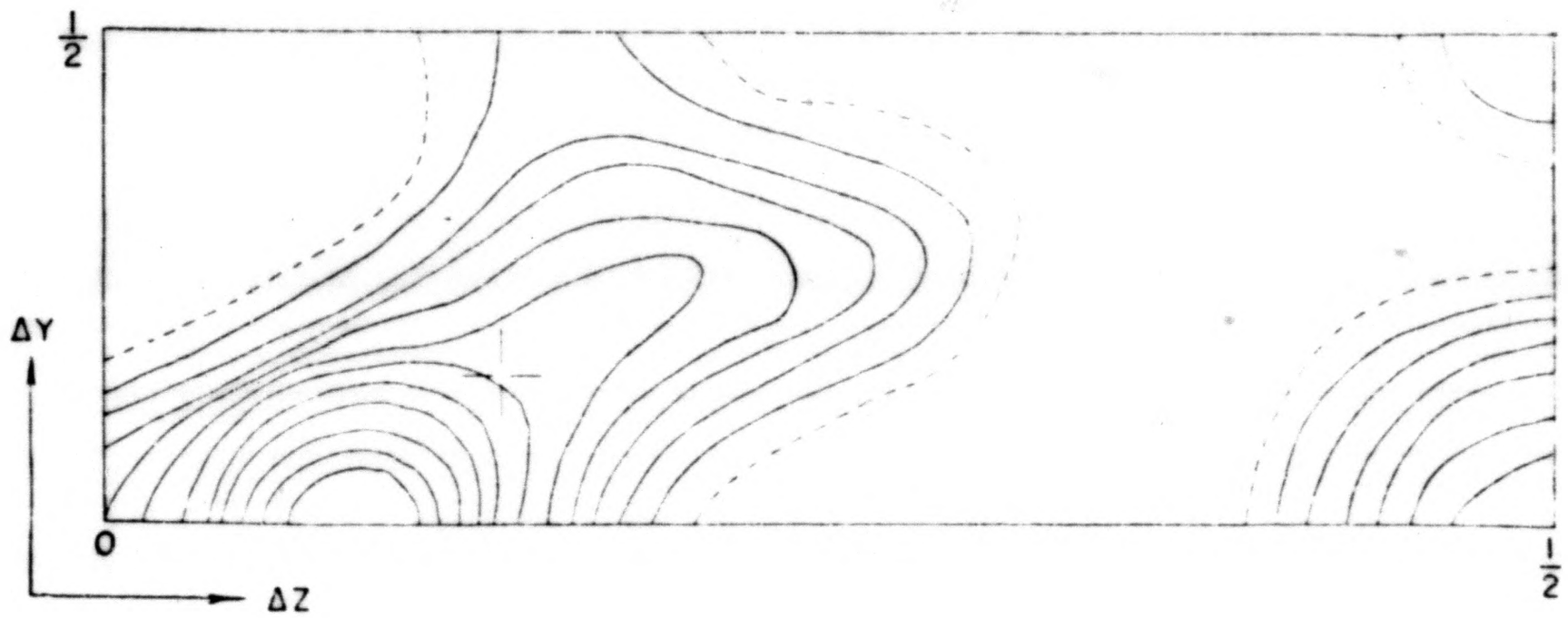


Figure 10. Three dimensional Patterson section at $\Delta x = 0.25$ with dashed arbitrary zero contours. Cross indicates 24-fold degenerate peak due to overlap of parallel carbon-carbon vectors from similar carbon atoms in the two benzene rings in a molecule of bis(meta-chlorobenzoyl)methane. The peak at $\Delta y = 0$, $\Delta z = .0843$ is the peak due to Cl_1O_2 vectors, and the peak at $\Delta y = 0$, $\Delta z = .5$ is the peak due to Cl_2Cl_1' vector, where Cl_1' is Cl_1 transformed to $\frac{1}{2} - x, y, \frac{1}{2} + z$

value on the (.25,Δy,Δz) section it was found that the out-of plane tilt was about 20.6°.

Initially the two chlorine atoms and two oxygen atoms were used to calculate least squares structure factor refinements of the (h,0,ℓ) data using the IBM 704 least squares program of Busing and Levy (57). Subsequent least squares cycles and fourier maps lead to the refinement of the x and z positional parameters and β_{11}, β_{13}, β_{33} anisotropic thermal parameters of all nineteen atoms in the molecule in the [0,1,0] projection, where the form of the anisotropic temperature factor was

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}\ell^2 - 2\beta_{12}hk - 2\beta_{13}h\ell - 2\beta_{23}k\ell).$$

Busing's program was modified somewhat so as to reject reflections with

$$\frac{|F_o - F_c|}{\sigma(F_o)} \geqq 6.0,$$

where F_o was the observed structure factor of the reflection, F_c was the calculated structure factor, and $\sigma(F_o)$ was the standard deviation of the observed structure factor, from the setting up of the normal equations in the least squares method. This was done to insure that erroneously recorded, or somehow otherwise adversely affected reflections did not influence the parameter shifts. Normally a value of

$$\frac{|F_o - F_c|}{\sigma(F_o)} = 3.0$$

gives a 99 percent confidence limit on the statistical data, so a value of the above ratio of 6.0 or greater must have been due to some mistake in working up the data, and not just statistical error; eleven such reflections out of 182 total were rejected in the (h,0,ℓ) data. The final agreement factor or R value defined by

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$$

obtained was .057 and the weighted R value was .087. Also, the value of

$$\sqrt{\frac{\sum w(F_o - F_c)^2}{M - N}} = 2.706$$

where $\sqrt{w} = \frac{1}{\sigma(F_o)}$, M was the number of reflections in the calculation, and N was the number of parameters varied. The fourier map of the asymmetric unit is shown in Figure 11.

Having the refined x and z coordinates of the nineteen atoms the next step was to refine the three dimensional data. The angle of tilt of the molecule out of the xz-plane had previously been found to be about 20°. To obtain the y-translation of the chlorine atoms the $\Delta x = .0875$ section of the three dimensional Patterson map was studied (Figure 12). The cross indicates the nonequivalent chlorine-chlorine vector between two molecules. From this, y-parameters were assigned to all nineteen atoms and several least squares cycles were run.

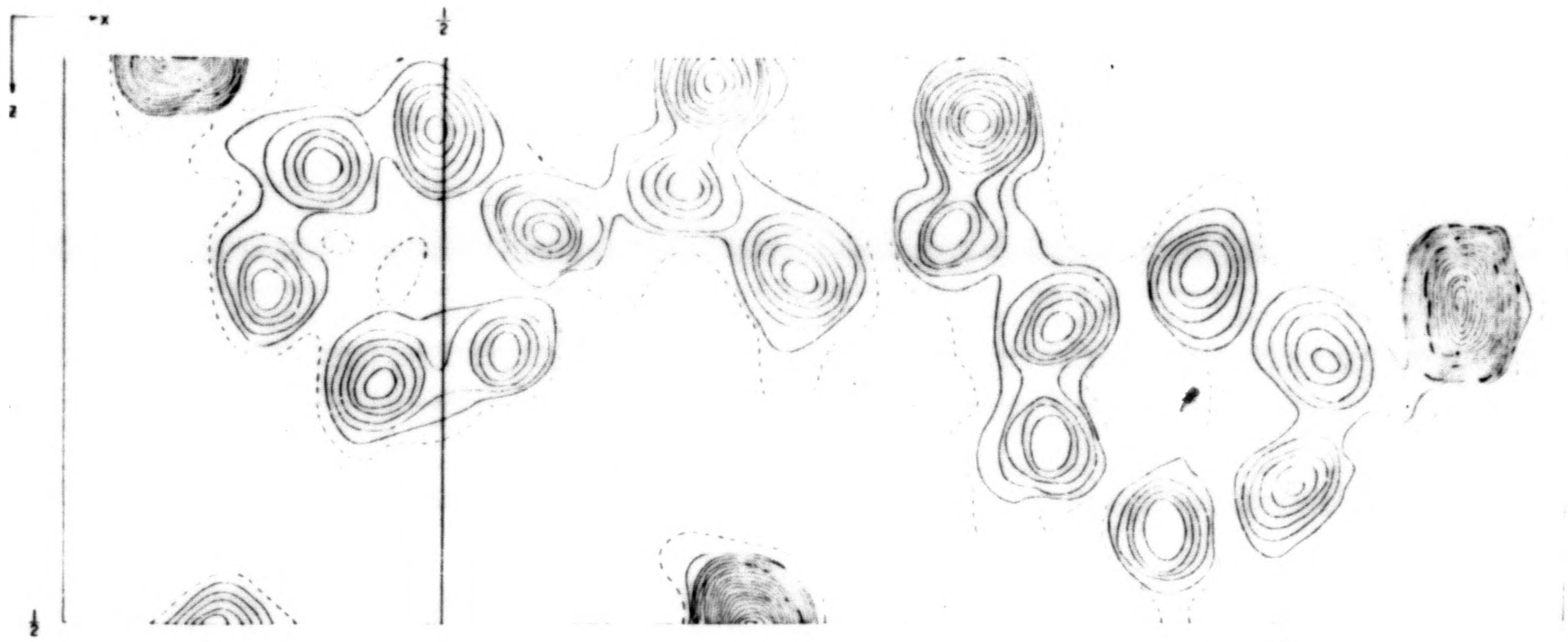


Figure 11. Fourier map of asymmetric unit of bis(meta-chlorobenzoyl)methane projected onto (0,1,0) plane. Contours are in $e^-/Å.^2$ with dashed $1e^-/Å.^2$ contour

