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The crystal structure of bis (meta-chlorobenzoyl) methane

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THE CRYSTAL STRUCTURE OF BIS(META-CHLOROBENZOYL)METHANE

by

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A Dissertation Submitted to the

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Signature was redacted for privacy.

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Signature was redacted for privacy.

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Ames, Iowa

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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 $\overset{o}{A}$. 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 intramolecular hydrogen bonds are the β-diketones in their enol form. This group of compounds can be represented by

$$
\begin{array}{ccc}
\text{O} & \text{O} & \\
\| & \| & \\
\text{R'}-\text{C}-\text{C}-\text{C}-\text{R'''} & \quad\text{or}\quad & \\
\quad\quad\;/\backslash & & \\
\quad\quad\text{H}\;\text{R''} &
\end{array}
\qquad
\begin{array}{cc}
\text{O-H} & \text{O} \\
| & \| \\
\text{R'}-\text{C}=\text{C}-\text{C}-\text{R'''} \\
\quad\quad\;| \\
\quad\quad\text{R''}
\end{array}
$$

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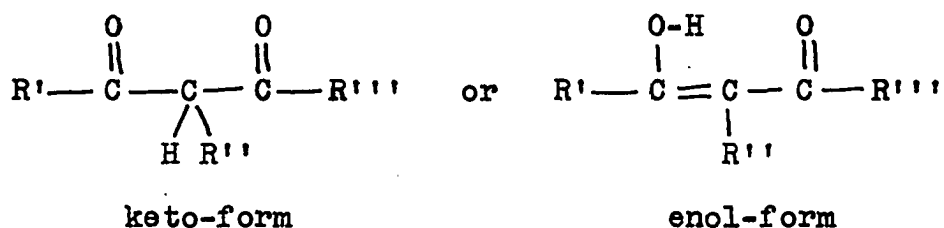
where R', R'', and R''' may or may not be the same group. These compounds have received much attention from the spectroscopists, but their results proved to be conflicting and inconclusive. The simplest group of β-diketones investigated were the diaroylmethanes, where the R'' group is a hydrogen atom.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

$$
\begin{array}{c}
\text{O}-\text{H}\ldots\text{O} \\
|\quad\quad\quad\| \\
\text{R'}-\text{C}=\text{C}-\text{C}-\text{R'''}. \\
\quad\quad\;| \\
\quad\quad\text{H}
\end{array}
$$
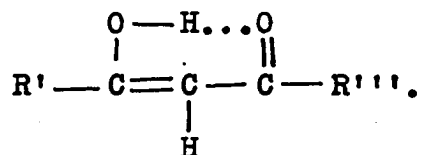
The simplest diaroylmethane is dibenzoylmethane where R' and R''' are both phenyl groups. In diaroylmethanes the primary

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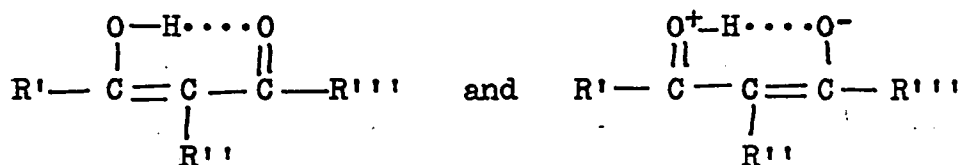
where decrease in the CO double bond character accounted for the band shift and the increase in charge accounted for the intensity. Several other interpretations of the infrared spectra of dibenzoylmethane have been made. Bratož, Hadži, and Rossmy (31) assigned several bands as follows:

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 $C \rightleftharpoons O$

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 interpre-

tation 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

$$O-H\cdots O$$
$$R'-C=C-C-R'''$$
$$\qquad\qquad H$$

and

$$O\cdots H-O$$
$$R'-C-C=C-R'''.$$
$$\qquad\qquad H$$

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

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 $\overset{o}{A}$. If the true situation was the double well model, the OH bond length would have been about 1.07 $\overset{o}{A}$. This left a resulting separation of 0.40 $\overset{o}{A}$. between the two "half hydrogens" so that the hydrogens lay 0.20 $\overset{o}{A}$. to each side of the center of symmetry. But the fourier projection showed a root-mean-square amplitude of 0.30 $\overset{o}{A}$. for the hydrogen atom peak. The centered model seemed to be the likely choice.

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

a
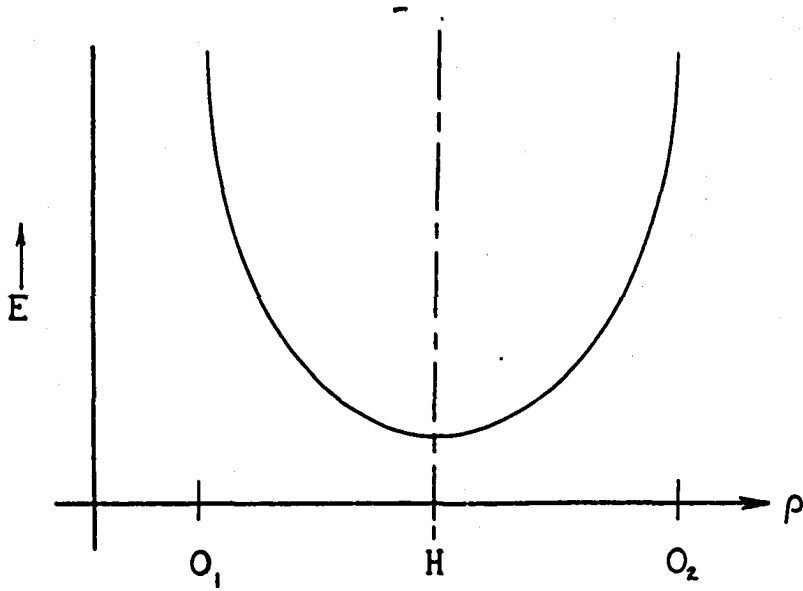
b
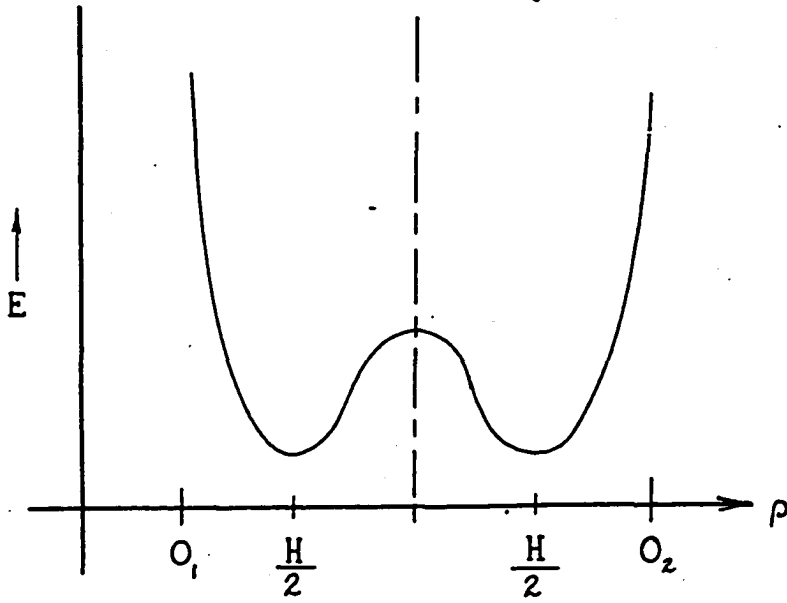
A neutron diffraction investigation of potassium hydrogen maleate (44) was made in an effort to locate the true position of the hydrogen atom. A difference fourier showed the hydrogen atom to be directly between the two oxygen atoms. Least squares cycles were run first with the hydrogen atom exactly between the oxygen atoms and then the model in which two half hydrogens were placed 1.05 $\overset{o}{A}$. 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
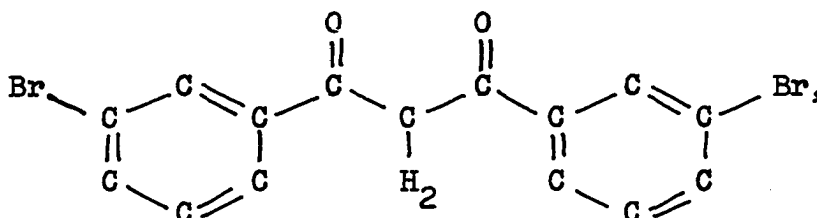
and it was selected for study because its unit cell volume was one half that of dibenzoylmethane. The heavy bromine atom would help in the initial investigation. The intensity data were collected with a General Electric single crystal orienter in order to get the best data obtainable. In this case also 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

$$Cl-\phi-\overset{\overset{\text{O}}{\|}}{C}-OC_2H_5 + Cl-\phi-\overset{\overset{\text{O}}{\|}}{C}-CH_3 \quad \xrightarrow[\text{Et}_2\text{O}]{\text{NaNH}_2} \quad Cl-\phi-\overset{\overset{\text{O}}{\|}}{C}-CH_2-\overset{\overset{\text{O}}{\|}}{C}-\phi-Cl.$$
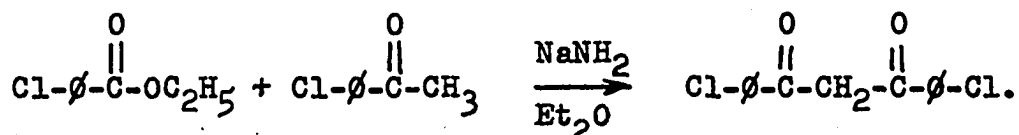
An ether suspension of sodium amide was prepared by reacting 1.5 grams of clean, dry sodium with 100 mls. of liquid ammonia. After stirring for 20 minutes the ammonia was allowed to evaporate and enough ether was added to keep the liquid level constant.

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 preci-

pitate 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 com-

bined 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 extinc-

tions 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$_\alpha$ 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 float-
ation 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 pro-
jection 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
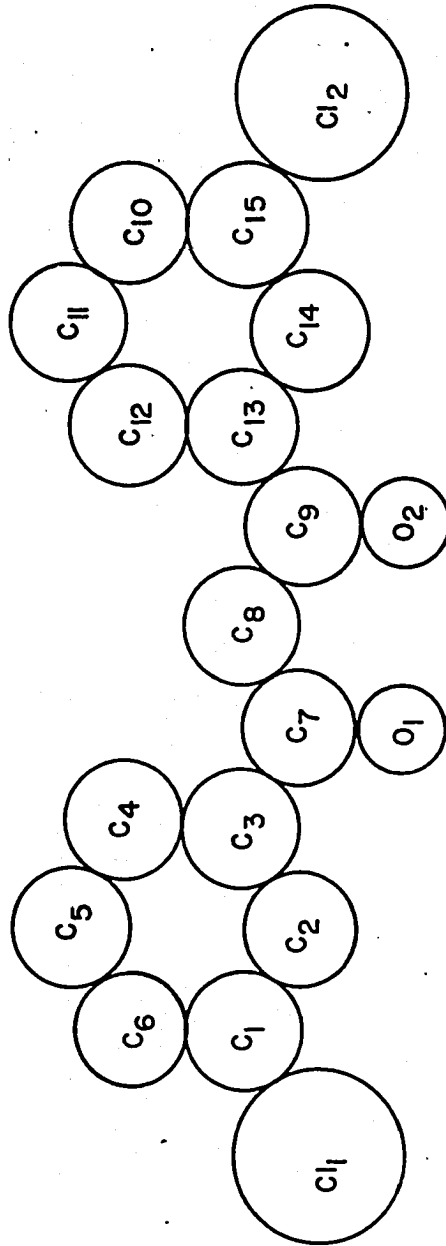
terminal hydrogens this width is 5.18 Å. There is clearly not enough room to allow for the Van der Waals interactions of the atoms between unit cells. The choice of Pca2$_1$ as the space group is then seen to be correct.

