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Hardgrove, George Lind

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THE CRYSTAL STRUCTURES OF SEVERAL
cis-1,2- DIHALOBENZOCYCLOBUTENES

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

August 13, 1959

ERRATA

To: Recipients of UCRL-8803 - Chemistry-General
From: Technical Information Division
Subject: THE CRYSTAL STRUCTURES OF SEVERAL
cis-1, 2-DIHALOBENZOCYCLOBUTENES
by George Lind Hardgrove, Jr. (thesis)

Please make the following changes:

Page 27 Line 2 $C_8H_6Cl_2$ should read $C_8H_6Br_2$
Line 17 Column(a) 1.34 should read 1.35
Page 28 Line 9 halogen should be halogen

Please insert pages 41-42 in place of the one now in subject report. Please note that page 41 reads the same as before - the change is on page 42 where additional information has been added to the table.

Cycles 12 and 13

These cycles were calculated by weighting the individual reflections according to the variable scale described in the section on least squares. On the 13th cycle the shifts remained smaller than one-half the corresponding standard deviations. The output parameters of Cycle 12 are listed in Table XIII.

Cycle 14

Several of the bond distances still varied from the expected values by many standard deviations. A set of structure parameters was derived by imposing the expected values on the bond distances, which constituted the input for this cycle. The reliability factors were higher and the shifts tended to move the atoms in the direction of the previously refined coordinates. The observed and calculated structure factors listed in Table XIV are from this cycle. The foginess of the films severely limited the measurement of weak intensities.

Discussion of the Structure

The atomic parameters calculated on Cycle 12 and the reliability factors and standard deviations from Cycle 13 are presented as the final results of the least-squares refinement of the structure of $C_8H_6Cl_2$ at room temperature.

The interatomic distances and angles are shown in Fig. 9 and the interatomic distances are listed in Table XV. The standard deviations of bond lengths were calculated from the diagonal least-squares matrix elements by using the corrections of Templeton (1959) for the x- and z-axis correlation and assuming a spherical standard deviation surface.

The chlorine-chlorine distance of 3.175A is much shorter than twice the Van der Waals radius of 3.60A suggested by Pauling (1948), but longer than the chlorine-chlorine distance in CCl_4 of 2.887A. The carbon-chlorine distance of $1.802 \pm 0.019A$ is in agreement with the value for 1, 2-dichloroethane of $1.78 \pm 0.01A$. All published values of interatomic distances are from the Tables of Interatomic Distances (1958) unless otherwise noted.

Table XIII

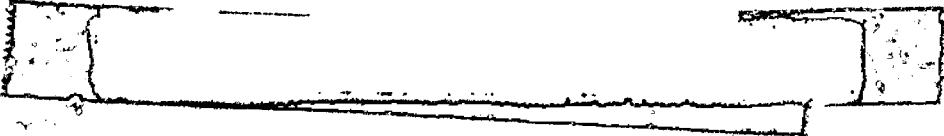
Final least squares parameters for $C_8H_6Cl_2$ at $25^\circ C$
(Output from cycle 12)

	x	y	z	$B(A^2)$	σ_x	σ_y	σ_z	σ_B
Cl_1	.16393	.01843	.28912	4.693	.00054	.00047	.00052	.014
Cl_2	.08509	.25302	.06669	5.936	.00073	.00053	.00065	.019
C_1	.2458	.4830	.6256	5.05	.0024	.0019	.0023	.06
C_2	.2033	.3625	.5125	4.59	.0022	.0018	.0021	.05
C_3	.3869	.3377	.5755	4.38	.0021	.0017	.0020	.05
C_4	.4262	.4404	.6745	3.86	.0019	.0017	.0018	.05
C_5	.4170	.5213	.2355	5.31	.0025	.0020	.0024	.07
C_6	.2964	.6010	.2511	5.14	.0024	.0020	.0023	.06
C_7	.3188	.6939	.3355	5.00	.0023	.0022	.0022	.06
C_8	.4852	.7338	.4368	6.76	.0034	.0024	.0031	.09

$R_1 = 0.208$, $R_2 = 0.226$, and $R_3 = 0.327$ for the three-dimensional data including the unobserved reflections.