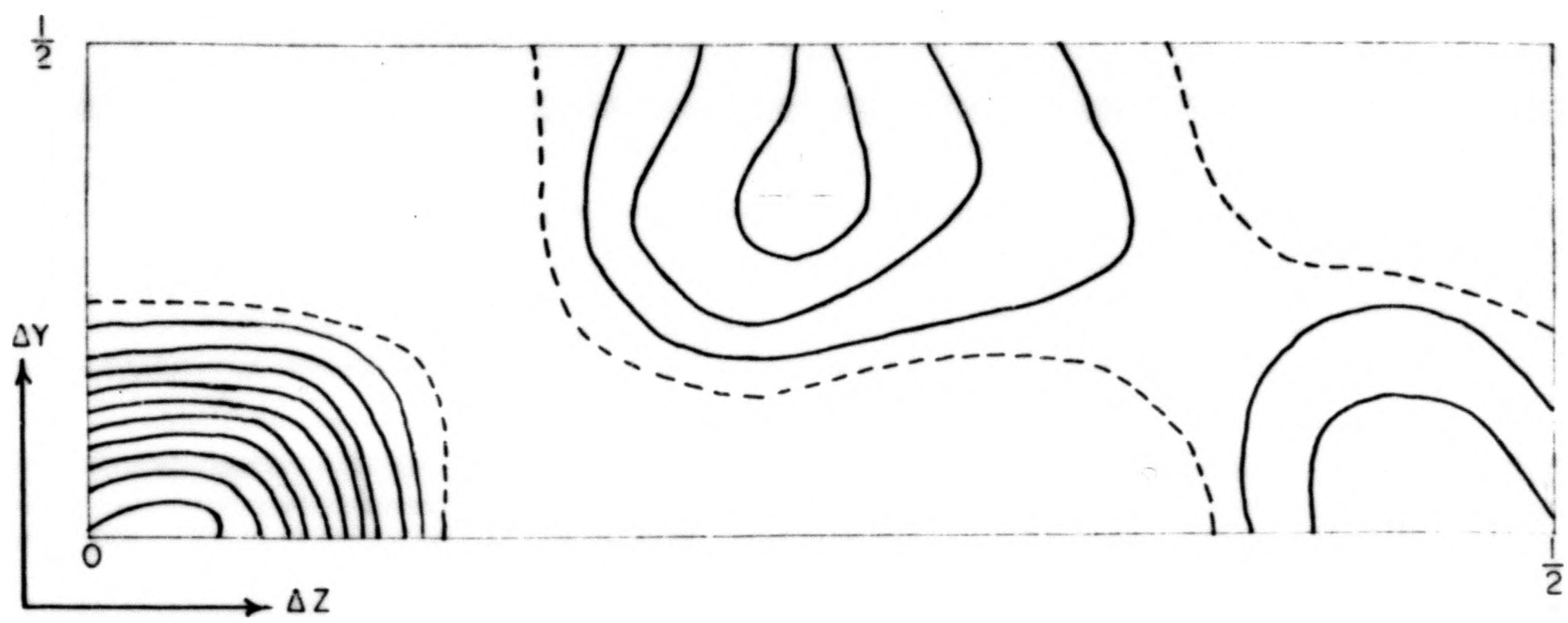


Figure 12. Three dimensional Patterson section at $\Delta x = 0.0875$ with dashed arbitrary zero contour. Cross indicates the chlorine-chlorine vector between the two nonequivalent chlorine atoms in two different molecules

The calculation stopped refining at an R value of .230. Upon investigation of the calculated structure factors it was found that when the h index was odd, the agreement between the calculated and observed structure factors was very poor. For the space group $Pca2_1$ when the h index is odd, the real structure factor coefficient, $A(h,k,\ell)$ and the imaginary structure factor coefficient, $B(h,k,\ell)$, are given by

h odd, ℓ even:

$$A(h,k,\ell) = -\sin 2\pi hx \sin 2\pi ky \cos 2\pi \ell z$$

$$B(h,k,\ell) = \sin 2\pi hx \sin 2\pi ky \sin 2\pi \ell z$$

h odd, ℓ odd:

$$A(h,k,\ell) = \cos 2\pi hx \sin 2\pi ky \sin 2\pi \ell z$$

$$B(h,k,\ell) = \cos 2\pi hx \sin 2\pi ky \cos 2\pi \ell z.$$

If the x-coordinate of each atom in the asymmetric unit were increased by one quarter unit cell translation, it was seen that when h was odd

$$\cos 2\pi h(x + 1/4) = -\sin 2\pi hx$$

and

$$\sin 2\pi h(x + 1/4) = \cos 2\pi hx$$

which gave a numerical change in value of the calculated structure factor for the reflections which had an odd h index. This situation did not arise in the $(h,0,\ell)$ refinement because the h index was always even which gave

$$\cos 2\pi h(x + 1/4) = -\cos 2\pi hx$$

$$\sin 2\pi h(x + 1/4) = -\sin 2\pi hx$$

but since $F_c = \sqrt{A^2 + B^2}$

this change in algebraic sign did not enter in.

Each x-coordinate was increased by 1/4 and after several cycles the R value dropped to .138. At this time anisotropic thermal refinement was begun. Since the β_{11}, β_{33}, β_{13} anisotropic thermal parameters had already been refined, these, along with the anisotropic thermal parameters calculated from the three dimensional isotropic thermal parameters were used. For β_{11}, β_{33}, β_{13} the mean value of the two quantities was calculated and β_{22} scaled to this. Three more least squares cycles gave an R value of .064 without unobserved reflections, and .109 including 601 unobserved reflections. During these last three least squares cycles the rejection test was again used which rejected a reflection from the setting up of the normal equations when the inequality

$$\frac{|F_o - F_c|}{\sigma(F_o)} \geqq 6.0$$

was valid. Fourteen reflections were rejected on this basis. The intensities of these fourteen reflections were remeasured on another crystal as the original crystal had been accidently lost, and it was found that all the reflections were acceptable when the remeasured intensities were properly reduced to structure factors. Another rejection test was used on the data

which tested to see if $F_o > F_c$ for unobserved reflections. If this inequality were valid, this indicated that the calculated intensity of that reflection was too high, and hence in error. The reflection was then given zero weight and thereby excluded from the normal equations and R value. Two hundred seventy six or 45.9 percent of the total 601 unobserved reflections were rejected in this manner.

It was then decided to include nine of the ten hydrogen atoms (the enolic hydrogen was omitted) in the least squares calculation. The positions of the hydrogen atoms were calculated by considering three carbon atoms forming a 120° angle. The hydrogen atom of interest was considered attached to the vertex carbon atom. The direction cosines were determined of the vector through the two non-vertex carbon atoms and the coordinates of the midpoint of the line joining these two atoms were found. The direction cosines were then calculated for the vector through this midpoint and the vertex carbon atom. The coordinates of the hydrogen atom were then found by going 1.0 Å out along this vector from the vertex carbon atom. Coordinates for the nine hydrogen atoms were calculated in this manner. A three dimensional difference fourier was calculated in hopes of seeing these hydrogen atoms. Six of the hydrogen atoms, H_2, H_6, H_8, H_{10}, H_{12}, H_{14}, showed peaks at the calculated positions. The H_5 difference fourier peak was somewhat off from the calculated position, and H_4 and H_{11} did not show any peaks on the difference map.

The nine calculated hydrogen positions were included along with the nineteen other atoms in another anisotropic least squares cycle. The anisotropic temperature coefficients for the hydrogen atoms were calculated using an isotropic temperature factor of 5.0. The positional parameters and the anisotropic coefficients of the hydrogens were not allowed to vary. At least one of the coordinates of each carbon attached to a hydrogen atom shifted by two standard deviation units. The final agreement factors were found to be .104 with unobserved reflections and .060 without unobserved reflections. Also,

$$\sqrt{\frac{w(F_o - F_c)^2}{M - N}} = 1.456.$$

Figure 13 lists the final structure factors for the chloro-compound. In each column the first entry is the ℓ index, an asterisk after the ℓ index indicates that the reflection was unobserved. The second entry is the observed structure factor multiplied by $10/s_q$, where s_q is the Busing's overall scale factor, the third entry is the calculated structure factor, the fourth entry is the real part, $A(h,k,\ell)$, of the calculated structure factor multiplied by 10.0 to retain significant digits, and the fifth entry is the imaginary part, $B(h,k,\ell)$, of the calculated structure factor also multiplied by 10.0. Tables 2 and 3 list atomic coordinates and anisotropic thermal parameters for each atom.

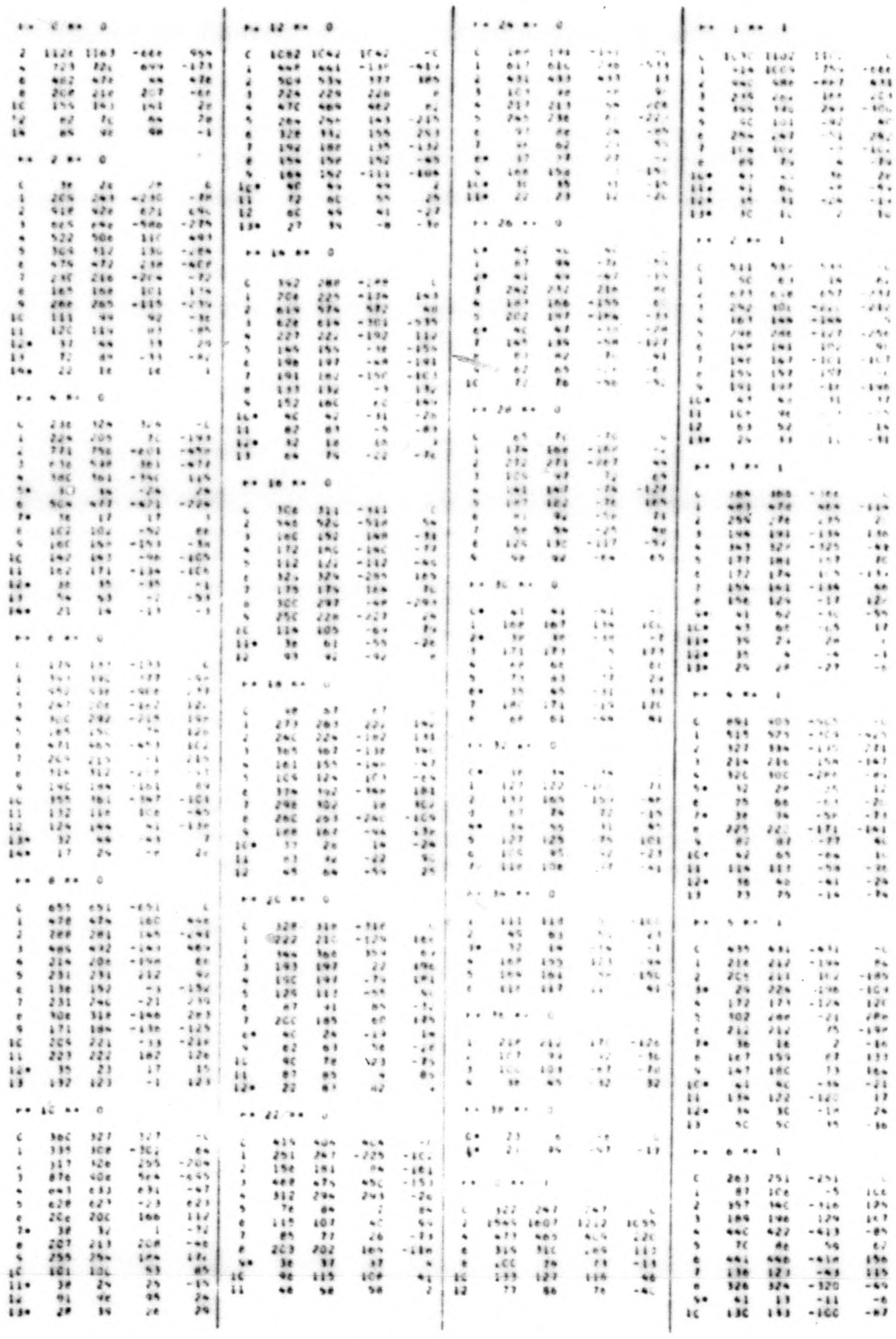


Figure 13. List of final structure factors for bis(meta-chlorobenzoyl)methane. The first column is the ℓ index, an asterisk after the ℓ index indicates an unobserved reflection. The second column is the observed structure factor x $10/s_q$, where s_q is Busing's overall scale factor (.2023); the third column is the calculated structure factor x $10/s_q$. The fourth and fifth columns are A_c x 10 and B_c x 10 respectively