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

FREQUENCY (CM⁻¹)

WAVELENGTH (MICRONS)

21
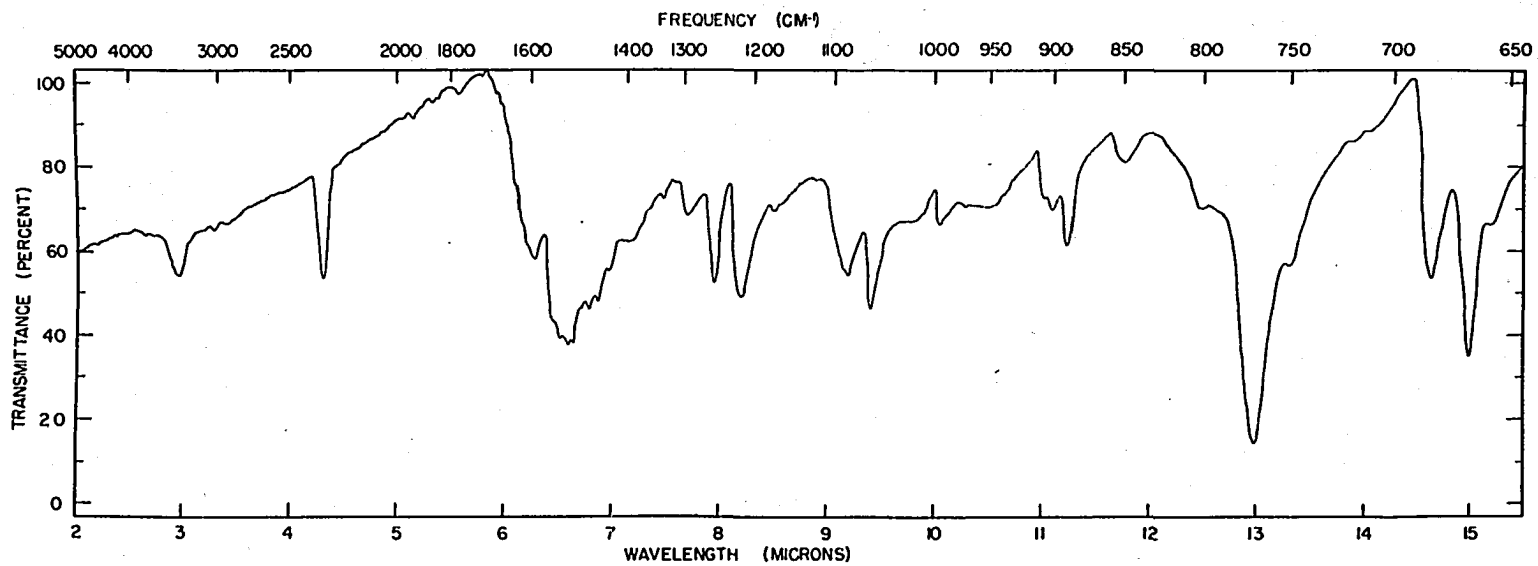
but after taking many Weissenberg photographs of crystals with
striae and a few without, no difference was found in the quality
of the photographs, so it was concluded that the quality of the
crystals was not dependent on the striae.

A suitable crystal was finally chosen which measured 115
microns along its needle axis and had an approximate trape-
zoidal 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 equa-
torial 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 $\bar{S}_o$ emerging from the X-ray tube and impinging on a crystal. Let this vector have length $\frac{1}{\lambda}$, where λ is the wave length of the X-rays. The vector sum of the negative of this vector and the vector $\bar{S}$ emerging from the crystal, also of length $\frac{1}{\lambda}$, 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 $\bar{S}_o$ and $\bar{S}$ 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 $\bar{S} - \bar{S}_o$ (Figure 4).

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, $\overline{S} - \overline{S}_0$, 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, $\overline{S} - \overline{S}_0$, 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

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

a

RECIPROCAL LATTICE POINT

χ

ϕ

ORIGIN

BASAL PLANE

b

RECIPROCAL LATTICE POINT

ω

ORIGIN

BASAL PLANE
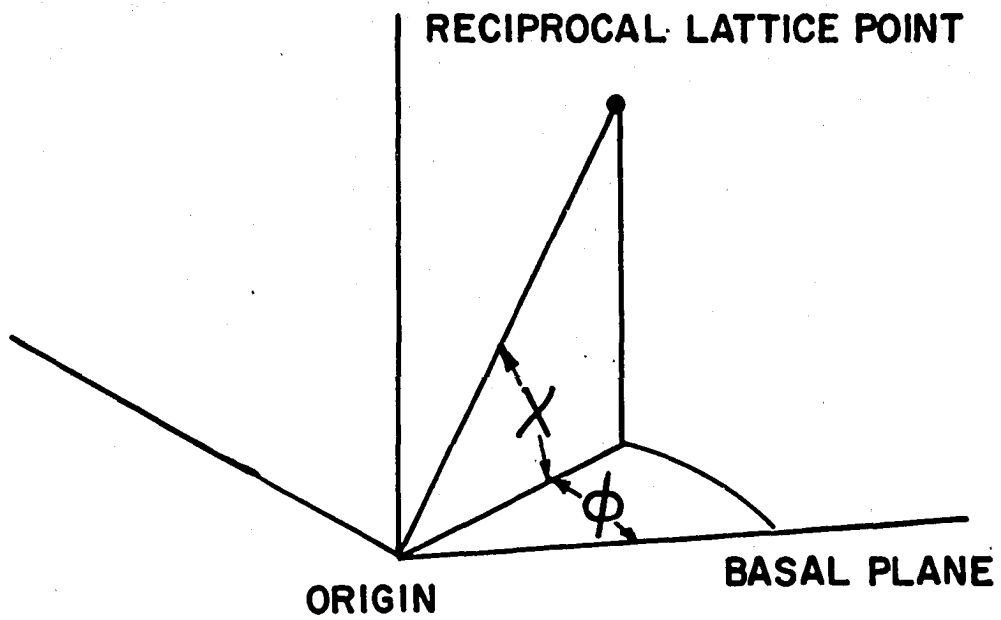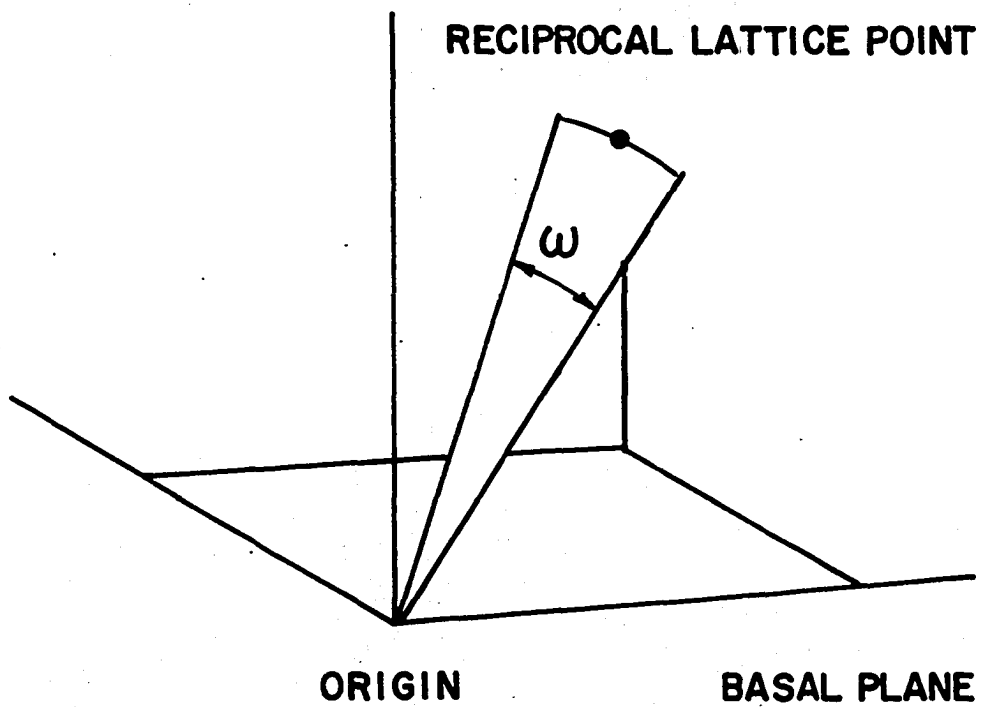
Figure 5. Schematic representation of the diffraction vector, $S - S_O$, to a reciprocal lattice point P showing its relation to the incident X-ray beam, S, and the diffracted X-ray beam, S_O
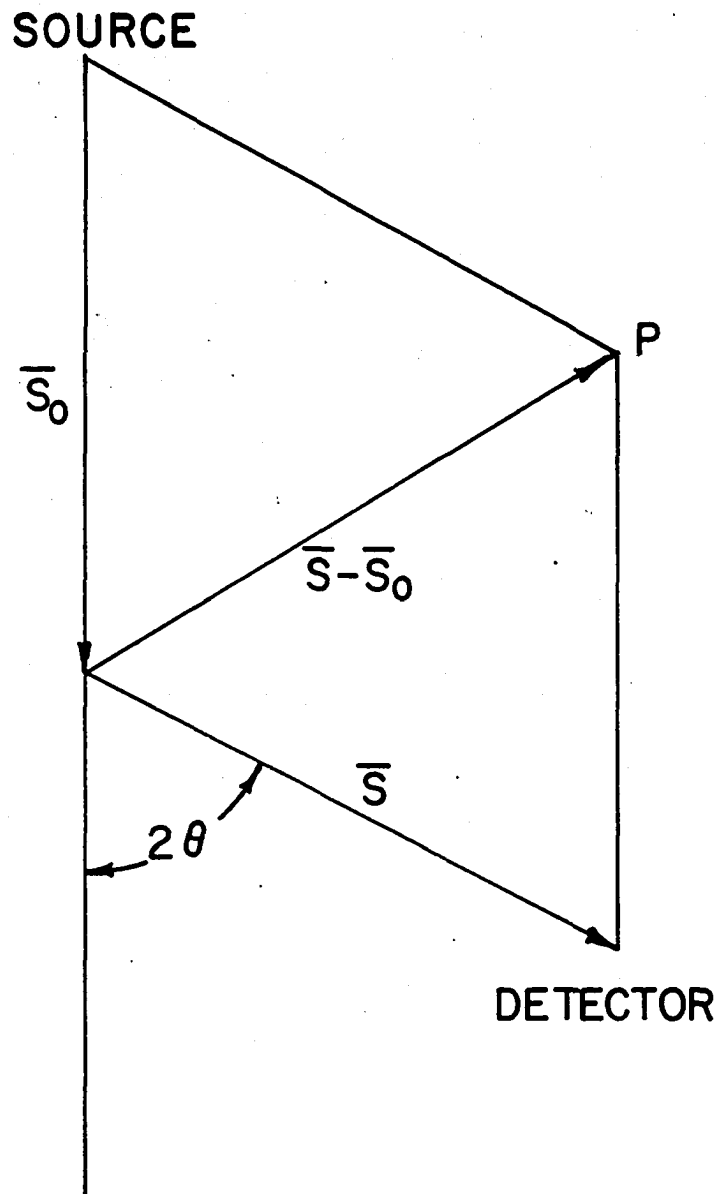
happily no reflections fell into this region. Below these values of χ and 2θ it was found that the background was a function of 2θ only and independent of χ.

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 $\qquad \exp(-\mu R)$

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 $\phi = \chi = 2\theta = 0°$ 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

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

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

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

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

$$A \cong \frac{1}{V} \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m (b-a)\left[d(x_i) - c(x_i)\right]$$

$$\left[f(x_i,y_{ij}) - e(x_i,y_{ij})\right] P_i P_j P_k \exp\left\{-\mu\left[R_p(x_i,y_{ij},z_{ijk})\right.\right.$$
$$\left.\left. -R_d(x_i,y_{ij},z_{ijk})\right]\right\}$$

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.