Parameters used to calculate Table XIV
(Input to cycle 14)

	x	y	z	$B(A^2)$	
Cl_1	.16393	.01857	.28901	4.831	
Cl_2	.08511	.25302	.06648	6.085	
C_1	.2456	.4837	.6255	5.10	$R_1 = 0.213$,
C_2	.2043	.3624	.5126	4.67	$R_2 = 0.232$,
C_3	.3864	.3373	.5753	4.45	$R_3 = 0.339$, for the
C_4	.4262	.4399	.6745	3.96	three-dimensional data
C_5	.4177	.5211	.2355	5.49	including the unobserved
C_6	.2970	.5910	.2410	5.19	reflections.
C_7	.3250	.6930	.3400	5.03	
C_8	.4844	.7324	.4358	6.95	



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cis-1, 2-DIHALOBENZOCYCLOBUTENES

George Lind Hardgrove, Jr.

Thesis

June 22, 1959

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THE CRYSTAL STRUCTURES OF SEVERAL
cis-1, 2-DIHALOBENZOCYCLOBUTENES

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THE CRYSTAL STRUCTURES OF SEVERAL
cis-1, 2-DIHALOBENZOCYCLOBUTENES

George Lind Hardgrove, Jr.

Lawrence Radiation Laboratory

and

Department of Chemistry and Chemical Engineering
University of California, Berkeley, California

June 22, 1959

ABSTRACT

The crystal structures of the cis-1, 2-diiodo-, dibromo-, and dichloro- derivatives of benzocyclobutene have been determined by single-crystal X-ray diffraction methods. The halogen-substituted double ring system shows a combination of resonance and steric strain effects on the bond distances and molecular configurations.

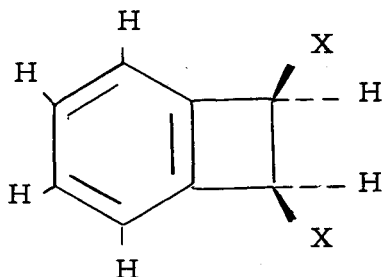
$C_8H_6Br_2$ and $C_8H_6I_2$ are isomorphous, crystallizing in space group $Pna2_1$ with four molecules per unit cell. The structure of the dibromo- derivative has been determined by three-dimensional least-squares refinement with 613 independent reflections. The full-matrix least-squares refinement technique is compared to the diagonal approximation method. The four- and six-membered rings are nearly coplanar, sharing a bond shortened by ring strain. The other bond lengths are in agreement with values predicted for nonstrained systems. A similar arrangement was found to be consistent with the data for $C_8H_6I_2$.

The crystal structure of $C_8H_6Cl_2$ has been determined at room temperature and at liquid nitrogen temperature by single-crystal X-ray diffraction methods, including three-dimensional least-squares refinements. At both temperatures the crystals have essentially the same monoclinic structure in space group $P2_1/c$ with four molecules in the unit cell. The bond distances derived from the room-temperature determination differ from those found at low temperature in a manner

attributable to anisotropic thermal motions. The low-temperature determination shows the side bonds of the four-membered ring shortened to $1.448 \pm 0.010\text{A}$, presumably because of cooperative resonance effects of the chlorine atoms and the phenyl ring. The two carbon atoms attached to the chlorine atoms are $1.562 \pm 0.014\text{A}$ apart, with the steric strain effects predominating over resonance shortening.

INTRODUCTION

The structural formula for the cis-1,2-dihalobenzocyclobutene series of compounds is as follows, where X represents iodine, bromine, and chlorine for the three cases.