11	100	113	-105	41
12	105	131	-56	-54
13*	28	46	29	28

** 7 ** 1

0	351	352	352	0
1	169	173	-22	171
2	192	198	-187	54
3	101	91	73	-55
4	224	225	124	-136
5	150	162	45	135
6	120	121	7	121
7	92	127	94	-62
8	125	116	116	-6
9	236	228	25	227
10	153	148	-129	32
11	125	125	-123	-20
12	112	115	61	-98
13*	28	27	19	-19

** 8 ** 1

0	251	224	-229	-6
1	295	296	33	295
2*	90	104	-98	-56
3	258	24	-95	226
4	134	131	-131	17
5	157	167	-69	136
6	56	54	51	24
7	210	195	-51	193
8	139	127	-107	-71
9	117	134	119	63
10*	63	66	-65	2
11	86	67	50	53
12*	33	23	20	-17
13	64	76	16	61

** 9 ** 1

0*	25	15	-15	0
1	195	194	170	-86
2	119	105	105	25
3	357	356	-360	105
4	130	118	-61	-89
5	311	315	114	-291
6*	36	225	219	-56
7	175	180	52	173
8	244	184	52	174
9	94	81	57	-56
10	101	110	31	-112
11*	39	30	0	1
12*	33	41	9	1
13*	26	24	-22	-15

** 10 ** 1

0	204	195	195	0
1	192	225	127	-181
2	355	361	347	-104
3	346	337	233	193
4	270	271	261	-6
5	238	251	243	61
6	242	243	245	42
7	57	72	72	54
8	143	144	139	55
9	82	56	-2	56
10	147	145	145	17
11	87	77	8	77
12*	32	13	12	-3
13	45	60	59	46

** 11 ** 1

0*	51	48	-48	0
1	207	204	-194	64
2	164	175	-177	-23
3	425	414	182	-392
4	117	131	62	-115
5	135	138	64	122
6	54	50	9	49
7	144	189	-59	-180
8*	39	35	-4	-34
9	53	65	73	44
10*	19	12	-3	-13
11	94	86	-71	-46
12*	31	7	7	-2
13*	74	9	9	-1

** 12 ** 1

0	245	254	254	0
1	494	490	308	-299
2	484	486	4 8	161
3	217	222	-18	-211
4	354	363	1 5	146
5	191	193	17	-191
6	151	154	138	73

7	71	75	9	74
8*	41	54	41	43
9	118	119	103	-80
10	84	87	69	23
11	77	73	1	-73
12	48	52	46	-25
13*	22	20	-1	-20

** 13 ** 1

0	570	554	554	0
1	278	267	58	-264
2	510	483	-425	230
3	152	152	52	120
4	274	268	97	-249
5	123	134	-62	-114
6	144	133	-95	107
7	87	79	65	45
8	98	101	-41	-92
9*	40	50	-45	-22
10*	40	45	-4	45
11*	35	25	25	2
12*	30	25	-25	-2
13*	20	20	-20	0

** 14 ** 1

1	182	185	-182	-19
2*	34	32	28	-17
3	162	161	-145	-71
4	205	211	-65	201
5	227	211	6	-211
6	82	89	80	-39
7	205	210	-45	-213
8*	40	3	2	2
9	147	148	-55	-135
10	78	47	-30	-38
11	63	57	-24	-52
12*	24	23	-23	-1

** 15 ** 1

0	128	123	-121	-6
1	191	187	177	60
2	198	182	140	117
3	105	117	-118	17
4	313	304	-265	142
5	186	183	172	64
6	225	236	64	-227
7	199	195	-172	92
8	161	160	31	156
9	90	82	14	-82
10	81	75	-46	-58
11*	34	36	2	30
12*	24	31	20	27

** 16 ** 1

0	240	231	-231	0
1*	35	47	24	40
2	285	284	-277	-82
3	101	112	-38	-110
4	202	207	-199	-54
5*	30	47	-1	47
6	254	262	-233	-120
7	98	95	-46	15
8	139	146	-140	40
9	103	91	-30	81
10*	17	15	-19	-3
11	93	81	-69	-45
12	72	72	-72	-2

** 17 ** 1

0	165	97	97	-0
1	235	224	-222	56
2*	34	32	30	-10
3	203	208	208	-13
4*	47	43	-22	37
5	111	114	-13	110
6	124	130	-54	-110
7	137	150	21	135
8	153	143	142	-31
9	74	80	-65	-1
10	87	70	-18	67
11	61	56	53	-20
12*	24	32	30	10

** 18 ** 1

0	107	115	-115	0
1	175	173	92	148
2	230	220	-205	80
3	170	144	-69	126
4	232	235	-147	183
5	187	201	66	190
6	172	170	-169	12
7	160	153	1	153

8	131	135	-127	-45
9	100	45	-15	7
10	90	95	-87	-47
11	102	109	-74	50
12*	23	17	-20	-24

** 19 ** 1

0	238	235	235	1
1	176	178	150	-81
2	142	135	-127	51
3	62	71	-53	50
4	145	151	151	-4
5	135	131	122	-47
6*	41	25	-22	12
7	138	131	14	130
8	62	76	69	-32
9	87	88	-88	5
10*	38	48	45	11
11*	30	32	22	-21

** 20 ** 1

1	225	227	17	224
2	104	121	-4	-20
3	98	116	-13	116
4*	40	76	-4	71
5	144	146	19	145
6*	42	18	2	-16
7*	42	17	-17	-2
8	55	53	-4	53
9	139	129	26	126
10	61	45	26	-42
11	49	61	58	24

** 21 ** 1

0	213	206	-211	-0
1*	35	40	31	-37
2	207	202	191	-84
3*	40	44	-10	-41
4	109	93	-69	44
5	105	105	82	-65
6	139	147	94	-109
7	80	74	-55	65
8	113	124	-24	121
9	65	71	-29	-65
10	68	72	-29	-66
11*	29	31	-21	-23

** 22 ** 1

0	122	123	123	0
1	159	160	75	-147
2	146	137	104	84
3	110	115	14	-115
4	281	270	262	-65
5	138	137	109	84
6	135	140	140	0
7*	73	51	48	-21
8	72	92	69	-21
9	57	64	64	-5
10	122	118	118	7
11*	24	28	22	-17

** 23 ** 1

0	65	64	69	0
1	374	354	-350	14
2	311	298	-267	-69
3	371	368	219	-298
4	199	191	169	-94
5	155	198	-54	193
6	83	93	-43	83
7	118	107	-44	-54
8*	37	30	-17	-25
9*	34	22	2	21
10*	30	16	-9	-13

** 24 ** 1

0	306	316	306	-0
1	312	293	207	-207
2	91	45	85	33
3	191	192	77	-177
4	84	103	41	49
5	140	137	81	-104
6*	40	55	7	54
7	104	85	-8	-80
8	51	56	47	-31
9*	33	45	-9	-44
10	44	27	4	-26

** 25 ** 1

0	226	233	-233	0
1	143	149	140	-49
2	145	145	-3	-145

3	72	89	-54	70
4	76	70	62	32
5	117	94	74	-66
6	73	54	-51	30
7*	38	71	-20	68
8*	15	21	-21	4
9*	32	45	-25	-37
10*	24	36	-16	25

** 26 ** 1

0	101	110	-110	-0
1	119	120	-22	-124
2	80	77	-4	76
3	91	111	-98	-54
4*	41	60	-60	5
5*	40	29	-23	18
6	71	54	-52	-17
7	142	110	-50	-107
8	82	75	-35	5
9*	29	46	-24	-31
10*	19	40	-40	-13

** 27 ** 1

0*	40	40	-40	-0
1*	34	20	14	14
2*	41	82	-8	-81
3*	40	51	2	51
4*	40	53	33	36
5	62	54	-47	29
6*	38	27	16	-21
7*	35	29	15	25
8	77	70	4	69

** 28 ** 1

0	76	117	-117	0
1	135	131	86	59
2	175	180	-175	-14
3*	40	51	2	51
4	95	97	-63	-41
5*	50	44	-3	44
6	108	108	-107	15
7	118	85	-51	81
8*	10	15	-9	12
9	45	65	-59	29

** 29 ** 1

0*	35	41	41	0
1	78	95	-80	52
2	78	84	-79	26
3*	39	64	63	-11
4	131	117	76	-89
5	67	45	-27	38
6	80	70	35	64
7	85	52	50	-36
8	63	54	25	-46

** 30 ** 1

0*	38	53	-53	-0
1*	38	70	48	54
2*	37	22	22	1
3	138	117	-42	109
4*	33	52	-39	34
5	134	128	48	120
6	50	40	-33	24
7	127	125	9	124
8*	22	24	-21	11

** 31 ** 1

0*	37	62	62	0
1	109	122	118	-39
2*	38	24	-18	-19
3	115	115	-107	42
4*	38	60	60	-4
5	130	128	20	-105
6*	31	24	-20	-8
7	70	80	6	80

** 32 ** 1

0*	38	33	33	0
1*	55	65	-20	64
2	79	98	94	19
3*	35	53	32	42
4	61	65	64	24
5*	32	34	29	17
6	48	51	47	20
7*	22	24	24	-4

** 33 ** 1

1*	34	61	-61	3
2	104	111	101	-44

Figure 13. (Continued)