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 $\phi = \chi = 2\theta = 0°$, 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 substitution 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 deviation 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

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

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

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

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

[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 $(h,0,\ell)$ 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
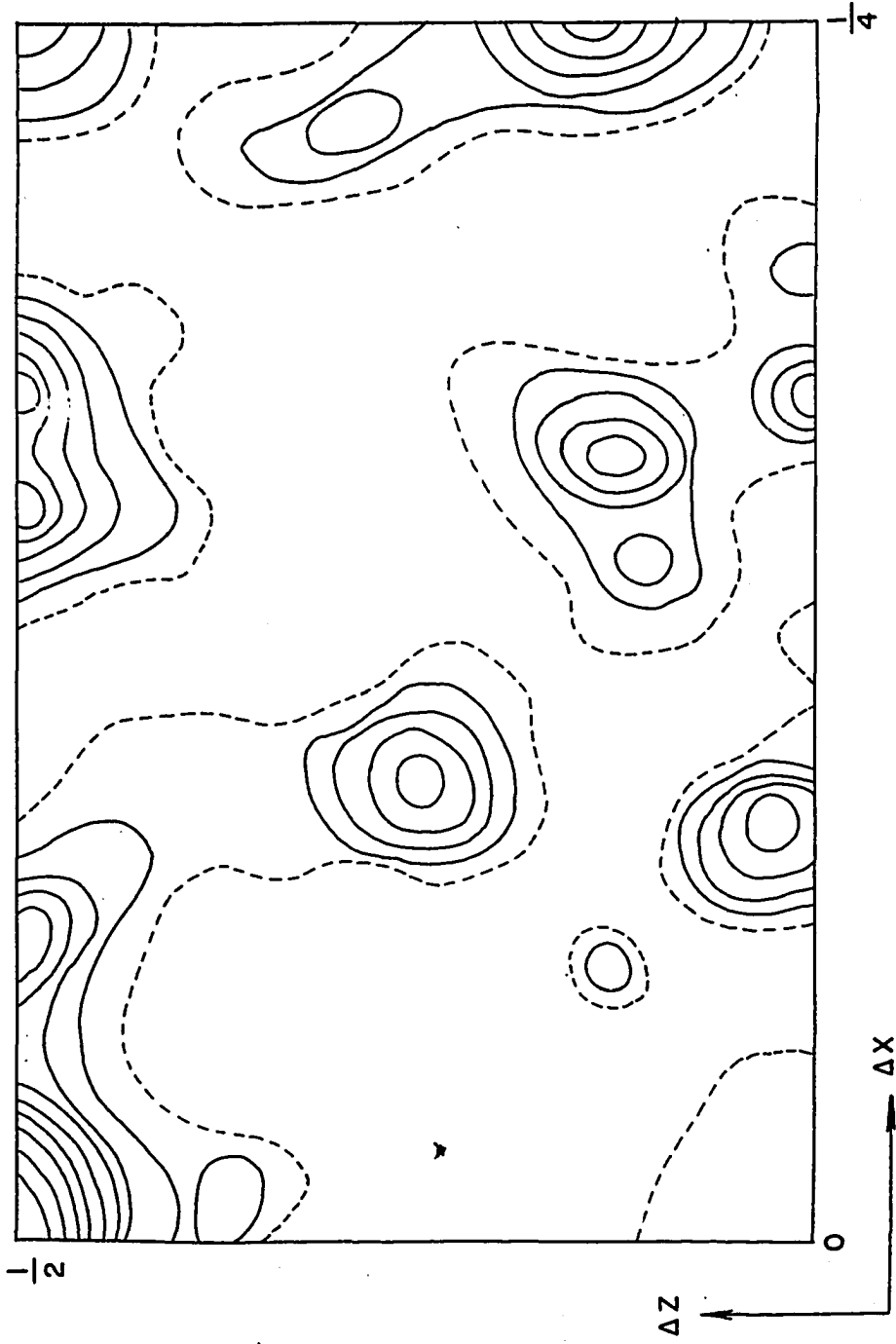
Figure 7. Weighted reciprocal lattice of the $[h,0,\ell]$ zone of
bis(meta-chlorobenzoyl)methane
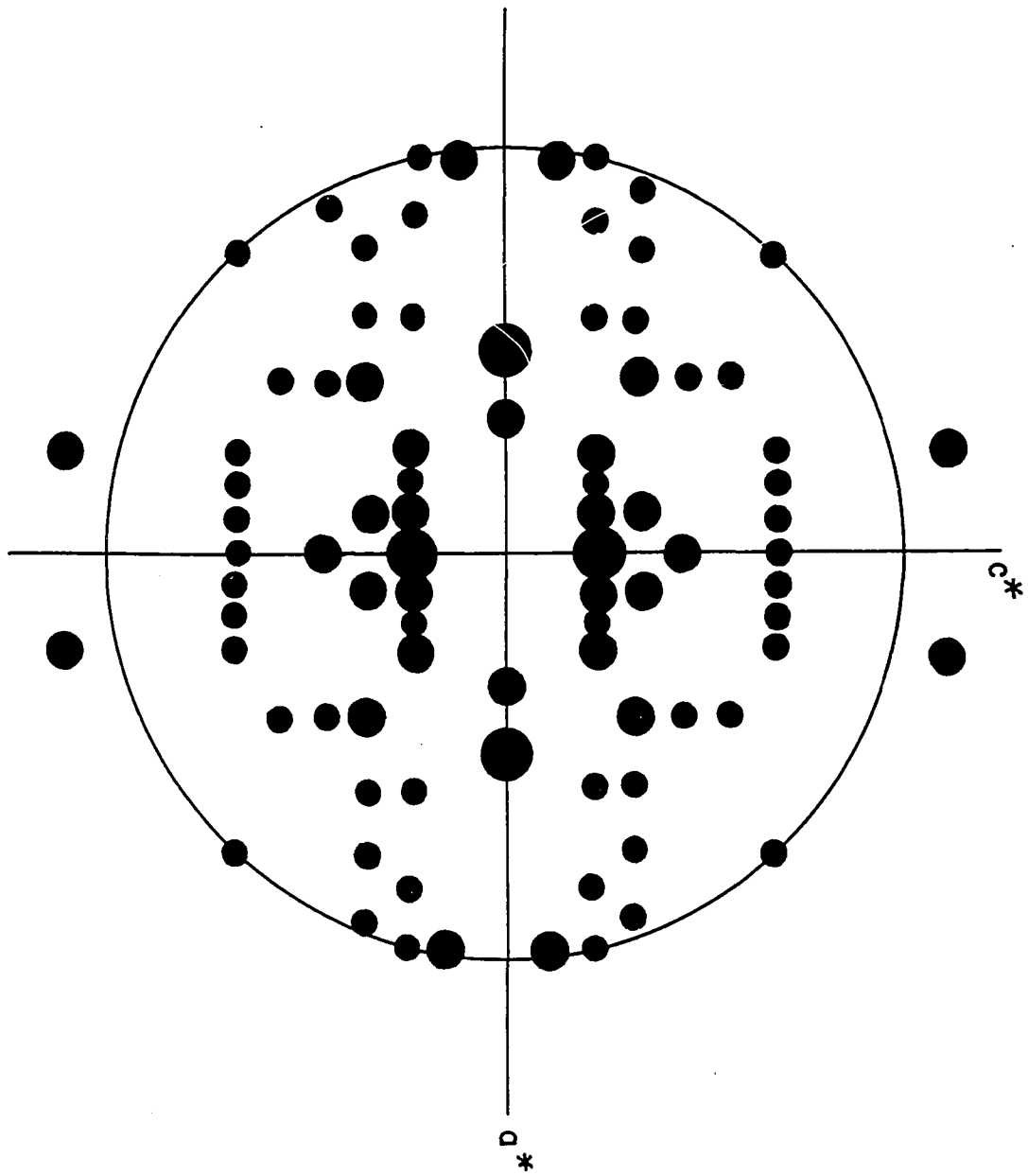
that zone. The reflections were then divided into groups according to the value of the ratio of their structure factor to the largest valued structure factor

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 Å^{-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 Å 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:

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

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 $(h, 0, \ell)$ 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"
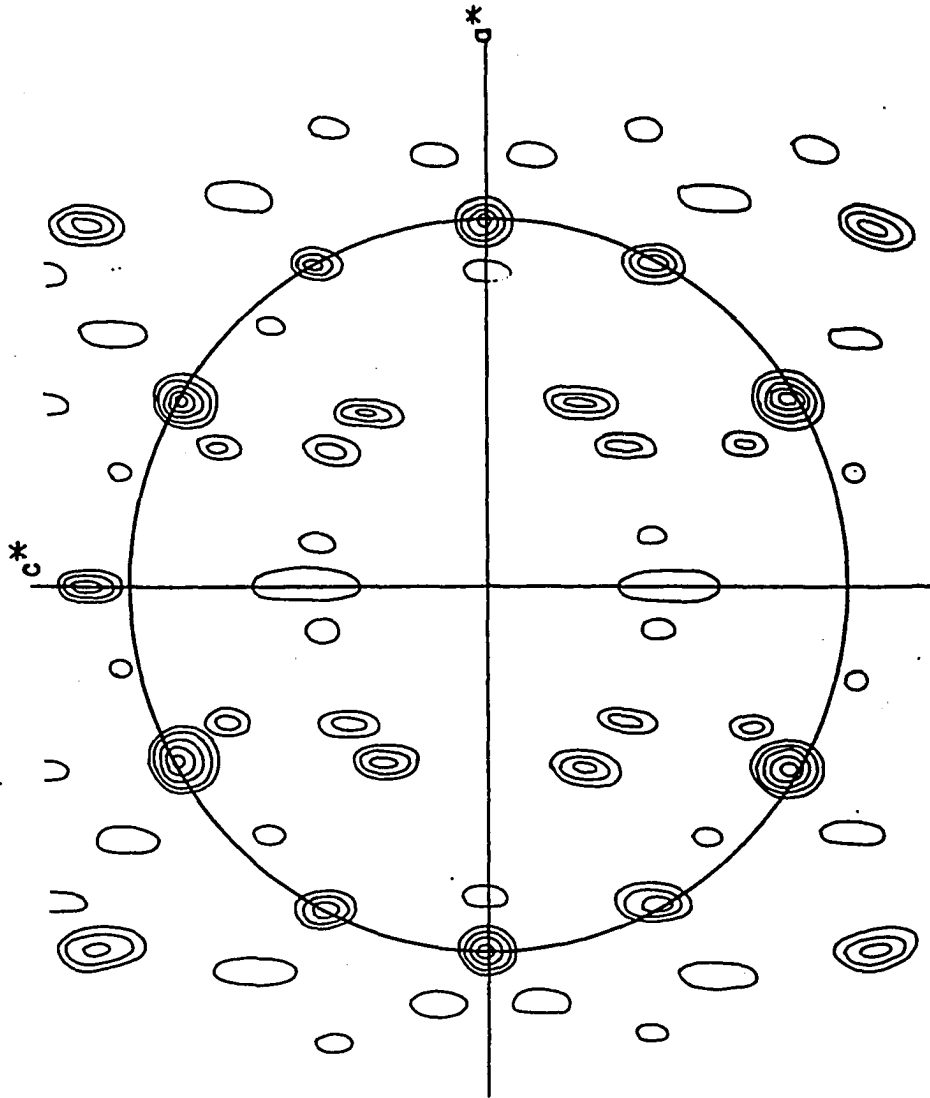
Figure 9. Fourier transform of the $(h, 0, \ell)$ data for bis(meta-chlorobenzoyl)-methane with the length of the molecule tilted 13° to the real space x-axis and the molecule tilted 24° out of the $(0,1,0)$ plane. Circle is the "benzene circle"
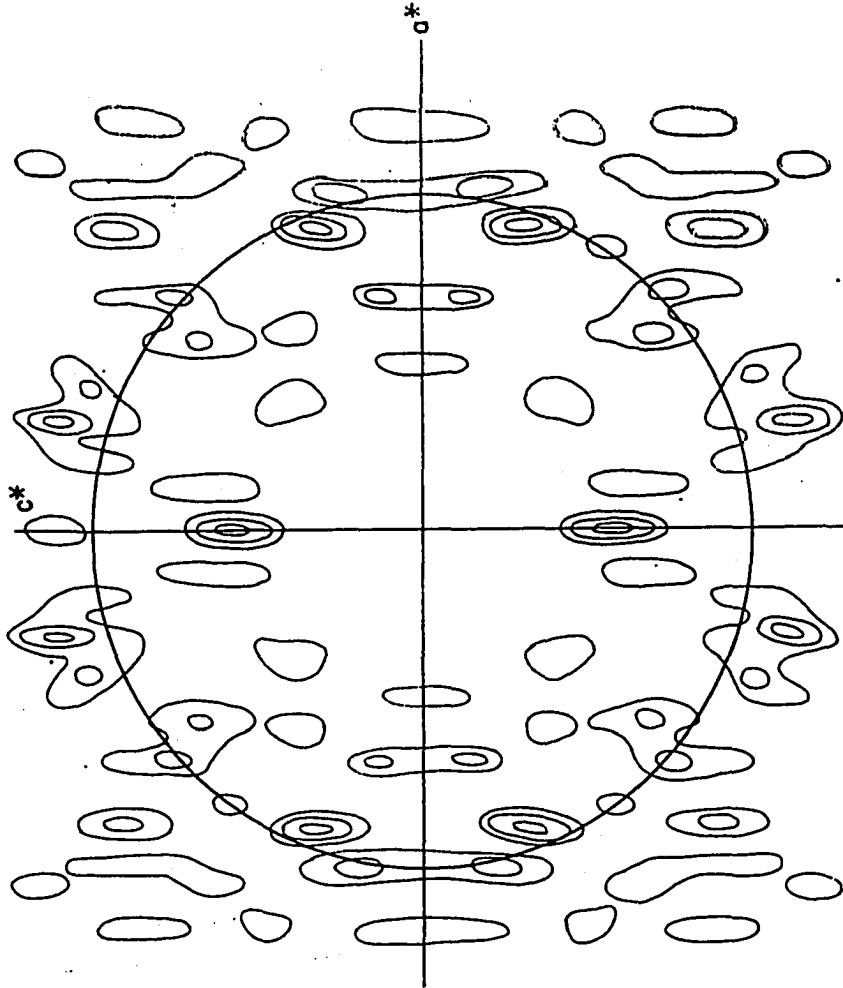
Figure 10. Three dimensional Patterson section at $\Delta x = 0.25$ with dashed arbitrary zero contours. Cross indicates 24-fold degenerate peak due to overlap of parallel carbon-carbon vectors from similar carbon atoms in the two benzene rings in a molecule of bis(meta-chlorobenzoyl)methane. The peak 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, $\frac{1}{2} + z$
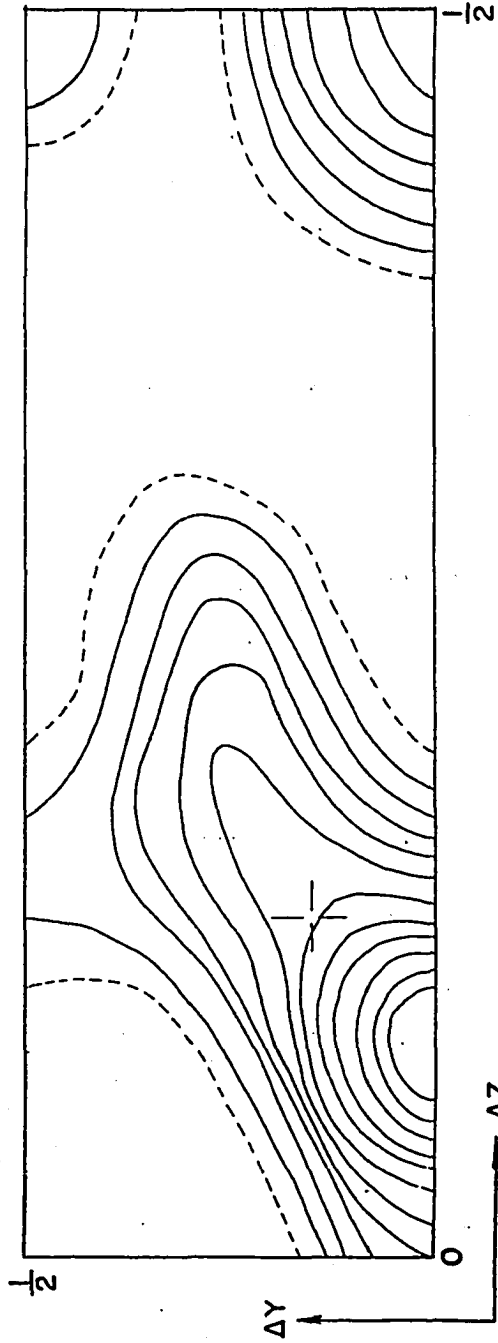
value on the $(.25, \Delta y, \Delta z)$ section it was found that the out-of plane tilt was about $20.6°$.