The samples were prepared by Professor F. R. Jensen and W. E. Coleman (1958) of this laboratory, who kindly provided the samples. They prepared a mixture of sodium iodide and potassium iodide and $\alpha, \alpha, \alpha', \alpha'$ -tetrabromo-*o*-xylene which was refluxed in ethanol for 10 days. The reaction yielded a mixture of trans- and cis-isomers of $C_8H_6I_2$. The cis- isomer was easily separated because of its much higher melting point ($150^\circ C$), and infrared and ultraviolet spectrographic analysis showed that the sample was free of trans- material and other substances. The dibromo-derivative was prepared by treatment of the diiodo- compound with Br_2 . Crystals of cis- $C_8H_6Br_2$ melted over the range 101.1 to $101.9^\circ C$. In like manner the dichloro- derivative was prepared by treatment of the diiodo- compound with chlorine water. The purified crystals of cis- $C_8H_6Cl_2$ melted over the range 91 to $92^\circ C$. The crystal-structure determinations were undertaken as a further check on the assignment of cis- and trans- isomers and to study the bond distances in the strained ring system.

LEAST-SQUARES METHODS

The crystal-structure determinations of these cis-1, 2-dihalo-benzocyclobutenes have involved study and comparison of the various mathematical methods for the analysis of crystallographic data. The following brief description of the least-squares procedure serves to define the notations and facilitate the explanation of variations in procedure.

The least-squares method is used in crystal-structure investigations to find the best values for the atomic position and temperature parameters to fit a set of measured intensity values of X-ray reflections. The observed structure factors ($F_{o(hkl)}$) are compared to calculated structure factors ($F_{c(hkl)}$) given by the formula

$$F_{c(hkl)} = \sum_{i=1}^n f_i(\theta) \exp(-B_i \sin^2 \theta / \lambda^2) \exp[-2\pi i(hx_i + ky_i + lz_i)], \quad (1)$$

where the part dependent on $h, k, l, x_i, y_i,$ and z_i is the usual geometrical structure factor and the $f_i(\theta)$ the usual atomic form factor for each atom in the unit cell. The part involving the individual isotropic temperature factor B_i is used to account for the drop in intensities over increasing θ due to thermal vibrations. The summation is carried out over the n atoms in the unit cell. An arbitrary scale factor puts the structure factors on absolute scale.

For a given set of parameters in a trial structure the shifts toward an improved structure are calculated by the least-squares relation

$$\underline{\epsilon} = \underline{A}^{-1} \underline{\Delta}, \quad (2)$$

where $\underline{\epsilon}$ and $\underline{\Delta}$ are column matrices of v elements for v independent parameters and \underline{A} and its inverse \underline{A}^{-1} are symmetric matrices each with v^2 elements. The elements $(\underline{\epsilon})_i$ of the $\underline{\epsilon}$ matrix are the shifts in the parameters calculated by Eq. (2). The other matrices in Eq. (2) have the following definitions in terms of arbitrary parameters q_i and

q_j with u the number of independent reflections used in the calculations:

$$(\underline{A})_{ij} = \sum_u \frac{\partial |F_c|}{\partial q_i} \frac{\partial |F_c|}{\partial q_j} w, \quad (3a)$$

$$(\underline{\Delta})_i = \sum_u \frac{\partial |F_c|}{\partial q_i} \left(|F_o| - |F_c| \right) w. \quad (3b)$$

If some of the parameters are not statistically independent, the correlation r_{ij} between two parameters q_i and q_j can be calculated by normalization of the \underline{A}^{-1} matrix as follows:

$$r_{ij} = (\underline{A}^{-1})_{ij} / \left[(\underline{A}^{-1})_{ii} (\underline{A}^{-1})_{jj} \right]^{1/2}. \quad (4)$$

The standard deviations σ_i due to uncertainties of the best values of the q_i are calculated by

$$\sigma_i = \left(\frac{(\underline{A}^{-1})_{ii} \sum_u w (|F_o| - |F_c|)^2}{(u-v)} \right)^{1/2}. \quad (5)$$

In the above equations w is the statistical weighting factor for the individual reflections based on an estimate of the accuracy of the individual measurements.