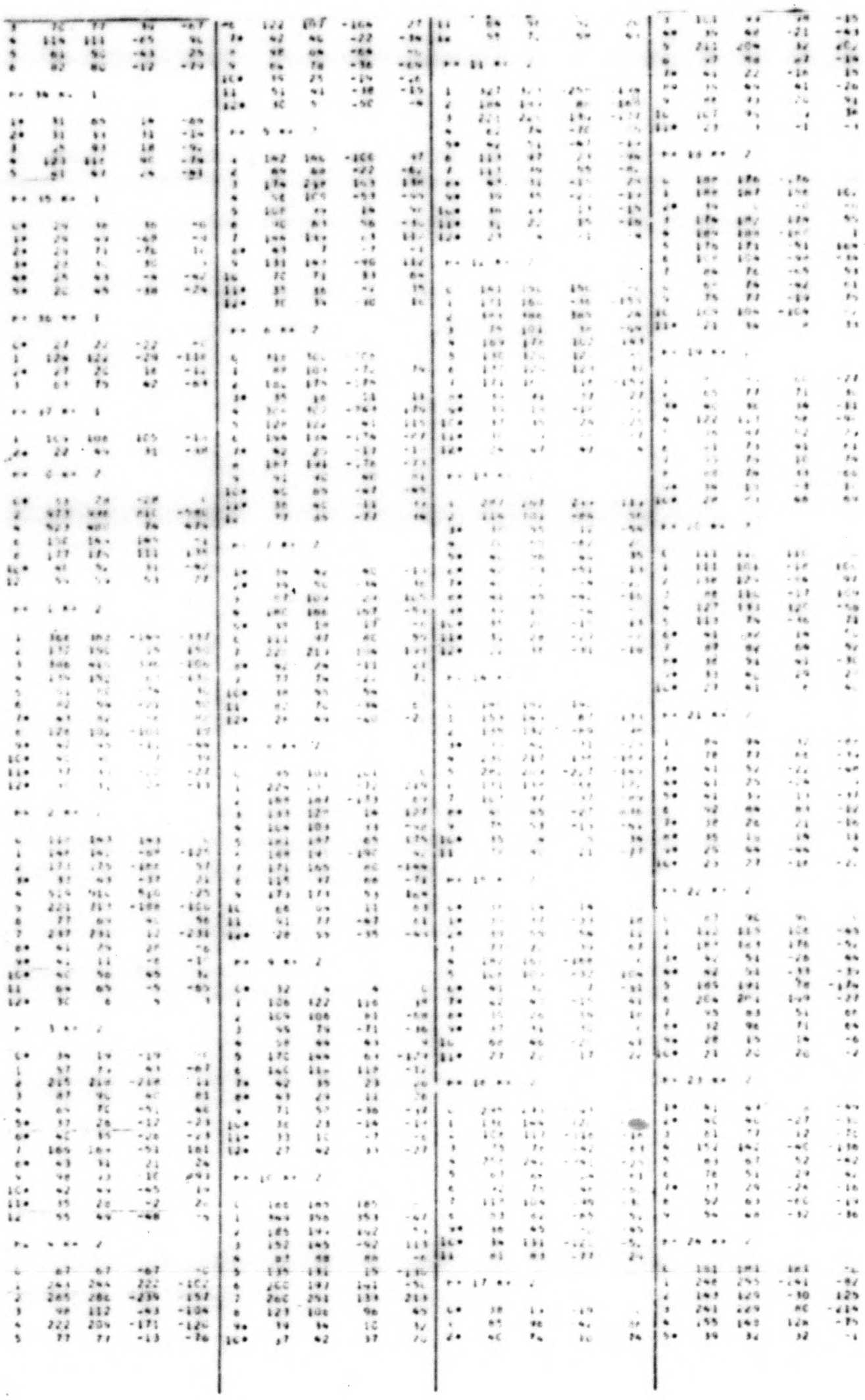


Figure 13. (Continued)

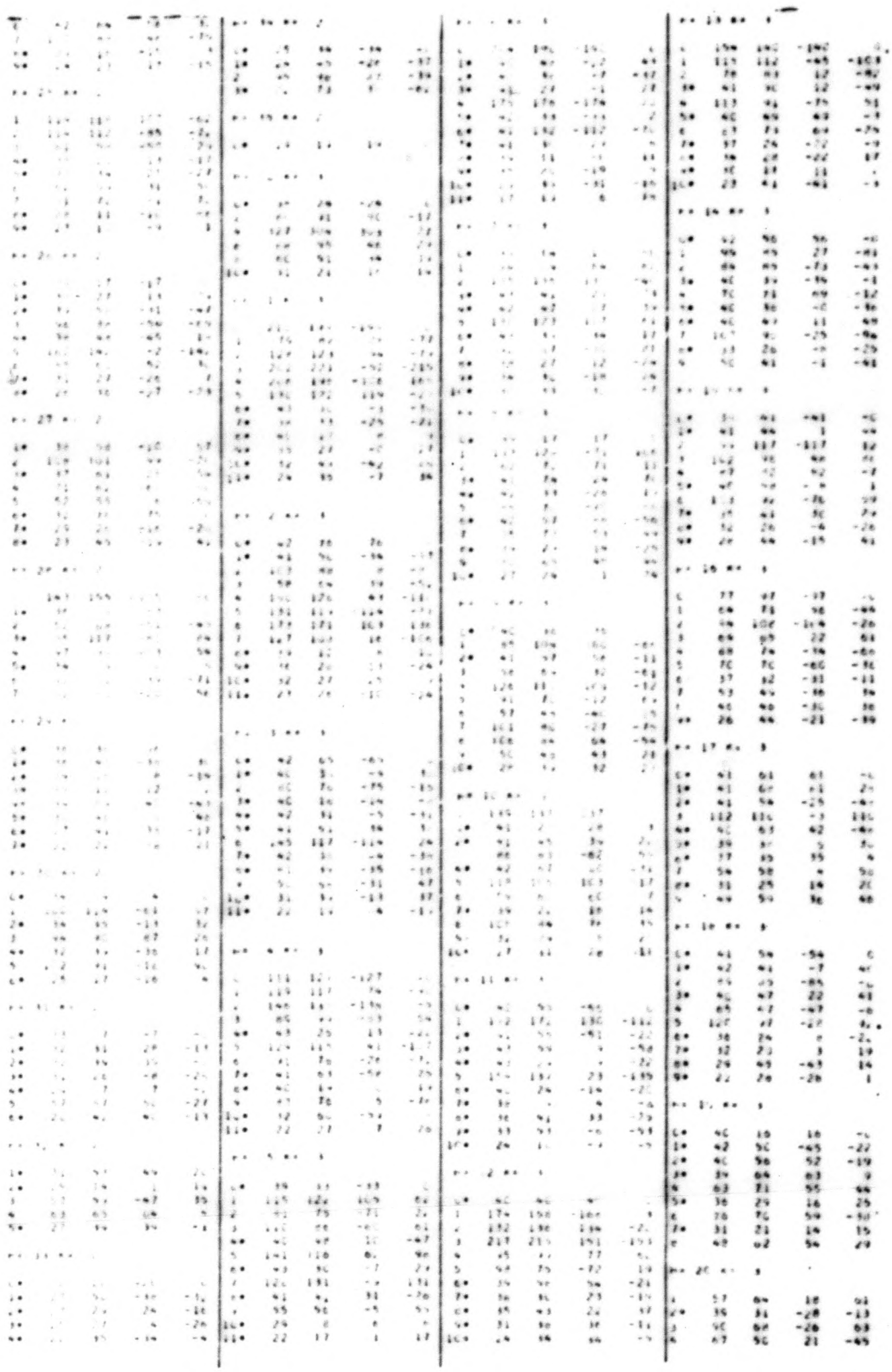


Figure 13. (Continued)

5*	35	18	13	-13
6*	35	37	9	36
7*	31	37	-12	35
8*	24	32	33	-17

** 21 ** 3

0*	37	86	86	-0
1*	41	44	-7	-43
2*	35	43	-51	-17
3*	38	58	43	-39
4	90	85	82	-25
5*	36	45	-29	-35
6	84	45	-46	-18
7	62	56	17	-54
8*	22	28	25	-12

** 22 ** 3

0*	38	31	-31	-0
1*	38	11	9	-6
2	67	75	25	-11
3*	37	36	-36	-0
4	60	66	53	27
5*	33	32	6	-32
6	118	100	58	-81
7	70	76	75	-10

** 23 ** 3

0*	38	47	-47	-0
1	138	134	89	-101
2	55	65	-55	-35
3	67	60	-51	32
4	88	70	-66	25
5	111	106	-23	-97
6	68	68	4	-67
7*	22	28	26	10

** 24 ** 3

0*	35	8	8	0
1	65	58	-16	12
2*	34	83	80	-23
3	133	113	12	-113
4*	32	43	-42	-7
5	57	53	11	-52
6	72	64	64	4

** 25 ** 3

0*	35	26	-6	0
1*	34	42	-42	5
2	111	104	-94	44
3	54	57	54	-19
4*	31	47	-30	-36
5*	27	24	1	24
6*	24	27	-19	-19

** 26 ** 3

0*	33	14	-14	-0
1*	32	27	-25	-10
2*	33	58	-58	3
3	84	77	-76	-14
4	49	47	47	-0
5	66	56	6	-56

** 27 ** 3

0*	30	44	44	0
1*	30	44	-17	41
2*	30	36	-36	4
3*	27	12	-1	12
4*	26	10	9	4
5*	22	53	-21	49

** 28 ** 3

1*	28	49	-7	49
2*	27	15	9	-12
3*	25	4	4	0
4	78	74	-71	-20

** 29 ** 3

0*	26	17	17	0
1*	24	43	37	22
2*	24	18	12	-13
3*	22	41	0	41

** 30 ** 3

0*	23	33	33	0
1*	21	50	-40	30

** 0 ** 4

0	89	112	112	0
2*	35	12	-8	11
4	85	64	-6	-83
6	108	98	79	55
8*	30	22	20	9

** 1 ** 4

0*	37	47	-47	0
1*	41	43	-17	-40
2*	40	23	1	-23
3*	40	57	-38	-43
4*	39	32	17	28
5	138	122	-42	-115
6	81	78	-74	-25
7*	33	31	26	17
8*	28	26	-14	21

** 2 ** 4

0*	42	60	-60	0
1*	40	22	-22	-4
2*	40	40	39	8
3*	35	34	-16	-36
4*	37	11	9	-7
5*	38	23	22	-8
6	84	72	53	-48
7*	32	37	-30	-21
8*	23	35	6	35

** 3 ** 4

0*	41	69	-69	-0
1	80	64	-58	26
2*	40	35	-33	-10
3*	39	29	27	-10
4*	37	45	-45	15
5	73	59	-59	4
6*	34	29	-3	29
7*	32	43	43	-6
8*	23	43	-40	-15

** 4 ** 4

0*	38	45	-45	-0
1*	39	13	-13	-3
2*	39	35	-18	-30
3*	39	38	5	-38
4*	40	61	-50	-34
5*	35	20	-17	10
6*	32	11	10	3
7*	30	22	-6	-21
8*	23	13	13	2