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

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

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

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

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 Δx = .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 le$^-/Å.^2$ contour
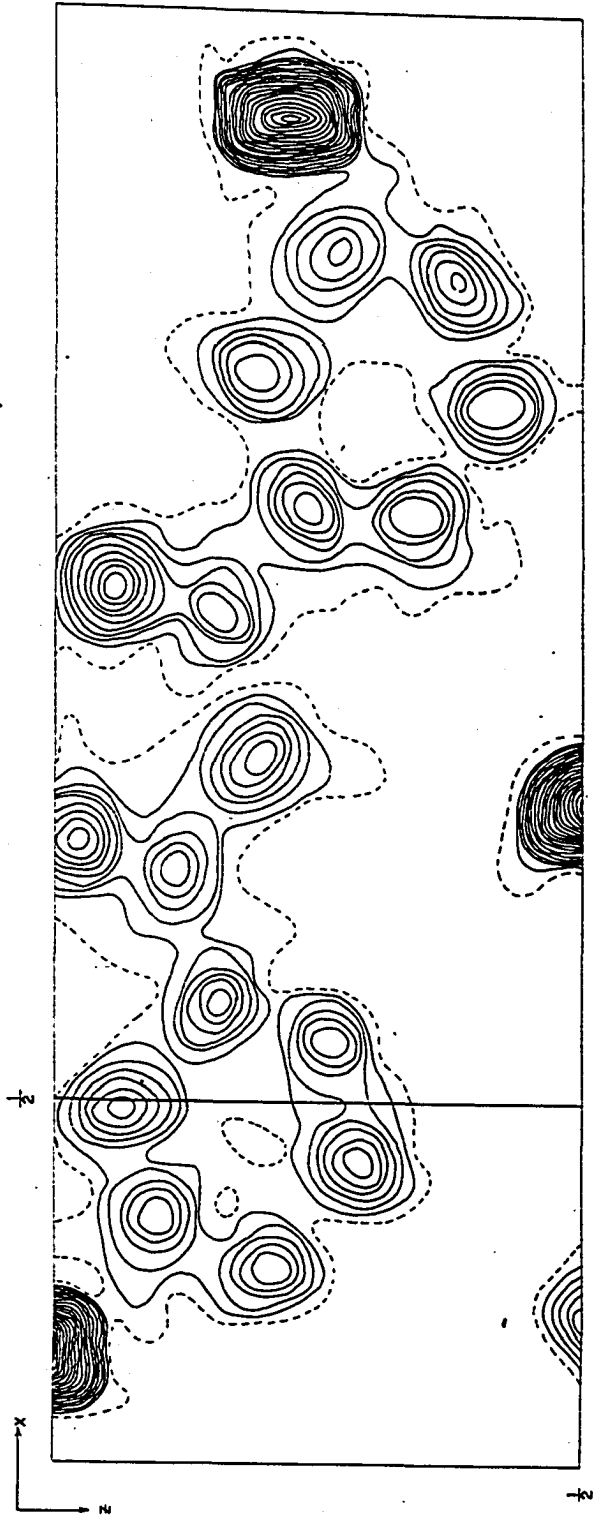
Figure 12. Three dimensional Patterson section at $\triangle x = 0.0875$ with dashed arbitrary zero contour. Cross indicates the chlorine-chlorine vector between the two nonequivalent chlorine atoms in two different molecules
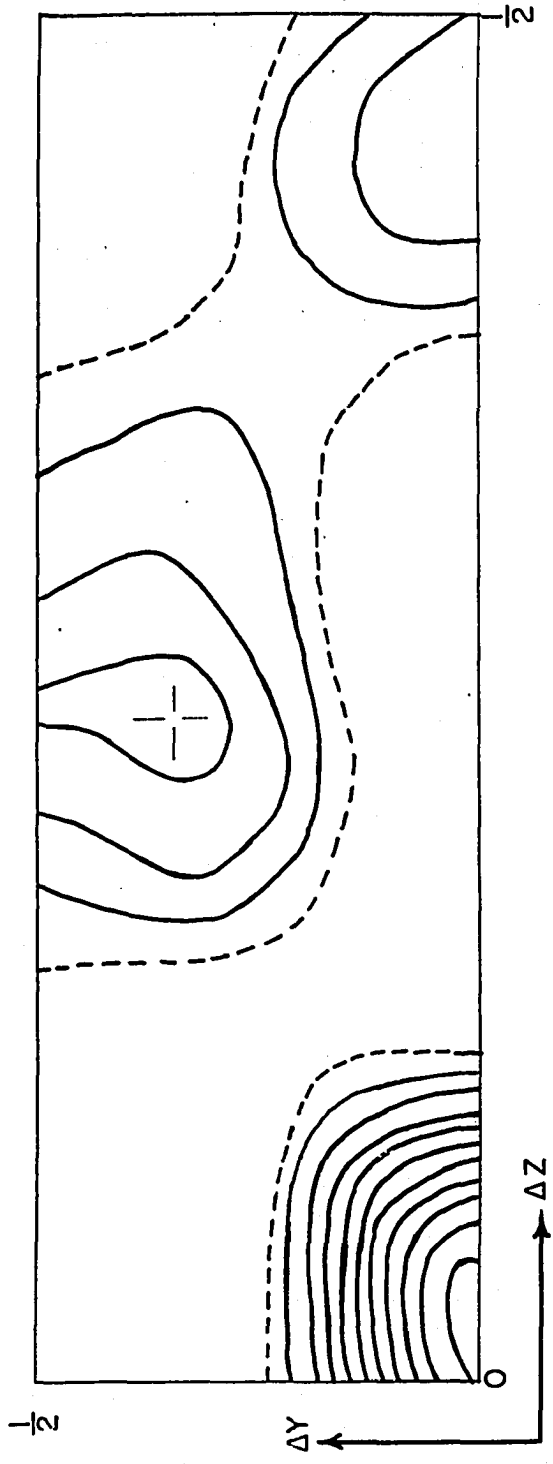
The calculation stopped refining at an R value of .230. Upon investigation of the calculated structure factors it was found that when the h index was odd, the agreement between the calculated and observed structure factors was very poor. For the space group $Pca2_1$ when the h index is odd, the real 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 $\qquad F_c = \sqrt{A^2 + B^2}$

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 was 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 $\overset{o}{A}$ 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