The \underline{A} matrix is often approximated by assuming that the off-diagonal elements are zero. Sparks (1958) and others have found that the shifts calculated by such diagonal approximation are too large and the least-squares process sometimes fails to converge unless partial shifts are taken. A partial shift factor, p , is introduced into the calculation of the new coordinates for the $(k+1)$ st cycle, based on least-squares refinement of the k th set of coordinates:

$$q_i^{k+1} = q_i^k + p \epsilon_i^k. \quad (6)$$

Senko (1957) has written the LS-II program for the IBM 650 computer for least-squares adjustment of the parameters in Eq. (1). Unit weights ($w = 1$) for individual reflections or a weighting scheme similar to that of Hughes (1941) may be chosen. In the latter case the weight w is taken as $(F_o^2)^{-1}$ or as a constant $(16F_{\min}^2)^{-1}$ if the uncorrected intensity is greater or less than 16 times the minimum value. For reflections too weak to be observed (unobserved) the quantity $(|F_o| - |F_c|)$ is set equal to zero for $|F_c| < |F_{\min}|$, or equal to $-F_c$ for $|F_c| > |F_{\min}|$. The following unreliability factors are computed:

$$R_1 = \sum_u \left| |F_o| - |F_c| \right| \div \sum_u |F_o| ,$$

$$R_2 = \left(\sum_u (|F_o| - |F_c|)^2 \div \sum_u F_o^2 \right)^{\frac{1}{2}} ,$$

$$R_3 = \left(\sum_u w (|F_o| - |F_c|)^2 \div \sum_u w F_o^2 \right)^{\frac{1}{2}} .$$

The program is designed to minimize R_3 by successive iteration. The diagonal elements of the least-squares matrix (A) and off-diagonal elements only of the type

$$\sum_u \frac{\partial F_c}{\partial x_i} \frac{\partial F_c}{\partial z_i}$$

are considered in calculation of the parameter shifts and standard deviations. Partial shift factors p of Eq. (6) are arbitrarily chosen as 0.5, 0.63, and 0.7 for shifts in the temperature factors, atomic position parameters, and the scale factor respectively.

The scattering factors used in the calculated structure factors in this research were those of Hoerni and Ibers (1954) for carbon. Those for hydrogen and chlorine were taken from the first edition of the Internationale Tabellen, and those of iodine and bromine were calculated by Thomas and Umeda (1957).

THE CRYSTAL STRUCTURES OF $C_8H_6Br_2$ AND $C_8H_6I_2$

Experimental Procedures

Both of these cis-1,2-dihalobenzocyclobutenes form colorless needle-like crystals with the long dimension in the [001] direction. Nearly cylindrical crystals of each were aligned to rotate about the needle axis. The dibromo-derivative was sealed in a thin-walled glass capillary because of its appreciable vapor pressure. Weissenberg photographs of the hk0, hk1, hk2, and hk3 layers were taken on multiple films with CuK α X-rays at room temperature. In addition h0l, h1l, and 0kl precession photographs were obtained with MoK α X-rays.

The intensities of the reflections were measured by visual comparison with an intensity standard. No absorption correction was made for the $C_8H_6Br_2$ crystal for such a small value of μ_r . (See Table I) The intensities from the $C_8H_6I_2$ crystal were corrected for absorption by the method of Bond (1959) using the tables of Bradley (Klug and Alexander 1954). The usual corrections for Lorentz and polarization effects were made. The relative scaling among the Weissenberg layers was determined by comparison with the precession data.

Unit Cell and Space Group

The rotation axes for the orthorhombic unit cells were determined from quartz-calibrated rotation photographs. The other axes were determined from hk0 quartz-calibrated Weissenberg films. The cell dimensions of $a = 4.913A$ and $c = 5.405A$ were assumed for quartz. The standard quartz crystal has been checked with a NaCl pattern to an accuracy of one part in 3000.