** 5 ** 4

0*	37	22	22	0
1*	41	44	-0	44
2*	40	38	-34	-16
3	70	72	17	70
4*	35	6	0	6
5*	35	32	29	27
6*	33	27	-12	-24
7*	30	41	-21	39
8*	19	14	-9	17

** 6 ** 4

0*	35	34	-34	-0
1*	37	21	1	21
2	62	62	-59	19
3*	37	13	-12	4
4*	38	51	-38	-33
5*	34	10	10	1
6*	31	27	11	-25
7*	28	13	-13	1

** 7 ** 4

0*	37	1	-1	-0
1*	37	21	-17	12
2	86	33	33	1
3*	38	29	28	15
4	57	47	15	43
5	37	37	0	37
6*	31	27	7	-27
7*	27	25	1	24

** 8 ** 4

0*	38	25	-25	1
1*	39	34	5	34
2*	37	5	-4	2
3*	39	52	-51	10
4	65	51	-27	-40
5*	35	43	42	1
6*	31	18	18	1
7*	27	25	-5	25

** 9 ** 4

1*	37	21	-10	-11
2*	37	26	-4	-7
3	78	60	75	-20
4*	35	37	-5	27
5	58	43	-43	-2
6*	29	24	18	-18
7*	26	35	8	-35

** 10 ** 4

0*	37	16	-16	0
1*	38	47	-24	42
2*	36	22	21	-4
3*	38	43	19	-39
4*	34	31	24	-12
5*	32	24	5	24
6*	30	39	38	9
7*	26	10	-5	9

** 11 ** 4

0*	38	61	61	0
1	135	113	61	-95
2	58	63	-58	24
3*	37	64	-61	-12
4*	35	52	-2	-52
5*	33	61	37	-47
6*	28	3	-2	3
7*	22	25	1	-25

** 12 ** 4

0*	36	32	32	0
1*	36	24	15	-19
2*	35	14	17	-9
3*	34	46	-46	-4
4*	32	33	28	-18
5*	31	46	43	-16
6*	27	32	26	18

** 13 ** 4

1*	35	42	-41	9
2*	34	29	-29	6
3	94	92	67	-75
4*	32	31	-30	8
5*	28	11	-8	-8
6*	25	12	-10	-6

** 14 ** 4

0	73	72	-72	-6
1*	34	14	-8	13
2*	32	39	37	-22
3	69	54	-17	-51
4*	30	5	-2	5
5*	28	23	9	-20
6*	24	15	8	-13

** 15 ** 4

0*	33	28	-28	6
1*	34	35	15	32
2	59	54	-26	-48
3*	30	52	-49	19
4*	30	4	-4	2
5*	27	26	12	23
6*	22	38	-35	30

** 16 ** 4

1*	31	5	-2	4
2*	31	50	-25	-44
3*	30	27	-27	-0
4*	28	1	-1	1
5*	25	1	1	1

** 17 ** 4

0*	32	53	-53	-0
1*	30	52	42	31
2*	30	21	17	-11
3	84	70	-23	66
4*	27	31	31	-1
5*	23	4	4	-1

** 18 ** 4

0*	30	32	-32	-0
1*	30	29	19	22
2*	29	33	-31	-11
3*	28	31	-19	24
4*	24	23	-9	-22

** 19 ** 4

0*	28	4	4	-0
1*	28	16	11	12
2	87	70	68	-19
3*	24	17	10	-14
4*	22	4	4	0

** 20 ** 4

0*	28	31	-31	0
1*	27	32	-9	30
2*	25	14	10	-9
3*	22	18	-17	4

** 21 ** 4

0*	25	15	15	0
1*	24	29	-12	-26
2*	23	17	9	15

** 22 ** 4

0*	23	20	20	0
1*	20	22	-16	13

Figure 13. (Continued)

Table 2. Atomic coordinates of the atoms in the asymmetric unit of bis(meta-chlorobenzoyl)methane with standard deviations of each. All numbers are reported x 10^5

Atom	x/a	x/a	y/b	y/b	z/c	z/c
Cl_1	40885	7	4084	70	00000	0
Cl_2	83345	6	20930	89	21959	37
O_1	58082	18	2356	200	1947	53
O_2	66147	19	4761	214	6265	54
C_1	44940	25	18084	273	9929	77
C_6	43521	23	32426	247	20746	92
C_5	46833	26	44041	275	28823	86
C_4	51325	25	39178	238	26211	83
C_3	52582	25	23767	254	15394	75
C_2	49365	26	12687	228	7181	77
C_7	57333	25	17848	261	12126	76
C_8	60839	21	27812	258	19687	75
C_9	65236	24	21088	233	16383	71
C_{13}	61256	22	30734	225	23842	67
C_{12}	68564	28	46246	264	34856	77
C_{11}	72238	25	55478	283	41867	84
C_{10}	76558	29	48437	281	37647	86
C_{15}	76999	25	31868	273	27006	94
C_{14}	73304	23	22840	275	20002	88
H_6	40140		34750		22600	
H_5	45953		55104		36769	

Table 2 (Continued)

Atom	x/a	x/a	y/b	y/b	z/c	z/c
H_4	53736		46688		32020	
H_2	50274		-504		-951	
H_8 (non-enolic)	60195		40582		27661	
H_{12}	65399		50177		27542	
H_{11}	71757		67501		49587	
H_{10}	79521		54914		42258	
H_{14}	73600		10182		12062	

The Function and Error program of Busing and Levy (58) was used to calculate bond distances, bond angles, and orientation of the anisotropic thermal ellipse in relation to the molecule, the results of which are partially listed in Tables 4, 5, and 6. Table 6 lists direction cosines of each of the three axes of the thermal ellipse for each atom. The direction cosines are listed for each axis of the thermal ellipse with respect to a coordinate system defined by two vectors. The vectors were $\overrightarrow{C_7O_1}$ and $\overrightarrow{C_7C_8}$, where now the three axes of the coordinate system were given by the cross vector products

Axis 1: $\overrightarrow{C_7O_1}$

Axis 2: $(\overrightarrow{C_7O_1}) \times (\overrightarrow{C_7C_8})$

Axis 3: (Axis 1) x (Axis 2).

Where now cos α refers to the angle a principle axis makes with Axis 1 of the coordinate system, cos β refers to Axis 2 of the coordinate system, and cos γ refers to Axis 3.

Table 3. Anisotropic temperature factors of the atoms in the asymmetric unit of bis(meta-chlorobenzoyl)methane x 10^5

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl_1	88	9627	879	-26	-96	-139
Cl_2	73	11668	1463	45	36	135
O_1	114	12101	658	83	-7	-1153
O_2	92	12585	721	49	15	-932
C_1	83	7956	722	70	-14	117
C_6	75	8377	845	74	29	-39
C_5	97	9158	773	-7	-7	-81
C_4	97	8237	684	-61	-20	-345
C_3	95	6680	544	-21	-15	384
C_2	89	7213	767	63	-42	796
C_7	95	7256	569	9	3	-7
C_8	65	8699	585	-28	-7	184
C_9	88	6074	614	150	-12	98
C_{13}	74	8016	559	-33	-5	325
C_{12}	98	8183	702	-21	22	-71
C_{11}	83	9590	834	-114	-7	536
C_{10}	116	8322	791	-94	-67	211
C_{15}	67	8293	1096	66	26	491
C_{14}	78	8992	781	-55	-33	416
all H's	138	6433	1010	0	0	0

Table 4. Bond distances and errors in bis(meta-chlorobenzoyl) methane

atom pair	bond distance (Å.)	error (Å.)
O_2 O_1	2.4751	.0079
Cl_1C_1	1.7315	.0085
Cl_2C_{15}	1.7272	.0085
C_1 C_6	1.3910	.0122
$C_{10}C_{15}$	1.3511	.0136
C_6 C_5	1.4142	.0115
$C_{10}C_{11}$	1.4079	.0113
C_5 C_4	1.3949	.0107
$C_{11}C_{12}$	1.3985	.0097
C_4 C_3	1.3937	.0109
$C_{12}C_{13}$	1.3732	.0111
C_3 C_2	1.3815	.0101
$C_{13}C_{14}$	1.3617	.0100
C_1 C_2	1.3974	.0107
$C_{14}C_{15}$	1.4012	.0102
C_3 C_7	1.4922	.0102
C_9 C_{13}	1.4819	.0097
C_7 O_1	1.2993	.0098
C_9 O_2	1.3179	.0089
C_7 C_8	1.4024	.0107
C_8 C_9	1.3970	.0089

Table 4 (Continued)

atom pair	bond distance (Å.)	error (Å.)
C_2 H_2	1.0728	.0093
C_4 H_4	1.0133	.0084
C_5 H_5	1.0162	.0098
C_6 H_6	1.0416	.0070
C_8 H_8	1.0324	.0090
$C_{10}H_{10}$	1.0582	.0086
$C_{11}H_{11}$	0.9862	.0104
$C_{12}H_{12}$	1.0094	.0030
$C_{14}H_{14}$	1.0126	.0105
H_8 H_4	2.0163	.0001
$H_{12}H_8$	1.9481	.0002
$H_{12}H_4$	3.5644	.0002

Table 5. Bond angles in bis(meta-chlorobenzoyl)methane molecule in degrees with error in degrees. Center atom is vertex

atoms	bond angle	error
Cl_1C_1 C_6	117.327	.590
$Cl_2C_{15}C_{10}$	119.314	.666
Cl_1 C_1 C_2	119.396	.701
$Cl_2C_{15}C_{14}$	118.923	.772

Table 5 (Continued)

atoms	bond angle	error
$C_6\ C_1\ C_2$	123.150	.774
$C_{10}C_{15}C_{14}$	121.756	.794
$C_1\ C_6\ C_5$	117.309	.680
$C_{15}C_{10}C_{11}$	118.268	.804
$C_6\ C_5\ C_4$	120.518	.829
$C_{10}C_{11}C_{12}$	119.634	.853
$C_5\ C_4\ C_3$	119.976	.755
$C_{11}C_{12}C_{13}$	120.716	.553
$C_4\ C_3\ C_2$	120.434	.732
$C_{12}C_{13}C_{14}$	119.368	.618
$C_3\ C_2\ C_1$	118.469	.806
$C_{13}C_{14}C_{15}$	120.155	.856
$C_4\ C_3\ C_7$	122.342	.712
$C_{12}C_{13}C_9$	120.752	.563
$C_2\ C_3\ C_7$	117.217	.735
$C_{14}C_{13}C_9$	119.821	.716
$C_3\ C_7\ O_1$	116.645	.685
$C_{13}C_9\ O_2$	115.676	.613
$C_3\ C_7\ C_8$	122.169	.714
$C_{13}C_9\ C_8$	123.641	.695
$O_1\ C_7\ C_8$	121.176	.668
$O_2\ C_9\ C_8$	120.671	.687
$C_7\ C_8\ C_9$	120.236	.738
$C_7\ O_1\ O_2$	89.056	.686
$C_9\ O_2\ O_1$	88.857	.652