Figure 13. (Continued)

```
11  1CC  113  -105    41        7    71   75     9    74        8   131  135  -127   -45        3    72   89   -54    70
12. 105  131   -86   -99        8.   41   59    41    43        9   100   94   -18    92        4    76   7C   62    32
13.  29   4C   29    28         9   118  119   103   -6C       1C    9C   99   -87   -47        5   117   99   74   -66
                               1C    84   87    84    23       11   102  109   -94    56        6    73   59  -51    3C
   h= 7 K= 1                    11    77   73     1   -73      12.   23   37   -28   -24        7.   38   71  -20    68
                               12    48   52    46   -25                                        8.   35   21  -21     4
C   351  352  352     C        13.   22   2C    -1   -2C         h= 19 K= 1                     9.   32   45  -25   -37
1   149  173  -22    171                                                                       1C.   24   3C  -16    25
2   192  196  -187    59         h= 13 K= 1                   C   238  235  235     C
3   101   91   73    -55                                      1   176  176  156   -81            h= 26 K= 1
4   286  279  208   -186       C   578  554  554     C        2   142  135  -127    46
5   15C  142   45    135       1   276  267   54   -262       3    62   79   -53    56         C   101  116  -116    -0
6   12C  121    7    121       2   51C  483  -425   230       4   149  151  151    -4          1   119  126  -22   -124
7    96  125   94    -82       3   152  152   82    128       5   135  131  122   -47          2.   8C   77   -4    76
8   125  116  116     -6       4   274  268   97   -249       6    41   25  -22    12          3    91  111  -94   -59
9   236  228   25    227       5   123  134  -62   -119       7   138  131   14   130          4.   41   68  -68     5
1C  153  148  -129    72       6   194  193  -95    167       8    62   76   69   -32          5.   4C   29  -23    16
11  125  125  -123   -20       7    87   79   65     45       9    87   66  -66     5          6    71   54  -52   -17
12  112  115   61    -98       8    98  101  -41    -92      1C.   36   46   45    11          7   142  118  -5C  -1C7
13.  28   27   19    -19       9.   4C   50  -45    -22      11.   3C   32   22   -23          8    82   75  -75     5
                               1C.   4C   45   -4     45                                       9.   29   4C  -24   -33
   h= 8 K= 1                    11.   35   25   25      2        h= 20 K= 1                     1C   19   48  -46   -13
                               12.   3C   25  -25     -2
C   251  229  -229   -C        13.   2C   26  -26      0      1   225  227   37   224            h= 27 K= 1
1   295  292   33    290                                     2   104  121   94   -75
2.   3C  108  -94    -54         h= 14 K= 1                   3    98  11C  -13   11C          C.   4C   49  -49    -C
3   258  245  -95    226                                     4.   4C   76   -4    76          1.   39   2C   14    14
4   134  133  -131    18       1   182  18C  -162   -78      5   144  136   39   13C          2.   41   82   -8   -81
5   157  147  -68    130       2.   34   32   26    -17      6.   42   18    2   -18          3.   4C   51    2    51
6    54   59   51     24       3   162  161  -145   -71      7.   42   17  -17    -2          4.   4C   53   39    3b
7   210  199  -51    193       4   209  211  -65    201      8    55   53   -4    53          5    62   54  -47    2H
8   137  127  -107   -7C       5   222  211    6   -211      9   138  129   20   128          6.   38   27   16   -21
9   117  134  119     63       6    82   89   8C   -39      1C    61   45   26   -37          7.   35   29   15    25
1C.  43   66  -65      2       7   205  218  -45   -213      11    49   61   56    24          8    77   7C    4    69
11   84   67   58     33       8.   4C    3    2      2
12.  33   23   20    -12       9   147  146  -55   -135        h= 21 K= 1                      h= 28 K= 1
13   64   7C   34     61       1C   74   47  -30    -36
                               11   63   57  -24    -52      C   213  20C  -20C   -C          C    76  117  -117    C
   h= 9 K= 1                    12.   29   23  -23     -3      1.   39   48   31   -37          1   135  131   86    99
                                                             2   202  202  181   -89          2   175  18C  -179   -14
C.   29   19  -19      C         h= 15 K= 1                   3.   4C   44  -16   -41          3.   39   64   63   -11
1   195  194  178    -78                                     4   108   93  -89    44          4    99   93  -83   -41
2   119  108  105     25       C   126  123  -123    -C      5   1C5  105   82   -65          5.   38   44   -3    44
3   357  356  -34C   105       1   191  187  177     60      6   138  147   99   -1C9         6   1C6  108  -1C7    15
4   13C  118  -63    -99       2   188  182  14C    117      7    86   74  -35    65          7   116   85  -61    6C
5   311  315  119   -291       3   105  117  -116    15      8   119  124  -25   12C          8.   3C   15   -7    12
6.   36  225  218    -56       4   313  304  -265   148      9    65   71  -28   -65          9    45   65  -59    2C
7   175  18C   52    173       5   166  183  172     64      1C   68   72  -79   -60
8   21C  181  -52    174       6   229  236   64   -227      11.   25   31  -21   -23            h= 29 K= 1
9    94   81  -57    -58       7   198  175  -172    92
1C  101  116  -31   -112       8   161  16C   36    156        h= 22 K= 1                     C.   39   91   91    C
11.  38   3C   30      2       9    90   82   34    -72                                       1    76   95  -8C    52
12.  33   41   41      1       1C   81   75  -48    -58      C   122  123  123     C          2    76   84  -79    2b
13.  26   26  -22    -15       11.   34   38   -2     38      1   159  16C   75   -142        3.   39   64   63   -11
                               12.   29   33   2C     27      2   146  137  1C8    84          4   131  117   76   -84
   h= 10 K= 1                                                3   11C  115   14   -115         5    63   45  -27    3C
                                 h= 16 K= 1                   4   281  27C  262   -64          6.   6C   7C   15    61
C   204  195  195     U                                      5   138  137  1C8    84          7    55   52   50   -16
1   192  205  -127   -161      C   24C  231  -231     C      6   135  14C  14C     6          8    63   54   25   -48
2   355  362  347   -1C4       1.   35   47   24     40      7    73   51   46   -21
3-  349  337  283    183       2   285  288  -277   -82      8    72   92   89   -21            h= 3C K= 1
4   27C  261  261     -6       3   1C1  117  -38   -11C      9    57   64   64    -5
5   236  251  243     61       4   202  207  -199   -53      1C   122  118  118     7         C.   38   53  -53    -C
6   242  248  245     42       5.   38   47   -1     47      11.   24   28   22   -17         1.   38   7C   46    54
7    57   72   7C     19       6   254  262  -233   -12C                                      2.   37   22   22     1
8   143  149  139     55       8   139  146  -14C    40        h= 23 K= 1                     3   138  117  -42   109
9    62   54   -2     54       9   103   91  -30     86                                       4.   3C   52  -39    34
1C  147  145  144     17       1C.   37   19  -19     -3     C    65   68   68     C          5   134  128   46   12C
11   87   77    6     77       11   93   82  -69    -45      1   372  381  -38C   33          6.   5C   4C  -33    24
12.  32   13   12     -3       12   72   72  -72     -2      2   311  296  -282   -89         7   127  125    9   124
13   45   6C   38     46                                     3   371  362  219   -296         8.   22   24  -21    11
                                 h= 17 K= 1                   4   198  191  168   -91
   h= 11 K= 1                                                5   199  196  -32   193            h= 31 K= 1
                               C   1C5   97   97    -C       6    83   93  -43    83
C.   31   46  -46      C        1   235  229  -222    56      7   116  1C8  -44   -99         C.   37   62   62    C
1   207  204  -194    62        2.   34   32   30   -1C      8.   37   3C  -17   -25          1   1C9  122  116   -38
2   164  179  -177   -23        3   203  206  206   -13      9.   34   22    2    22          2.   36   24  -16   -19
3   425  414  132   -392        4.   37   43  -22    37      1C.   3C   16   -9   -13          3   115  115  -107    42
4   137  131   62   -115        5   111  119  -13    118                                      4.   3C   6C   60    -9
5   135  138   64    122        6   124  13C  -58   -11C       h= 24 K= 1                     5.   13C  12b   7C  -1C5
6.   54   5C    9     49        7   137  118   21    11C                                      6.   31   26  -26    -4
7   194  189  -59   -180        8   153  143  142   -1C      C   306  30C  3C6   -C           7    7C   8C    6    8C
8.   39   35   -4    -34        9    94   86  -86    -1      1   312  293  207   -2C7
9    93   85   73     44        1C   87   7C  -16     68      2    91   95   89   -33            h= 32 K= 1
1C.  39   12   -3    -11        11   68   56   53    -2C      3   193  192   77   -177
11   96   86  -71    -48        12.   24   32   30     1C     4    84  103   91    44         C.   3b   33   33    C
12.  31    7    7     -2                                      5   146  137   83   -1C4        1.   35   69  -26    64
13.  24    9    9     -1          h= 18 K= 1                   6.   4C   55    7    54          2    79   96   94    19
                                                             7   1C4   89   -8   -8C          3.   35   53   32    42
   h= 12 K= 1                   C   107  115  -115     0      8    51   56   47   -31          4    61   69   64    24
                               1   175  173   92    146      9.   33   45   -9   -44          5.   32   34   29    17
0   745  754  754     0        2   23C  22C  -205    8C      1C   44   27    4   -26          6.   48   51   47    20
1   494  490  388   -259       3   17C  144  -69    126                                       7.   22   24   24    -4
2   484  486  458    161       4   232  235  -147   183        h= 25 K= 1
3   217  222  -68   -211       5   187  201   66    19C                                         h= 33 K= 1
4   354  363  335    140       6   172  17C  -169    12      C   226  233  -233    C
5   191  193   27   -191       7   16C  153    1    153      1   143  149  14C   -49          1.   34   61  -61     8
6   151  154  136     73                                     2   145  145   -3   -145         2   104  111  1C1   -44
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Figure 13. (Continued)

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  3   7C   77   39  -67     -6  122  107 -104   27     11   84   56   52   2C      3  1C1   97   98  -15
  4  114  111  -65   9C      7*  42   4C  -22  -34     12   55   72   58   43      4*  39   48  -21  -43
  5   61   5C  -43   25      8   98   64  -64   -C                                  5  211  204   32  202
  6   82   8U  -12  -79      9   64   78  -36  -49     H= 11 K= 2                   6   47   88   87  -14
                            1C*  39   25  -19  -16                                  7*  41   22  -16   15
H= 34 K= 1                   11   51   41  -38  -15      1  327  323 -258 -194      8*  39   49   41  -26
                            12*  3C   5C   -5C  -4      2  184  187   88 -168      9*  8C   93  -2C   91
 1*   31   65   14  -64                                  3  221  245  139 -177     1C  107   95   99   34
 2*   31   31   31  -14     H= 5 K= 2                    4   62   74  -7C   25     11*  23    3   -1   -3
 3    95   93   18  -92                                  5*  42   51  -47  -19
 4   123  116   4C  -7*      1  142  14C -1CC   97       6  113   97   23  -94     H= 18 K= 2
 5    41   47   24  -41      2   69   66  -22  -62       7  113   99   55  -8c
                             3  174  238  193  136      8*  43   31  -15   28      C  188  176 -176    C
H= 35 K= 1                   4   56  1C9  -53  -45       9*  39   15  -29  -19      1  188  187 -156  1C2
                             5  1C8   94   14   5a     1C*  36   13   13  -15      2*  39    C   -0   -0
 C*   29   36   36   -0      6   9C   63   56  -3C     11*  31   22   15  -16      3  174  182  174   55
 1*   29   49  -48   -4      7  144  119   63  112     12*  23    4   -1   -4      4  189  188 -188    1
 2*   29   71  -7C   1C      8*  43    7   -7   -1                                  5  176  171  -51  164
 3*   28   3C   3C    5      9  131  143  -9C  112     H= 12 K= 2                   6  1C8  104  -98  -14
 4*   25   43   -4  -42     1C   7C   71   33   64                                  7   84   76  -55   53
 5*   2C   45  -38  -24     11*  35   36   -7   35      C  141  15C  15C   -C       8   68   74  -42   61
                           12*  3C   34  -30   16       1  171  16C  -36 -155      9   75   77  -19   75
H= 36 K= 1                                              2  193  386  385   24     1C  1C9  104 -104   -7
                           H= 6 K= 2                    3   75  101   38  -94     11*  21   34    8   35
 C*   27   22  -22   -0                                 4  169  176  102  143
 1   124  122  -29 -118      C  318  30C -1C6    C      5  13C  12C  12C   -5     H= 19 K= 2
 2*   27   2C   16  -12      1   88  103  -74   74      6  132  124  123   37
 3    63   75   42  -63      2  18C  175 -175    9      7  171  16C   16 -15v      1   88   85   6C  -27
                             3*  35   16   11   11      8*  34   91   97   27      2   65   77   71   3C
H= 37 K= 1                   4  3C4  3C7 -243  179      9*  39   1d  -18   -2      3*  4C   36   34  -11
                             5  128  122  -41  115    1C*  37   35   24  -25      4  122  113   56  -9e
 1   1C9  106  1C5  -1a      6  194  194 -174  -87    11*  3C    9   -6   -7      5   96   87   82   29
 2*   22   49   31  -38      7*  42   25  -17  -1a    12*  24   47   47    4      6   61   73   41   61
                             8  187  191 -176  -73                                 7   95   75   1C   74
H= 0 K= 2                    9   41   9C   4C   81     H= 13 K= 2                   8   68   74   33  -66
                           1C*  4C   65  -47  -45                                  9*  34   19   -3   1v
 C*   33   7d  -28    C     11*  36   4C  -11   39      1  287  267  239 -11v     1C*  28   83   46   69
 2   973  996  81C  -58C    12   77   85  -77   34      2  114  101  -84   56
 4   523  48C   74  474                                3*  38   55   12  -54     H= 2C K= 2
 6   15C  144  144   -1     H= 7 K= 2                   4   7C   65  -62   2C