The systematic absences suggest the space-group possibilities of either $Pna2_1$ or $Pnam$ with the mirror plane in question perpendicular to the short axis. With four molecules in the cell it would be necessary that the molecule have mirror symmetry in the latter space group. For molecules of the expected geometry the only arrangement possible would place the bromine atoms opposite the mirror plane. Both the hydrogen-hydrogen distance of 5A across the benzene ring and the

combined diameters of two bromine atoms exceed the 4.384A translation. These considerations ruled out Pnam, therefore the structure analyses were carried out in Pna2₁ (No. 33 C_{2v}⁹). The general equivalent positions for this group are x, y, z; \bar{x} , \bar{y} , 1/2 + z; 1/2 - x, 1/2 + y, 1/2 + z; 1/2 + x, 1/2 - y, z. With four molecules per unit cell only the general positions are considered.

Table I

Crystallographic data			
	C ₈ H ₆ Br ₂	C ₈ H ₆ I ₂	
Unit cell dimensions	<u>a</u>	16.177 ± 0.032A	16.427 ± 0.023A
	<u>b</u>	11.793 ± 0.024A	12.464 ± 0.030A
	<u>c</u>	4.384 ± 0.014A	4.494 ± 0.010A
Molecular weight	261.96	355.97	
Number of molecules per unit cell	4	4	
X-ray density	2.08	2.58	
Radius of the crystal needle	0.0019- 0.0026 cm	0.0020- 0.0029 cm	
Average absorption μ_r (CuK α X-rays)	0.136	0.582	
Number of observed reflections CuK α	443	599	
Number of unobserved reflections	170	266	

Determination and Refinement of the Structure of $C_8H_6Br_2$

The analysis of the well-resolved [001] projection began with the calculation of the Patterson projection by using the IBM 701 computer program of Dodge (1958). The bromine-bromine vectors were well resolved and a trial structure with the two bromines at (0.16, 0.48) and (0.18, 0.19) was found to be consistent with the vectors.

These coordinates, two isotropic temperature factors, and the scale factor were refined by the LS-II least-squares program for six cycles on the observed reflections with a final R_1 of 0.288. The signs of the final structure factors were used to calculate a [001] Fourier projection which clearly resolved the eight carbon atoms. Two further least-squares cycles with ten atoms resulted in a structure with $R_1 = 0.136$, and a second Fourier projection was calculated based on the final phases. The best coordinates from this Fourier map were refined by three further least-squares cycles with $R_1 = 0.121$. The refinement of this projection was concluded with the calculation of another Fourier projection and three more cycles of least squares, giving a final $R_1 = 0.096$ for the $hk0$ reflections, including all the observed and unobserved reflections.

Three-Dimensional Refinement

The best three-dimensional parameters for the bromine atoms were determined by least-squares refinement of the limited MoK α data. A series of structure factor calculations was made, varying the parameter $z_{Br_1} - z_{Br_2}$. A minimum in R_1 was found for the choice of 0.14 for the above parameter. A Patterson projection [100] calculated with the Beevers and Lipson strips gave a large vector supporting this choice. The subsequent refinement of parameters in three dimensions was carried out by using the complete CuK α data.

Cycle 1

The input for x, y, and B coordinates was that derived from the refinement of the [001] projection. The bromine atoms were placed 0.14 z apart, and the z parameters of the carbon atoms were estimated from the tilt of the molecule. Three-dimensional Fourier sections with phases based on this structure were calculated to give improved z coordinates.

Cycle 2

The agreement factor R_1 (Table II) was 0.141 for the improved coordinates. A further calculation of Fourier sections led to the input for the next cycle.

Cycle 3

The temperature factors were reset to average values with a resulting increase of R_3 .

Cycles 4 and 5

Two of the carbon temperature factors were reset and several carbon atoms shifted to impose bond lengths of the expected values.

Cycles 6 and 7

The input for each of these cycles consisted of the output from the previous cycle.