Table 6. Direction cosines of the three principal axes of the anisotropic thermal ellipse for each atom

atom	principal axis	cos α	cos β	cos γ	length (Å.)
Cl_1	1	-.36941	.15329	-.91990	.171
	2	-.90231	.19187	.38601	.253
	3	-.23566	-.96937	-.06906	.268
Cl_2	1	.27984	-.05057	-.95871	.181
	2	-.01303	-.99871	.04888	.293
	3	-.95995	-.00116	-.28013	.302
O_1	1	-.98631	.08150	-.14328	.174
	2	-.14831	-.05939	.98715	.231
	3	.07193	.99490	.07067	.315
O_2	1	.94024	-.12386	-.31718	.195
	2	.31276	-.05413	.94828	.203
	3	.13462	.99082	.01216	.323
C_1	1	-.01265	.27401	-.96164	.183
	2	.84270	-.51473	-.15774	.215
	3	-.53822	-.81237	-.22439	.268
C_6	1	.43867	-.02197	-.89837	.183
	2	.79478	-.45705	.39926	.223
	3	-.41937	-.88916	-.18302	.247
C_5	1	-.10381	.05934	-.99282	.200
	2	.91669	-.38157	-.11866	.238
	3	-.38587	-.92243	-.01478	.257
C_4	1	-.73876	.05437	-.67176	.200
	2	-.64713	.22019	.72957	.210
	3	-.18824	-.97371	.12822	.247
C_3	1	-.60146	.74819	-.28008	.175
	2	-.08533	.27525	.95587	.207
	3	.79226	.60369	-.08870	.237
C_2	1	-.24182	.74423	-.62261	.168
	2	-.28736	.55793	.77854	.197
	3	-.92679	-.36718	-.07893	.273
C_7	1	-.88486	.45243	-.11096	.180
	2	-.13941	-.02993	.98977	.216
	3	-.44448	-.89130	-.08957	.235

Table 6 (Continued)

atom	principal axis	cos α	cos β	cos γ	length (Å.)
C_8	1	.02373	.00310	-.99971	.163
	2	.81248	-.58271	.01748	.195
	3	-.58249	-.81266	-.01633	.259
C_9	1	-.00570	.65503	-.75558	.173
	2	-.95571	.21874	.19687	.197
	3	-.29424	-.72324	-.62476	.232
C_{13}	1	-.55993	.52409	-.64171	.173
	2	-.47887	.42715	.76694	.189
	3	-.67606	-.73678	-.01180	.245
C_{12}	1	.77656	-.35861	-.51801	.203
	2	.50428	-.13905	.85226	.223
	3	-.37766	-.92307	.07289	.237
C_{11}	1	.14505	-.26708	-.95269	.181
	2	.58886	-.75046	.30004	.212
	3	.79511	.60453	-.04841	.287
C_{10}	1	-.55339	.31962	-.76915	.203
	2	-.15507	.86775	.47218	.236
	3	.81836	.38058	-.43062	.259
C_{15}	1	.11074	.17485	-.97834	.167
	2	-.17330	.97271	.15423	.233
	3	-.97862	-.15247	-.13801	.281
C_{14}	1	-.14183	.12376	-.98212	.174
	2	-.60431	.77500	.18493	.207
	3	-.78401	-.61974	.03514	.283

DISCUSSION OF THE STRUCTURE

Least squares planes were calculated for the entire molecule and several subgroups of the molecule. The IBM 650 program of Stewart[1] was used. Least squares planes were calculated for the Cl_1 atom and its attached phenyl group (plane 1), Cl_2 and its attached phenyl group (plane 2), the enol subgroup, $O_1C_7C_8C_9O_2$ (plane 3), and the entire molecule (plane 4). The planes were of the form

$$Ax + By + Cz + 1 = 0.$$

The coefficients are listed in Table 7.

Table 7. Least square plane coefficients for bis(meta-chlorobenzoyl)methane

Plane	A	B	C
1	-.053071	-2.098751	1.029589
2	-.050345	-0.992145	0.508572
3	-.058742	-0.922791	0.492784
4	-.060025	-1.410536	0.710613

For each of the least squares planes the perpendicular distance to the least squares plane was calculated for every atom forming the least squares plane. The perpendicular

[1]Stewart, J. M. University of Washington. Seattle, Washington. Private communication. 1960.

distances to the plane of the atoms not forming the least squares plane were also calculated. The least squares plane which gave the best fit was through the enol subgroup, $O_1C_7C_8C_9O_2$. The two next best fits were the planes through the two chlorine atoms with their attached phenyl groups. The plane through the entire molecule gave the next best fit. There was some degree of non-coplanarity of the least squares planes through the three subgroups; the angles between planes were calculated to be

$$\angle \text{(plane 1, plane 2)} = 2.0^\circ$$
$$\angle \text{(plane 1, plane 3)} = 2.9^\circ$$
$$\angle \text{(plane 2, plane 3)} = 1.4^\circ.$$

It can be seen from Table 8 that the plane through the entire molecule fitted quite well. The average deviation from this plane was .023 Å. with a maximum deviation of .068 Å. The entire molecule was taken to be planar and the perpendicular distance between least squares planes was found to be 3.463 Å. The deviations of all the atoms from all the least squares planes mentioned above are listed in Table 8.

Table 8. Perpendicular distances in Å. of atoms in a molecule of bis(meta-chlorobenzoyl)methane to several least squares planes

plane	perpendicular distance of plane from origin	atom	perpendicular distance to plane
1	0.4276	Cl_1	.0058
		C_1	-.0288
		C_2	.0135
		C_3	-.0038
		C_4	.0037
		C_5	-.0051
		C_6	.0147
		Cl_2	.2148
		O_1	.0397
		O_2	.1229
		C_7	.0038
		C_8	.0024
		C_9	.0480
		C_{10}	.0779
		C_{11}	.0687
		C_{12}	.0709
		C_{13}	.0521
		C_{14}	.1167
		C_{15}	.1157
2	0.8957	Cl_2	.0248

Table 8 (Continued)

plane	perpendicular distance of plane from origin	atom	perpendicular distance to plane
		C_{10}	-.0277
		C_{11}	.0102
		C_{12}	.0286
		C_{13}	-.0193
		C_{14}	.0005
		C_{15}	-.0171
		Cl_1	.1216
		O_1	.0159
		O_2	.0384
		C_1	.0784
		C_2	.0760
		C_3	.0494
		C_4	.0910
		C_5	.1273
		C_6	.1575
		C_7	.0082
		C_8	-.0058
		C_9	-.0058
3	0.9[illegible]4	O_1	-.0084
		O_2	.0098
		C_7	.0071

Table 8 (Continued)

plane	perpendicular distance of plane from origin	atom	perpendicular distance to plane
		C_8	.0029
		C_9	-.0114
		Cl_1	.1249
		Cl_2	.0029
		C_1	.0918
		C_2	.0760
		C_3	.0619
		C_4	.1280
		C_5	.1772
		C_6	.1953
		C_{10}	-.0069
		C_{11}	.0469
		C_{12}	.0561
		C_{13}	-.0153
		C_{14}	-.0107
		C_{15}	-.0195
4	0.6328	Cl_1	.0237
		Cl_2	.0686
		O_1	-.0197
		O_2	.0313
		C_1	-.0165

Table 8 (Continued)

plane	perpendicular distance of plane from origin	atom	perpendicular distance to plane
		C_2	.0012
		C_3	-.0199
		C_4	.0075
		C_5	.0234
		C_6	.0476
		C_7	-.0387
		C_8	-.0461
		C_9	-.0256
		C_{10}	-.0206
		C_{11}	-.0038
		C_{12}	.0061
		C_{13}	-.0299
		C_{14}	.0100
		C_{15}	.0010

The C-C bond distances in the benzene rings were near the experimental value of 1.397 Å. (59, p. S-13) except for two shorter bonds between $C_{13}C_{14}$ and $C_{10}C_{15}$. No explanation could be given for these short bonds, however, the averages for the C-C bond distances for the two phenyl rings were 1.395 Å. and 1.382 Å., the latter containing the two short bonds. The bond

distances between C_3C_7 and C_9C_{13} indicated that these bonds were C-C single bonds trigonally coordinated. In the enol ring distances between C_7C_8 and C_8C_9 were indicative of 50 percent double bond character. This supported the hypothesis that these bond distances are determined by resonance between the two enol forms. The two CO bonds (1.31 Å.) were longer than the shorter of the CO bonds observed in HCO_2H and $\emptyset CO_2H$ (1.23 Å.) (59, p. S-13) and indicated that the CO bond was not a pure double bond but had some single bond character, again supporting resonance in the enol ring. The larger thermal amplitudes of the oxygen atoms were normal to the CO bond and hence did not affect the accuracy of this bond distance as much as if the larger amplitudes were parallel to the bond.. The average chlorine-carbon distance of 1.729 Å. agreed quite well with that observed for o-dichlorobenzene (1.735 Å.) and m-dichlorobenzene (1.70 Å.) (59, p. S-14). The observed O-O distance of 2.475 Å. confirmed the existence of a strong intramolecular hydrogen bond. When compared, the O-H-O distances of compounds with weak hydrogen bonds such as the acetic acid dimer (2.76 Å.) (59, p. M-171), or 4-aminosalicylic acid which has an O-H-O distance of 2.70 Å. and an intramolecular dimer O-H-O distance of 2.64 Å. (59, p. M-213), and to the O-H-O distances of strongly hydrogen bonded compounds such as maleic acid (2.46 Å.) (59, p. M-163), it can be seen that the O-H-O distance in bis(meta-chlorobenzoyl)-methane belongs to the latter group.

The bond angles in one of the benzene rings varied from 123.1° to 117.3° with the sum of the angles being 719.9°. The second benzene ring had angles varying from 121.7° to 118.2°, again with a sum of 719.9°. This near theoretical value of 720° indicated that both benzene rings were planar. The angles $C_7O_1O_2$ and $C_9O_2O_1$ were both less than 90° and showed that the two oxygen atoms were being forced apart by the hydrogen atom between them. The larger than normal angles $C_3C_7C_8$ and $C_8C_9C_{13}$ indicated that these angles "opened" to relieve the strain caused by the repulsion of H_8 from both H_4 (H_8H_4 distance of 2.016 Å.) and H_{13} (H_8H_{13} distance of 1.948 Å.).

If a hydrogen atom were placed on the line of centers of the two oxygen atoms, this would have given an exceedingly small C-O-H angle (90°), at least 15° less than normal. It seems likely that the hydrogen atom lies off the line of centers of the two oxygen atoms.