 8   177  175  111  135                                5*  4C   56   44  -35      C  111  11C  110    C
1C*   4C   52   31   -2      1*  34   42  -40  -13      6*  42   53  -51   13      1  111  101  -18  1CC
12    55   59   53   27      2*  34   5C  -34   36      7*  4C   22   -4  -22      2  138  129  -84   97
                             3   97  109   29  1C5      8*  41   45  -42  -16      3   86  11C  -17  1C9
H= 1 K= 2                    4  18C  160  157  -53      9*  35   1C   -4   -8      4  127  133  12C  -58
                             5*  38   1d   17   -6    1C*  35   2C  -15   13      5  113   75  -36   71
 1   366  368 -149 -337      6  111   97   8C   55    11*  31   2d  -27   -6      6*  41   52   14   56
 2   132  15C   15  150      7  225  213  104  193    12*  22   36  -31  -18      7   87   82   64   52
 3   386  416  396 -106      8*  42   24  -11   21                               8*  36   51   41  -3C
 4   139  152  -63 -13a      9   77   74  -22   71    H= 14 K= 2                  9*  33   4C   29   28
 5    91   8C  -74    6     1C*  38   55   54    6                              1C*  27   41    6   4C
 6    82   54  -21   50     11   82   7C  -34   67      C  14C  142  142    0
 7*   43   82   -6  -82     12*  28   49  -40  -26      1  153  149   67 -133     H= 21 K= 2
 8   126  102 -101   15                                2  135  132  -69   9a
 9*   42   45  -11  -44     H= 8 K= 2                   3*  39   42   31  -29      1   84   94   32  -88
1C*   4C   4C    7   39                                4  23C  217  136 -169      2   78   77   66  -34
11*   37   35  -22  -27      C   95  101  1C1    C      5  288  269 -227 -145     3*  41   52  -22  -48
12*   3C   31  -28  -13      1  224  43C  -72  219      6  131  138  -66  122     4*  41   25  -24    9
                             2  188  187 -173   69      7  1C3   97   37  -8v     5*  41   39   13  -37
H= 2 K= 2                    3  133  129   14  177      8*  4C   45  -27  -36      6   92   84   83  -12
                             4  1C4  103   33  -4d      9   75   53  -13  -51     7*  38   26   21  -16
 C   118  143  143    C      5  181  187  -65  175    1C*  35   34    5   34      8*  35   18   14   11
 1   146  142  -68 -125      6  188  195 -19C   42    11   78   9C   21  -77      9*  29   44  -44    4
 2   173  175 -166   57      7  171  165   8C -144                              1C*  23   27  -16  -22
 3*   33   43  -37   21      8  115   97   66  -71     H= 15 K= 2
 4   519  51C  510  -25      9  173  173   53  164                               H= 22 K= 2
 5   221  213 -188 -1CC     1C   66   64   11   63      C*  36   14  -14   -C
 6    77   69   4C   56     11   91   77  -47   61      1*  39   37  -33   18      C*  83   9C   90    C
 7   237  231   12 -231     12*  28   55  -35  -45      2*  39   55   54   11      1  112  115  1C6  -45
 8*   41   29   28   -6                                3   77   7e   39   67      2  188  163  176  -52
 9*   41   11   -6  -10     H= 9 K= 2                   4  182  16C -168    6     3*  42   51  -26   44
1C*   4C   56  -45   32                                5  1CC  109  -32  104     4*  42   51  -33  -34
11    64   65   -5  -65      C*  32    4    4    C      6*  41   32    7  -31      5  189  191   78 -174
12*   3C    6    5    5      1  106  122  116   38      7*  42   43  -15   41      6  204  201  199  -27
                             2  1C9  106   81  -68      8*  35   76  -19   18      7   95   83   51   66
H= 3 K= 2                    3   99   79  -71  -36      9*  37   51  -30    6     8*  32   96   71   64
                             4   58   44   43    9    1C   68   46  -20   41      9*  28   15   14   -6
 C*   34   19  -19   -0      5  17C  144   63 -129    11*  27   2e   17   2c    1C*  21   2C   20   -2
 1    57   79   43  -67      6  14C  116  118  -12
 2   215  218 -218   11      7*  42   35   23   26     H= 16 K= 2                 H= 23 K= 2
 3    87   9C   4C   81      8*  43   29   11   26
 4    65   7C  -51   48      9   71   52  -36  -37      C  295  293 -293   -C      1*  41   49    8  -49
 5*   37   36  -12  -23     1C*  38   23  -14  -1d      1  136  144  12C  -80     2*  4C   4C  -27  -30
 6*   4C   55  -26  -23     11*  33   1C   -7   -6      2  1C6  117 -116  -16     3   61   77   12  -76
 7   169  169  -51  161     12*  27   42   33  -27      3   75   76  -42   63     4  152  142  -4C -136
 8*   43   31   21   24                                4  256  242 -241  -25     5   83   67   52  -42
 9    98   93  -10  -93     H= 10 K= 2                  5   67   66   24   61     6   76   51   29   42
1C*   42   49  -45   19                                6   92   76   46  -6C     7*  37   29  -24  -16
11*   35   28   -2   2a      C  186  185  185   -0      7  119  104  -99  -3c     8   52   63  -6C  -19
12    55   49  -48   -5      1  349  356  353  -47      8   83   82  -65   51     9   54   48  -32  -36
                             2  185  199  192   53      9*  36   45   -0  -45
H= 4 K= 2                    3  152  145  -92  113    1C*  34  131 -120  -5c     H= 24 K= 2
                             4   63   88   88   -6     11   81   83  -77   2a
 C    67   67  -67   -C      5  135  131   15 -130                               C  181  181  181   -0
 1   243  244  222 -1C2      6  2CC  197  191  -50     H= 17 K= 2                 1  246  255 -241  -82
 2   285  286 -239 -157      7  26C  251  133  213                               2  143  129  -30  125
 3    98  112  -43 -104      8  123  10e   96   45      C*  38   19  -19    0     3  241  229   8C -214
 4   222  209 -171 -12C      9*  39   34   10   32      1   85   96  -42   8a     4  155  148  128  -75
 5    77   77  -13  -76     1C*  37   42   37   20      2*  4C   74   10   74     5*  39   32   32   -1
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Figure 13. (Continued)

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  C   62   64   50   32      h= 34 k= 2             h= 6 k= 3               h= 13 k= 3
  7  1CC   88   46  -75                              C  2C4  19C -19C   C•    C  154  14C -14C    0•
  6•  27   16  -15    3      C•  25   34  -34   -C   1•  4C   46  -22   43    1  115  112  -45 -1C3
  5•  24   23   17  -15      1•  24   45  -2e  -37   2•  4C   3e   -7  -37    2   78   83   12  -82
                            2   95   96   87  -34   3•  41   27   -1   27    3•  41   5C   12  -49
 h= 25 k= 2                  3•  72   73   38  -62   4  175  176 -174   28    4  113   91  -75   51
                                                    5•  42   33  -33    2    5•  4C   49   49   -3
  1  115  116  1CC  -62     h= 35 k= 2              6•  41  132 -112  -7C    6•  63   73  -69  -25
  2  114  112  -85  -72                              7•  41   5C   24    6    7•  37   24  -22   -9
  3   61   54  -50   29      C•  19   13   19    C   8•  35   11   -6   11    8•  34   28  -22   17
  4•  38   21   13  -17                              9•  35   2C  -19    5   1C•  23   41  -41   -3
  5•  39   14   21  -27     h= 0 k= 3               1C•  29   35  -31  -16
  6   62   59  -31   5C                             11•  17   13    6   1e   h= 14 k= 3
  7   91   72   -1   7c      C•  38   24  -24    C
  8•  28   11  -1C   -6      2   84   71   9C  -17  h= 7 k= 3                 C•  42   56   56   -C
  9•  23   13   -9    1      4  327  304  303   27                           1   99   85   27  -81
                            6   78   55   4c   29   C•  35   14   14   -C    2   84   85  -73  -43
 h= 26 k= 2                  8   6C   51   34   39   1   74   69   64   6c    3•  4C   34  -36   -1
                           1C•  31   21   1c   14   2  115  13c  130  -4U    4•  7C   71   69  -12
  C•  33   17  -17   -6                              3•  43   45   25   33    5•  4C   36   -C  -36
  1•  38   27   13   24     h= 1 k= 3                4•  42   47   27   3•    6•  4C   41   11   48
  2•  39   5a  -31  -4f                              5  13C  123  1C7   61    7  1C7   9e  -25  -94
  3   46   8d  -54  -69      C  21C  134 -145    C   6•  43   53   34   17    8•  35   26   -6  -25
  4•  38   4d  -45   19      1   79   82   28  -77   7•  42   47  -3C   21    9•  5C   41   -1  -41
  5  162  142   -2 -142      2  128  123   94  -79   8•  38   27   12  -24
  6   85   63  -52   3L      3  2C2  221  -52 -215   9•  35   11  -18   24   h= 15 k= 3
  7•  31   27  -26    7      4  206  196 -106  165  1C•  3C   33   32   -7
  8•  26   3c  -27  -23      5  13C  172  119  -26                           C•  34   41  -41   -C
                            6•  43   3C   -3  -3U  h= 8 k= 3                 1•  41   44    1   44
 h= 27 k= 2                  7•  3e   43  -25  -21                           2   95  117 -117   12
                            8•  4C   12    8    9   C•  39   17   17    0    3  1C2   99   48   8c
  1•  38   58  -1C   57      9•  35   27   -0  -27   1  153  12d  -71  1Ce    4•  e7   82   62   -7
  2  1C8  101   99  -26     1C•  32   45  -42  -25   2•  62   7c  -71   11    5•  4C   5d  -58    1
  3•  37   61   28   59     11•  24   35   -7  -34   3•  41   74   24   1C    6  1C3   92  -7C   59
  4   71   62  -62   -L                              4•  42   31  -26   1•    7•  3e   41   3C   29
  5   52   55    6   59     h= 2 k= 3                5•  85   7c  -7C   -c    8•  32   26   -4  -26
  6•  32   7e   75    6                              6•  42   57   -o  -5o    9•  28   44  -15   41
  7•  25   26  -1e  -2o      C•  42   76   76    C   7   75   72   53   49
  8•  23   45  -19   41      1•  41   5C  -34  -17   8•  35   23   14  -25   h= 16 k= 3
                            2  1C3   88    8  -8c   9•  4C   65   4e   44
 h= 28 k= 2                  3   58   64   39  -51  1C•  27   24    1   24    C   77   97  -97   -L
                            4  15C  126   43 -114                           1   64   71   3e  -44
  C  143  155 -155   -C      5  131  119 -114  -31  h= 9 k= 3                2   54  1Ce -1c4  -26
  1•  36    8   -3    8      6  173  171  1C3  130                           3   64   65   22   61
  2   52   68  -51  -45      7  127  108   1e -1C6   C•  4C   3e   36    c    4   88   74  -14  -6o
  3•  35  117  -81   84      8•  35   12    8   1e   1   85  1C4  -6C  -6c    5•  7C   7C  -6C  -3c
  4   97   99  -63   54      9•  3e   2e   13  -24   2•  41   57   56  -11    6•  37   32  -31  -11
  5•  34    5    C    5     1C•  32   27   25   -4   3•  58   63   37  -c1    7   53   45  -36   34
  6   92   61  -39  -71     11•  23   26  -1C  -24   4  12e  113  1C9 -12c    8•  4e   46  -3C   3e
  7   62   6C  -20   56                              5   91   7C  -12   63    9•  26   44  -21  -39
                           h= 3 k= 3                6•  57   49  -4C   25
 h= 29 k= 2                                          7  1C1   8C  -27  -75   h= 17 k= 3
                            C•  42   65  -65    C   8  1Ce   84   64  -54
  C•  36   30   3c    C      1•  4C   35   -4   3e   9•  5C   43   43   21    C•  41   61   61   -L
  1•  36   48  -38   3C      2   8C   70  -75  -15  1C•  26   33   32   23    1•  41   6c   c1   25
  2•  34   16    8  -14      3•  4C   1e  -14  -2e                           2•  41   54  -25  -4e
  3•  33   12   12    2      4•  42   31   -5  -31  h= 1C k= 3               3  112  11C   -3  11C
  4•  34   59   4C  -43      5•  41   51   34   3c                           4•  4C   63   42  -4e
  5•  3C   4c    C  -46      6  145  117 -114   24   C  135  137  137    C    5•  39   5e    5   3u
  6•  27   41   38  -17      7•  42   38   -4  -35   1•  41   23   28    3    6•  37   35   35    4
  7•  22   22   -8   21      8•  41   34  -35  -1o   2•  41   45   34   22    7   54   5e    4   5e
                            9   5C   55  -31   47   3•  8c   63  -62   55    8•  35   25   14   7C
 h= 3C k= 2                 1C•  31   33  -13   37   4•  42   67   6C  -31    9•  49   59   36   4e
                           11•  22   15   -4  -13   5  114  1C5  1C3  -17
  C•  34    4    4    C                              6•  55   6C   6C   -7   h= 18 k= 3
  1  1CC  114  -61   97     h= 4 k= 3                7•  39   22   16   14
  2•  34   35  -13   32                              8  1C8   84   7e   35    C•  41   54  -54    0
  3   94   9C   87   26      C  111  127 -127   -C   9•  32   24    8   2e    1•  89   83  -85   -u
  4•  32   39  -36   17      1  119  117   74  -9C  1C•  27   31   2e  -11    2•  4C   41   -7   4C•
  5  1C2   91  -16   9C      2  146  13c -138   -5                           3•  65   47  -47   -6
  6•  25   17  -16    4      3   89   97  -83   54  h= 11 k= 3               4  12C   97  -28   3z•
                            4•  43   26   13  -22                           5•  36   24    8  -2z
 h= 31 k= 2                  5  129  115   41 -1C7   C•  42   55  -55    c    6•  32   2C    3   19
                            6   91   7o  -26  -7c   1  172  172  13C -112    7•  29   43  -43   14
  C•  33    7   -7   -6      7•  41   63  -58   25   2•  41   55  -51  -22    8•  22   2d  -2e    1
  1•  32   31   28  -13      8•  4C   1e    C   1e   3•  43   59    9  -5d
  2•  32   39   39   -C      9   83   76    5  -7o   4•  41   24    5  -22   h= 19 k= 3
  3•  31  -2e   -8  -25     1C•  32   60  -59    e   5  154  137   23 -135
  4•  29    7    7   -2     11•  22   27    7   26   6•  4C   24  -14  -2C    C•  4C   1e   1e   -C
  5   57   57   50  -27                              7•  3e    9    4   -8    1•  42   5C  -45  -22
  6•  2C   42   4C  -13     h= 5 k= 3                8•  3e   41   33  -25    2•  4C   56   52  -19
                                                    9•  33   53   -o  -53    3•  34   64   63    9
 h= 32 k= 2                  C•  39   33  -33    C  1C•  24   1C   -3   -5    4•  63   71   55   44
                            1  115  122  1C5   62                           5•  36   29   16   25
  1•  31   53   49   2C      2   81   75  -71   22  h= 12 k= 3               6•  76   7C   59  -3d
  2•  29   14    1   14      3  11C   86  -60   61                           7•  31   21   14   15
  3   53   53  -47   35      4•  4C   48   1C  -47   C•  4C   4C   4C    c    8•  49   62   54   29
  4   63   65   64    5      5  141  110   62   98   1  174  158 -16e    5
  5•  22   39   39   -1      6•  43   3C   -7   29   2  132  13e  134  -22   h= 2C k= 3
                            7  128  131   -3  131   3  217  215  151 -153
 h= 33 k= 2                  8•  41   41  -31  -26   4   55   93   77   62    1   57   64   18   c1
                            9   55   56   -5   55   5•  38   75  -72   19    2•  35   31  -28  -13
  C•  2e   2C  -2C    C     1C•  29    8    6    o   6•  39   5e   54  -21    3•  9C   6e  -26   63
  1•  27   5C  -38  -32     11•  22   17    1   17   7•  38   3C   23  -19    4•  67   5C   21  -45
  2•  27   29  -24  -1e                              8•  35   43   22   37
  3•  25   27    4  -26                              9•  31   3d   3e  -11
  4•  22   35  -34   -4                             1C•  24   34   34   -5
```