Cycle 8

The six hydrogen atoms were included in the structure-factor calculations for this and subsequent cycles. The four benzene ring hydrogens were placed in the plane of the ring 1.1A from the neighboring carbon atoms. The carbon-hydrogen bonds in the unsaturated ring were assumed to be symmetrical in direction with the carbon-bromine bonds and a length of 1.1A was assumed. Table III shows the atomic positions used for the hydrogens with a temperature factor of $B = 2.38\text{A}^2$.

Cycles 9-13

The least-squares procedure continued to refine the output from the previous cycles. The input to Cycle 10 gave the lowest agreement factors of any cycle. Table II shows the oscillation of the R factors on later cycles.

Table II

Least-squares refinement of $C_8H_6Br_2$

Cycle	R_1	R_2	R_3	Comments
1	0.181	0.200	0.273	Observed reflections only
2	0.141	0.160	0.230	
3	0.139	0.172	0.283	Temperature factors reset to averages Unobserved data included
4	0.122	0.150	0.231	
5	0.128	0.161	0.246	Average temperature factors Normal carbon-carbon bond distances imposed
6	0.123	0.155	0.226	
7	0.125	0.158	0.233	same
8	0.137	0.154	0.216	
9	0.133	0.169	0.256	Input from previous cycle
10	0.117	0.149	0.213	
11	0.121	0.156	0.226	Hydrogen scattering introduced
12	0.121	0.155	0.220	
13	0.121	0.148	0.227	Reliability factors for the best structure
14	0.120	0.154	0.220	
15	0.122	0.148	0.223	Input based on average of output of Cycles 9 and 10
16	0.121	0.154	0.220	
17	0.122	0.154	0.232	z for Br_1 reset to starting value
18	0.117	0.149	0.213	
19	0.121	0.155	0.226	Shift rules similar to those of Vand and Pepinsky applied to Cycles 14 and 15
20	0.125	0.163	0.218	
21	0.126	0.162	0.224	Based on three-dimensional Fourier parameters
22	0.127	0.163	0.232	
23	0.126	0.161	0.229	Rerun of 10 accumulating the complete \underline{A} matrix
24	0.124	0.159	0.219	
				Cycles using constant \underline{A} matrix and the $\underline{\Delta}$ matrix from each cycle. Partial shift factors p were taken as 1/2 or 1 if the shifts on the two previous cycles were opposite or alike in sign.

Table III

Hydrogen atomic parameters for $C_8H_6Br_2$			
	x	y	z
H ₁	0.322	0.455	0.372
H ₂	0.452	0.503	0.096
H ₃	0.542	0.332	0.968
H ₄	0.535	0.151	0.209
H ₅	0.265	0.216	0.902
H ₆	0.395	0.040	0.720

These hydrogen parameters were not refined.

Cycles 14 and 15

The coordinate shifts oscillated in sign, indicating that their magnitudes were too large. The effect was especially marked in the z-coordinate shifts of the bromine atoms. The z origin of the space group $Pna2_1$ is not defined with respect to any symmetry element. The shifts in z of the bromine atoms were always opposite in sign and nearly equal in magnitude. The refinements were begun with the average structure of Cycles 9 and 10 or the best structure with one-half the shifts calculated by the LS-II program added to the coordinates. Before the 15th cycle the z parameter of the first bromine atom was reset to the constant value. These procedures did not result in a structure giving better agreement than Cycle 10.