Figure 14 represents the anisotropic thermal stereograms for selected atoms in a bis(meta-chlorobenzoyl)methane molecule. The length of each thermal axis is indicated in Å. The plane of the paper is the least squares molecular plane and the stereograms are in the same orientation as the molecule indicated at the top of the Figure. It is evident that both chlorine atoms have their shortest thermal vibration parallel to the Cl-C bond and their largest thermal vibrations normal to this bond. The carbon atoms in the enol ring all have their

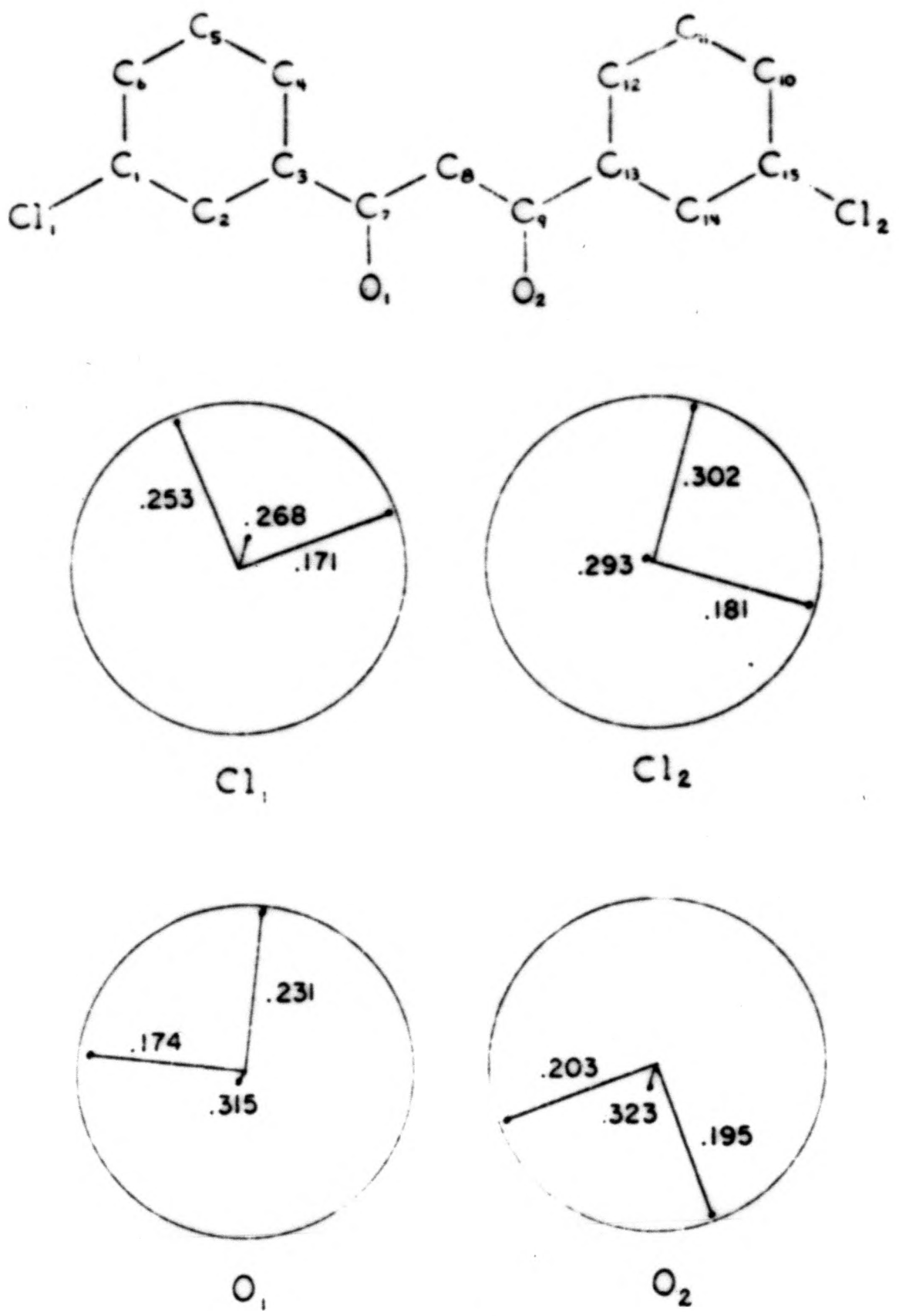
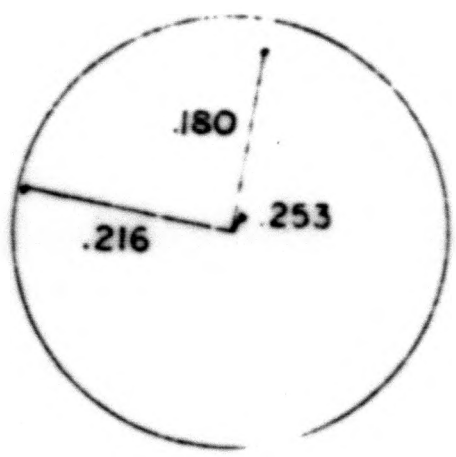
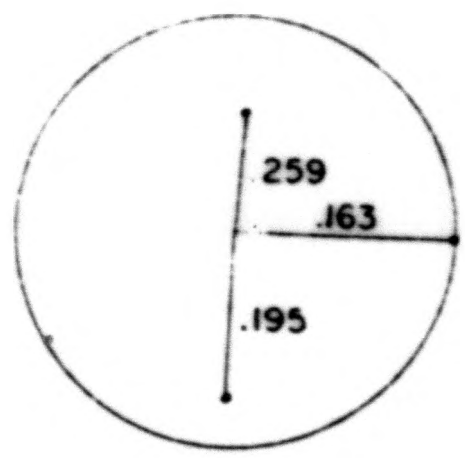


Figure 14. Anisotropic thermal stereograms for selected atoms in the bis(meta-chlorobenzoyl)methane molecule. The plane of the paper is the molecular least squares plane and the stereograms are oriented in the same manner as the molecule at the top of the Figure



C_7



C_8

C_9

Figure 14. (Continued)

greatest thermal vibration nearly perpendicular to the molecular least squares plane. A study of the data in Table 6 indicates that all the atoms have their greatest vibrations nearly normal to the molecular least squares plane, therefore it can be concluded that the molecule vibrates as a whole perpendicular to the molecular least squares plane. The two oxygen atoms have their lowest thermal vibration nearly parallel to the C-O bond. This confirms the hypothesis that the intramolecular hydrogen bond is the symmetrical type. For if it were not, the largest thermal amplitude of each oxygen atom would have been parallel to the C-O bond. The reason for this is that the anisotropic temperature factor is making an effort to correct the oxygen atom to a point atom when in reality it appeared to be an elongated atom in the C-O direction caused by a superimposed statistical distribution of carbon-oxygen single and double bonds. The large anisotropic thermal parameters of the oxygen atoms normal to the molecular least squares plane supported the hypothesis suggested by Williams et al. (48) that the oxygen atoms were warped out of the molecular plane due to the very short O-O contact.

Molecular Packing Efficiency

A comparison was made between the packing efficiencies of the nonisostructural compounds bis(meta-bromobenzoyl)methane and bis(meta-chlorobenzoyl)methane. The packing coefficient of Kitaigorodskii (60) was calculated for each of these compounds.

This coefficient represented the ratio of the volume occupied by all the atoms in the unit cell to the volume of the unit cell. The coefficient for the bromo- derivative was 0.686 and that of the chloro- derivative was 0.691. If the chloro-derivative was assumed to be isostructural with the bromo-derivative, the packing coefficient was 0.648. The difference in unit cell volumes of the two compounds was 83 Å.^{3} while the difference in molecular volumes was only 52 Å.^{3} This left an excess volume of 34 Å.^{3} of the bromo- derivative over the chloro- derivative. It was concluded, therefore, that the chloro- derivative packed more efficiently than the bromo-derivative. Figures 15 and 16 demonstrate the packing of the bromine atoms in bis(meta-bromobenzoyl)methane and the chlorine atoms in bis(meta-chlorobenzoyl)methane respectively. It can be seen that the bromine atoms tend to pack in sheets while the chlorine atoms pack in zigzag chains. The large congregation of bromine atoms may in some way compensate for the loss of packing efficiency. Figure 17 shows the packing of molecules of the chloro- derivative. The Figure is a projection of the asymmetric unit onto the (0,1,0) plane with the space group symmetry elements indicated.