Figure 13. (Continued)

```
5•   35    18    13   -13        1•   28    49    -7    49        4•   35     6     C     6        H= 13 K=  4
6•   34    37     9    36        2•   27    15     9   -12        5•   35    39    28    27
7•   31    37   -12    35        3•   25     4     4     C        6•   33    27   -12   -24        1•   35    42   -41     9
8•   24    37    33   -17        4    73    74   -71   -2C        7•   3C    45   -21    39        2•   34    29   -29     6
                                                                 8•   19    19    -9    17        3    94    92    47   -79
H= 21 K=  3                      H= 29 K=  3                                                      4•   32    31   -30     8
                                                                 H=  6 K=  4                      5•   28    11    -8    -8
C•   37    86    86    -C        C•   26    17    17     C                                         6•   25    12   -10    -6
1•   41    44    -7   -43        1•   24    43    37    22        C•   39    34   -34    -C
2•   39    43   -41   -13        2•   24    18    12   -13        1•   37    21   -17    12        H= 14 K=  4
3•   38    58    43   -39        3•   22    41     0    41        2    62    62   -59    18
4    90    85    82   -25                                         3•   37    13   -12     4        C    73    72   -72    -C
5•   36    45   -29   -35        H= 30 K=  3                      4•   38    51   -38   -33        1•   34    14    -6    13
6    64    49   -46   -18                                         5•   34    1C    10     3        2•   32    39    32   -22
7    62    56    17   -54        C•   23    33    33     0        6•   31    27    11   -25        3    69    54   -17   -51
8•   22    28    25   -12        1•   21    50   -40    30        7•   28    13   -13     3        4•   3C     5    -2     5
                                                                                                  5•   28    23     9   -2C
H= 22 K=  3                      H=  0 K=  4                      H=  7 K=  4                      6•   24    15     8   -13

0•   38    31   -31    -0        C    89   112   112     C        C•   37     1    -1    -0        H= 15 K=  4
1•   38    11     9    -6        2•   39    12    -6    11        1•   37    21   -17    12
2    67    75    74   -11        4    85    64    -6   -63        2    84    73    73     1        C•   33    28   -28     C
3•   37    36   -36    -0        6   108    96    79    55        3•   38    29    26    14        1•   34    35    15    32
4    60    6C    53    27        8•   30    22    20     9        4    57    47    19    43        2    59    54   -26   -48
5•   33    32     6   -32                                         5    77    77     0    77        3•   3C    52   -49    19
6   116   10C    58   -81        H=  1 K=  4                      6•   31    27     7   -27        4•   3C     4    -4     2
7    70    76    75   -10                                         7•   27    29    -3    29        5•   27    26    12    26
                                 C•   37    47   -47     0                                         6•   22    36   -2C    3C
H= 23 K=  3                      1•   41    43   -17   -40        H=  8 K=  4
                                 2•   4C    23     1   -23                                         H= 16 K=  4
0•   36    47   -47    -0        3•   4C    57   -38   -43        C•   38    29   -29     0
1   13C   134    89  -101        4•   39    33    17    28        1•   39    34     5    34        1•   31     5    -2     4
2    55    65   -55   -35        5   138   122    42  -115        2•   37     5    -4    -2        2•   31    5C   -25   -44
3    67    6C   -51    32        6    81    78   -74   -25        3•   39    52   -51    1C        3•   3C    27   -27    -C
4    66    7C   -66    25        7•   33    31    26    17        4    69    51   -29   -42        4•   28     1    -1     1
5   111   10C   -23   -97        8•   28    26   -14    21        5•   34    43    42     9        5•   25     3     1     3
6    68    68     4   -67                                         6•   31    18    18     3
7•   22    28    26    10        H=  2 K=  4                      7•   27    25    -5    25        H= 17 K=  4

H= 24 K=  3                      C•   42    6C   -60     C        H=  9 K=  4                      C•   32    53   -53    -C
                                 1•   4C    22   -22    -4                                         1•   3C    52    42    31
C•   35     8     8     0        2•   4C    4C    39     8        1•   37    21   -18   -11        2•   3C    21    17   -11
1    65    58   -56    12        3•   39    39   -16   -36        2•   37    26    24    -9        3    84    7C   -23    66
2•   34    83    80   -23        4•   37    11     9    -6        3    78    8C    75   -26        4•   27    31    31    -1
3   133   113    12  -113        5•   36    23    22    -8        4•   35    37    25    27        5•   23     4     4    -1
4•   32    43   -42    -7        6    84    72    53   -48        5    58    43   -43    -2
5    57    53    11   -52        7•   32    37   -30   -21        6•   29    24    18   -16        H= 18 K=  4
6    72    64    64     4        8•   23    35     6    35        7•   26    35     8   -35
                                                                                                  C•   3C    32   -32    -0
H= 25 K=  3                      H=  3 K=  4                      H= 10 K=  4                      1•   3C    29    19    22
                                                                                                  2•   29    33   -31   -11
C•   35    26    26     0        C•   41    69   -69    -C        C•   37    10   -1C     U        3•   28    31   -19    24
1•   34    42   -42     5        1    8C    64   -58    26        1•   38    47   -23    42        4•   24    23    -9   -22
2   111   104   -94    44        2•   4C    35   -33   -1C        2•   36    22    20    -9
3    54    57    54   -19        3•   39    29    27   -10        3•   36    43    19   -39        H= 19 K=  4
4•   31    47   -30   -36        4•   37    49   -45    19        4•   34    31    29   -12
5•   27    24     1    24        5    73    59   -59     4        5•   32    24     5    24        C•   28     4     4    -0
6•   24    27   -19   -19        6•   34    29    -3    29        6•   30    39    38     9        1•   28    16    11    12
                                 7•   32    43    43    -6        7•   24    1C    -5     9        2    87    7C    68   -19
H= 26 K=  3                      8•   23    43   -40   -15                                         3•   24    17    1C   -14
                                                                 H= 11 K=  4                      4•   22     4     4     C
0•   33    14   -14    -0        H=  4 K=  4
1•   32    27   -25   -10                                         C•   38    61    61     C        H= 20 K=  4
2•   33    58   -58     3        C•   38    45   -45    -0        1   135   113    61   -95
3    84    77   -76   -14        1•   39    13   -13    -3        2    56    63   -58    24        C•   28    31   -31     C
4    49    47    47    -0        2•   39    35   -18   -3C        3•   37    64   -63   -12        1•   27    32    -9    3C
5    66    56     6   -56        3•   39    38     5   -3B        4•   35    52    -2   -52        2•   25    14    10    -9
                                 4•   40    61   -50   -34        5•   33    6C    37   -47        3•   22    18   -17     4
H= 27 K=  3                      5•   35    20   -17    10        6•   28     3    -0    -3
                                 6•   32    11    10     3        7•   22    25     1   -25        H= 21 K=  4
0•   30    44    44     0        7•   30    22    -6   -21
1•   3C    44   -17    41        8•   23    13    13     2        H= 12 K=  4                      C•   25    15    15     C
2•   3C    36   -36     4                                                                          1•   24    29   -12   -26
3•   27    12    -1    12        H=  5 K=  4                      C•   36    32    32     0        2•   23    17     9    15
4•   26    1C     9     4                                         1•   36    24    15   -19
5•   22    53   -21    49        0•   37    22    22     0        2•   35    19    17    -9        H= 22 K=  4
                                 1•   41    44    -0    -4        3•   34    46   -46    -4
H= 28 K=  3                      2•   40    38   -34   -16        4•   32    33    28   -18        C•   23    2C    20     C
                                 3    79    72    17    70        5•   31    46    43   -16        1•   2C    22   -16    16
                                                                 6•   27    32    26    18
```