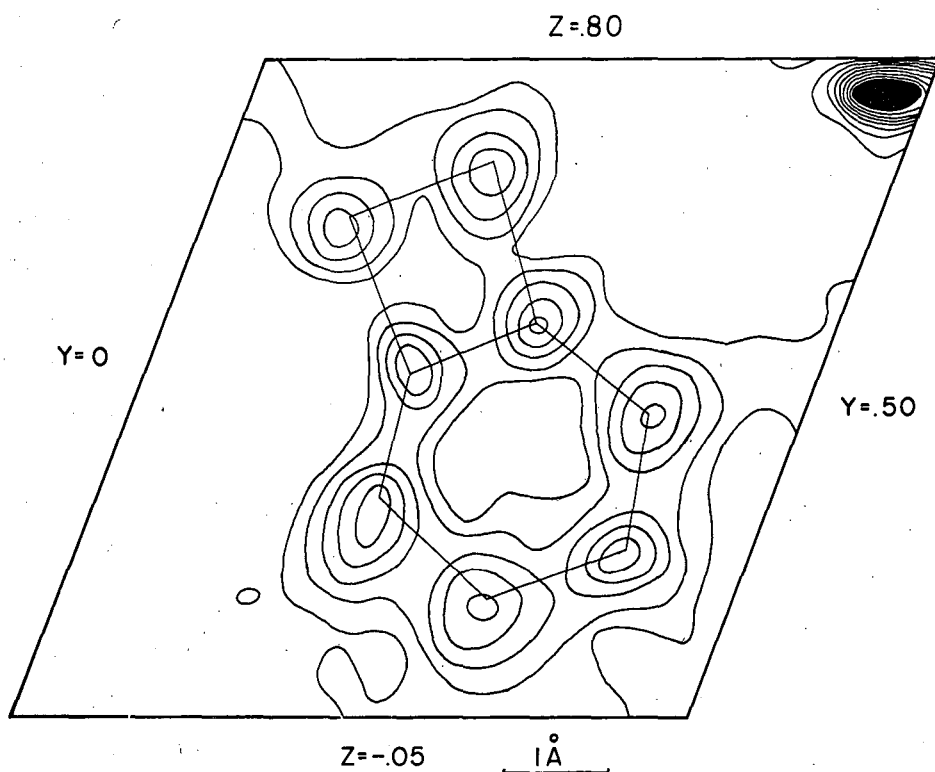
Cycle 16

Vand and Pepinsky (1958) have developed methods to speed the convergence of least-squares refinement. A procedure similar to theirs in spirit was adopted in this problem. If on two successive cycles the shifts calculated for a given parameter had the same sign, the shift was doubled on the second cycle. If two successive shifts were of opposite sign, the second-cycle shift was cut in half to cut down the oscillation.

The input structure to this cycle was derived by application of such methods to the shifts of Cycles 14 and 15. This procedure also failed to improve the agreement. On the 10th cycle there were only six out of 170 unobserved reflections with $F_c > F_{\min}$, so that shifts in the scaling usually caused by a large number of reflections of this type could not account for the oscillations in the refinement.

Cycle 17

A complete three-dimensional electron-density function was calculated based on the observed structure factors with the calculated phase constants from the 10th cycle. The locations of the maxima were determined from the parameters of the least-squares paraboloid fitted to the logarithms of the 27 electron density values nearest each of the maxima. Figure 1 shows a contour map of the electron density in the plane of the carbon rings. A similar set of calculations was made with the calculated structure factors in order to correct for series-termination effects. The corrected coordinates were the input for Cycle 17. The Fourier refinement failed to improve the agreement.



MU-17716

Fig. 1. Three-dimensional F_0 Fourier synthesis of $C_8H_6Br_2$. This section is taken in the plane of the carbon rings. The equation for this plane is $1.519x + 0.575y + 0.655z = 1$, with the variables in units of fractions of the unit-cell translations. Contours are drawn each electron/ \AA^3 with the zero contour omitted.

Full-Matrix Least-Squares Calculations on C₈H₆Br₂

Full matrix methods were applied in an effort to improve the convergence of the least-squares method. Since the origin in the space group Pna2₁ lies at any point along the 2₁ axis so that only relative values of the z parameters can be determined, the full-matrix method should speed the convergence by taking into account the correlations.

The LS-II program for the IBM 650 computer was altered to accumulate the 800 complete \underline{A} matrix cross terms in ten separate structure factor calculations. The z parameter for Br₁ was not considered a variable in order to avoid a singular \underline{A} matrix. The matrix inversion and multiplications were carried out on the IBM 701 computer. Representative portions of the \underline{A}^{-1} matrix were normalized and the resulting correlations are listed in Table IV. The results show the expected large correlations among the scale factor and the heavy-atom temperature factors. The correlations among all the z coordinates are shown in Table V. The z coordinates show much more systematic correlations than the other parameters.