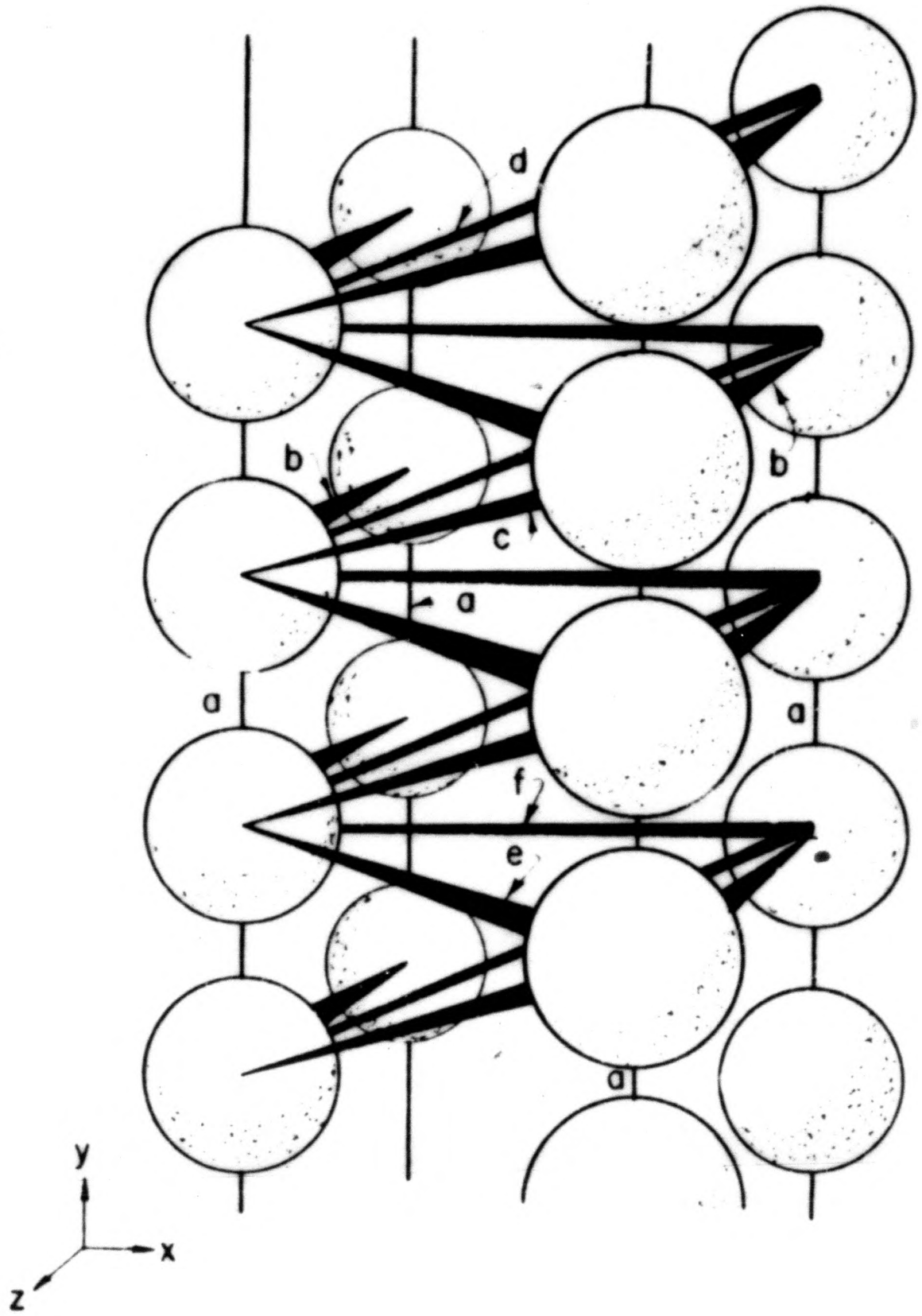


Figure 15. Packing of the bromine atoms in sheets in a crystal of bis (meta-bromobenzoyl) methane. a = 4.05 Å., b = 6.39 Å., c = 4.79 Å., d = 3.68 Å., e = 4.92 Å., f = 3.68 Å.

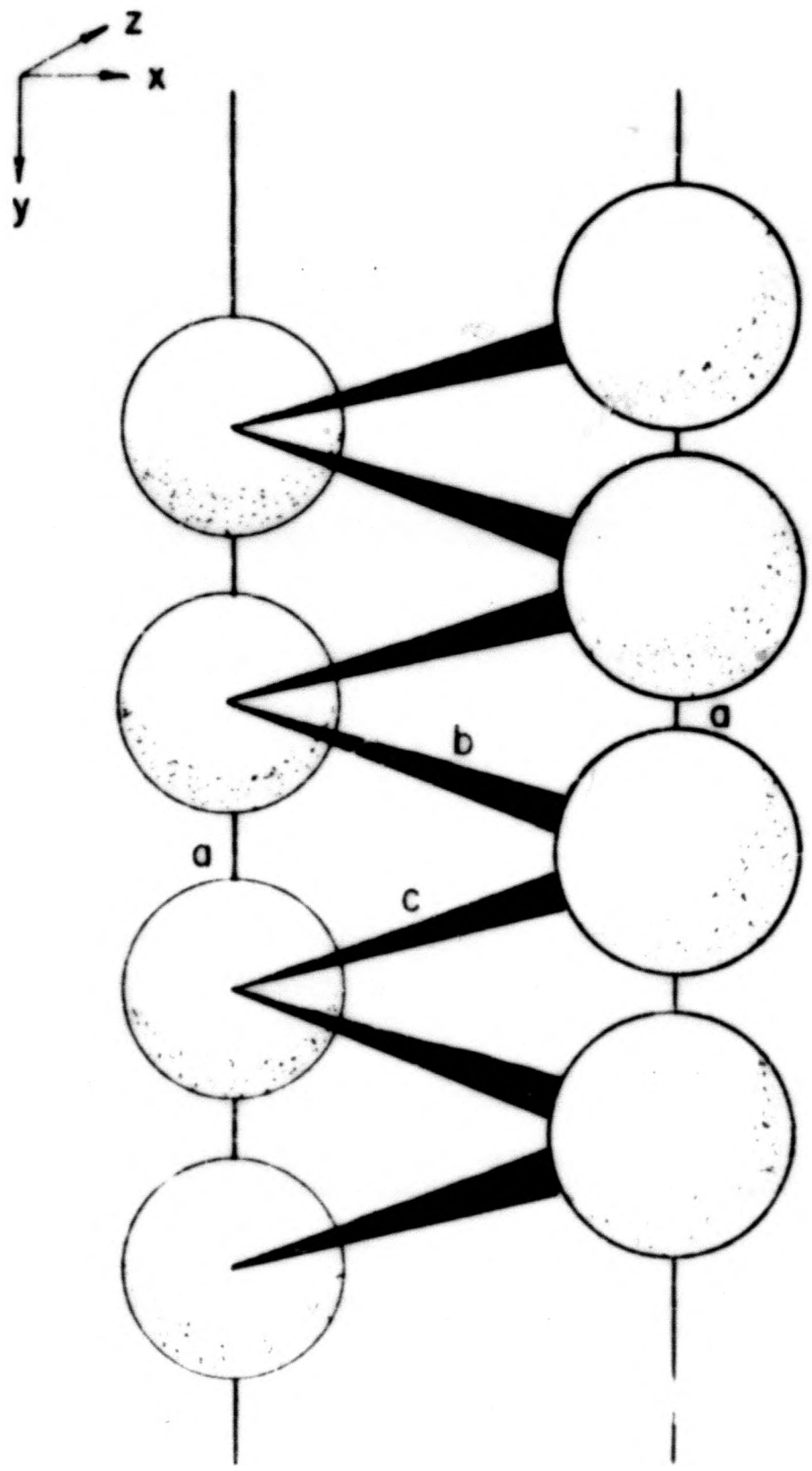


Figure 16. Packing of chlorine atoms in chains in a crystal of bis (meta-chlorobenzoyl) methane. a = 3.85 Å., b = 4.58 Å., c = 3.69 Å.

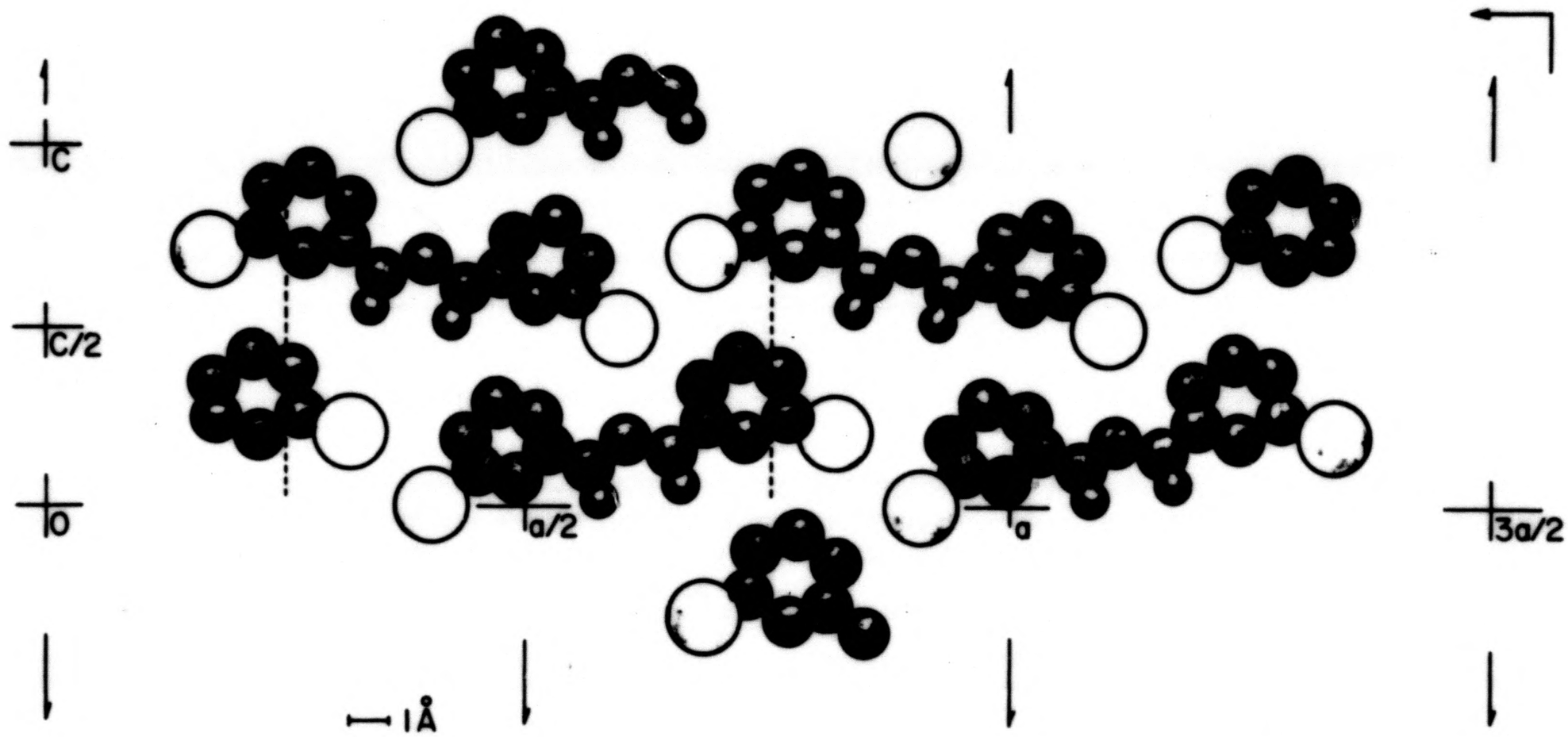


Figure 17. Molecular environment of a molecule of bis (meta-chlorobenzoyl)-methane projected onto the (0, 1, 0) plane with space group symmetry elements indicated.

SUMMARY

The structure of bis(meta-chlorobenzoyl)methane has provided proof that the enol form is the sole form in the solid state and is probably the only form in all β-diketones in the solid state. The bond distances, bond angles, and least squares plane calculations confirm a planar molecule and a planar enol group with a resonant structure. It has been demonstrated that the molecule contains a very strong hydrogen bond between the two oxygen atoms. The position of the hydrogen atom in the bond, although not directly obtainable, was deduced from anisotropic thermal parameters of the two oxygen atoms. The hydrogen atom was deduced to be equidistant between the two oxygen atoms but probably off the line of centers of the oxygen atoms.

A definite increase in packing efficiency was observed for bis(meta-chlorobenzoyl)methane over bis(meta-bromobenzoyl)-methane with the bromine atoms packing in sheets and the chlorine atoms packing in zigzag chains. The reason for the increase of packing efficiencies for the not too dissimilar compounds poses a very interesting problem.

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