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		37542	
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 $\overrightarrow{C_7 O_1}$ and $\overrightarrow{C_7 C_8}$, where now the three axes of the coordinate system were given by the cross vector products

Axis 1: $\overrightarrow{C_7 O_1}$

Axis 2: $(\overrightarrow{C_7 O_1}) \times (\overrightarrow{C_7 C_8})$

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

Where now $\cos\alpha$ refers to the angle a principle axis makes with Axis 1 of the coordinate system, $\cos\beta$ refers to Axis 2 of the coordinate system, and $\cos\gamma$ 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	8433	1010	0	0	0

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

atom pair	bond distance ($\overset{\circ}{A}$.)	error ($\overset{\circ}{A}$.)
$O_2 \, O_1$	2.4751	.0079
$Cl_1 C_1$	1.7315	.0085
$Cl_2 C_{15}$	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
$Cl_1 C_1 C_6$	117.327	.590
$Cl_2 C_{15}C_{10}$	119.314	.666
$Cl_1 C_1 C_2$	119.396	.701
$Cl_2 C_{15}C_{14}$	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	$\cos \alpha$	$\cos \beta$	$\cos \gamma$	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

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[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	0.9544	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 1.39 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 $\overset{o}{A}$.) were longer than the shorter of the CO bonds observed in HCO_2H and $\emptyset CO_2H$ (1.23 $\overset{o}{A}$.) (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 CC 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 $\overset{o}{A}$. agreed quite well with that observed for o-dichlorobenzene (1.735 $\overset{o}{A}$.) and m-dichlorobenzene (1.70 $\overset{o}{A}$.) (59, p. S-14). The observed O-O distance of 2.475 $\overset{o}{A}$. 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 $\overset{o}{A}$.) (59, p. M-171), or 4-aminosalicylic acid which has an O-H-O distance of 2.70 $\overset{o}{A}$. and an intramolecular dimer O-H-O distance of 2.64 $\overset{o}{A}$. (59, p. M-213), and to the O-H-O distances of strongly hydrogen bonded compounds such as maleic acid (2.46 $\overset{o}{A}$.) (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
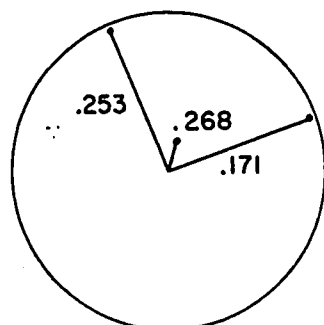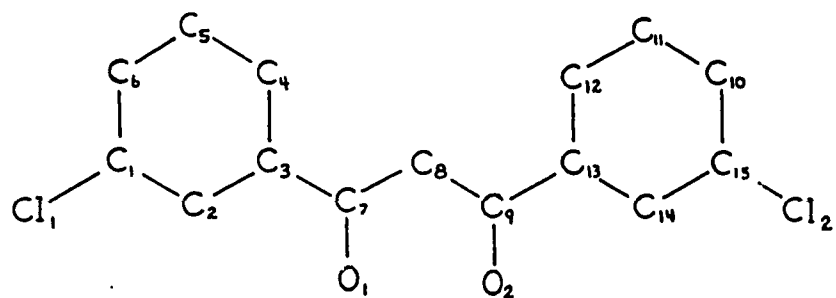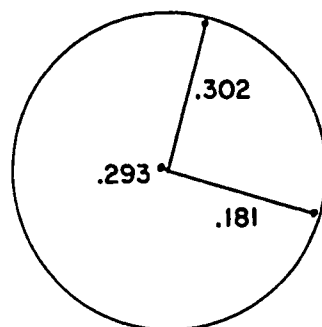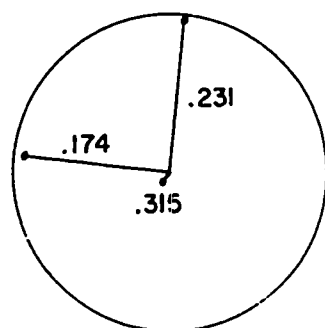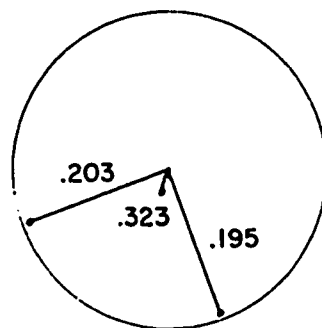
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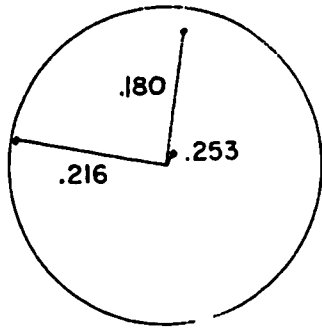
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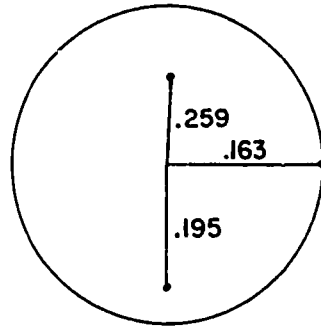
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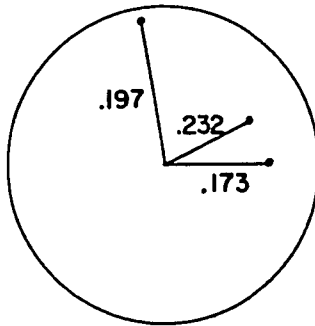
c_9

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 $\mathring{A}.^3$ while the difference in molecular volumes was only 52 $\mathring{A}.^3$ This left an excess volume of 34 $\mathring{A}.^3$ 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.
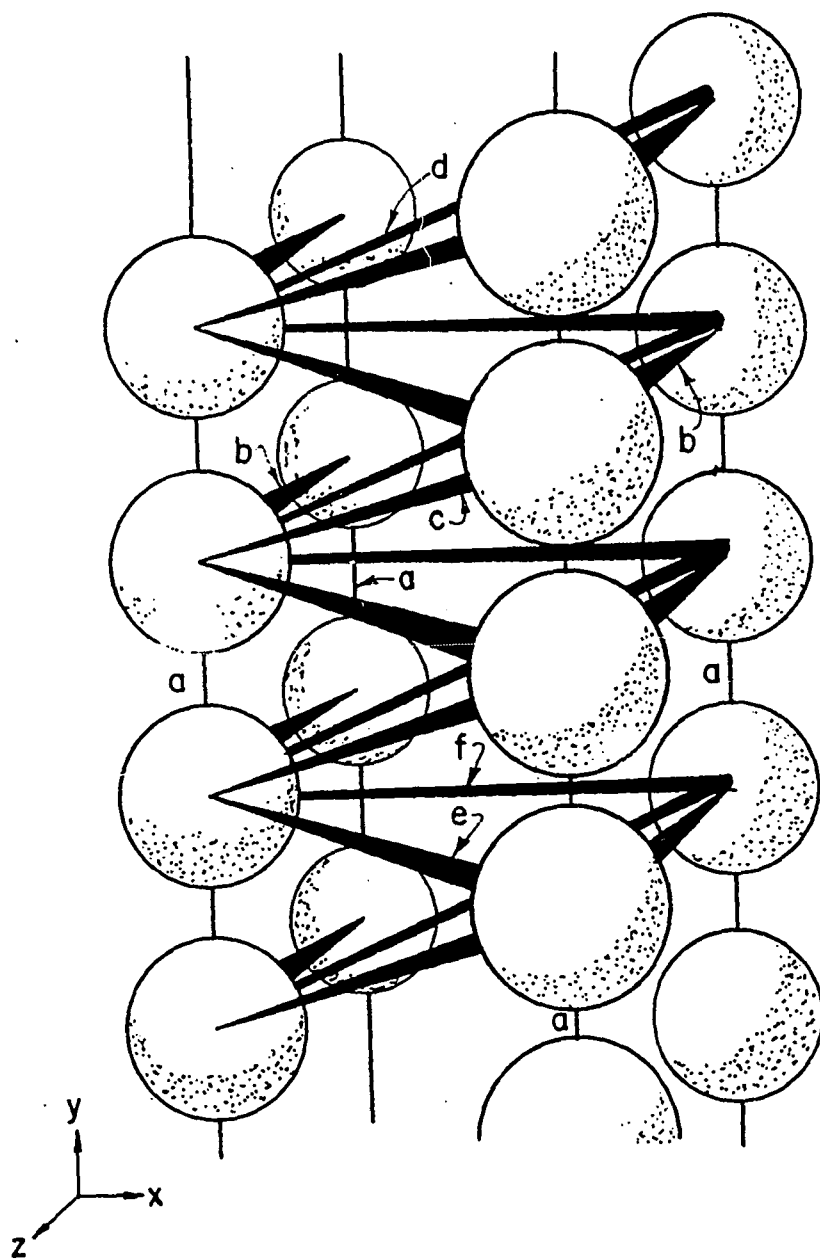
Figure 16. Packing of chlorine atoms in chains in a crystal of bis(meta-chlorobenzoyl)methane. $a = 3.85$ Å., $b = 4.58$ Å., $c = 3.69$ Å.
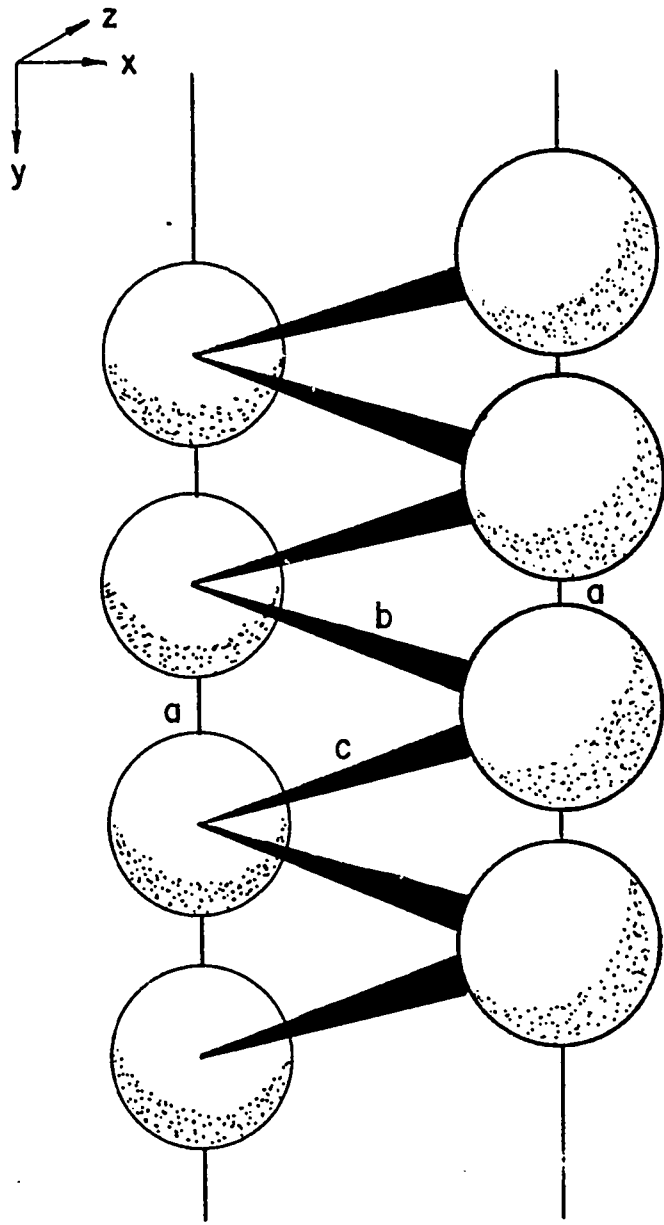
Figure 17. Molecular environment of a molecule of bis(meta-chlorobenzoyl)-methane projected onto the (0,1,0) plane with space group symmetry elements indicated
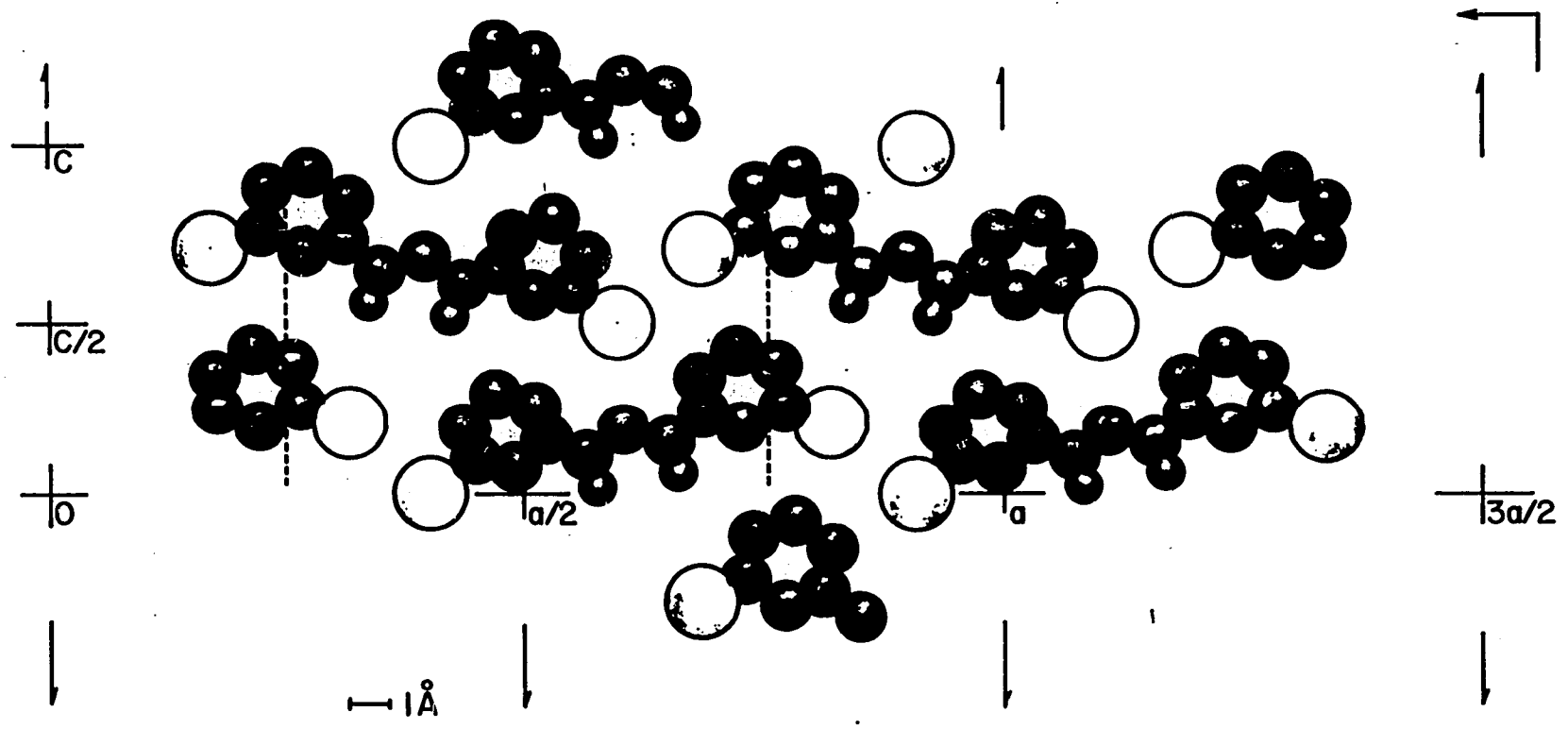
SUMMARY

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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