Least-squares Cycles 18-24 were made by calculating the shifts using the constant \underline{A} matrix and the appropriate $\underline{\Delta}$ matrix from each cycle. Calculation of several off-diagonal elements on each cycle showed that the assumption of a constant \underline{A} matrix is justified so near the end of the least-squares refinements. The coordinate shifts were taken by using partial shift factors p of 0.5 or 1.0 in Eq. (6) if the signs of ϵ_i values on two successive cycles were different or alike.

The coordinate shifts became significantly lower after the seven cycles, but the scale and temperature factors still had shifts larger than their standard deviations. This set of refinements failed to determine a better set of parameters than those calculated on the 9th cycle of the diagonal least squares.

Table IV

A portion of the correlation (r_{ij}) matrix for $C_8H_6Br_2$

K	x_{Br_1}	y_{Br_1}	B_{Br_1}	x_{Br_2}	y_{Br_2}	z_{Br_2}	B_{Br_2}	x_{C_6}	y_{C_6}	z_{C_6}	B_{C_6}	x_{C_7}	y_{C_7}	z_{C_7}	B_{C_7}	x_{C_8}	y_{C_8}	z_{C_8}	B_{C_8}	
K	1.00	.00	-.04	+69	.00	+01	+03	+74	-.03	+01	-.05	+08	-.05	.00	+01	+13	-.01	+01	+02	+15
x_{Br_1}	1.00	.00	.00	+06	+02	-.01	-.02	-.09	-.02	-.01	-.05	+03	-.04	-.06	.00	+04	+02	+06	-.04	
y_{Br_1}		1.00	-.03	+06	+02	-.05	-.04	-.04	-.13	-.02	+05	-.07	-.07	-.01	-.03	+08	+04	.00	+06	
B_{Br_1}			1.00	+04	-.01	+05	+54	.00	-.04	-.02	+05	-.05	.00	+01	+12	-.03	-.03	+02	+10	
x_{Br_2}				1.00	-.03	+02	-.06	-.09	.00	+05	-.02	-.03	-.10	-.01	+04	+12	-.02	+02	-.04	
y_{Br_2}					1.00	+01	+03	-.01	+02	-.02	-.01	+03	+15	.00	-.03	+04	-.06	-.02	-.04	
z_{Br_2}						1.00	+05	.00	+02	+23	+01	+02	.00	+14	.00	.00	-.02	+14	-.01	
B_{Br_2}							1.00	-.04	+07	-.06	+09	.00	-.02	-.02	+05	+02	+06	-.06	+02	
x_{C_6}								1.00	+02	+01	.00	+03	-.04	-.01	-.06	+03	-.04	+04	-.05	
y_{C_6}									1.00	.00	+04	-.04	-.04	+03	.00	+03	+06	+02	-.05	
z_{C_6}										1.00	+05	+01	+04	+04	-.08	-.08	+03	+20	-.03	
B_{C_6}											1.00	-.05	+03	+04	-.08	+10	+05	+04	-.01	
x_{C_7}												1.00	.00	-.03	+01	-.04	-.01	.00	+01	
y_{C_7}													1.00	-.04	-.06	-.04	+02	-.04	+09	
z_{C_7}														1.00	+04	+02	.00	+22	+08	
B_{C_8}															1.00	+03	.00	-.05	-.02	
x_{C_8}																1.00	+02	+01	-.01	
y_{C_8}																	1.00	.00	+04	
z_{C_8}																		1.00	+02	
B_{C_8}																				1.00

Table V

Correlations (r_{ij}) among z parameters in $C_8H_6Br_2$									
	z_{Br_2}	z_{C_1}	z_{C_2}	z_{C_3}	z_{C_4}	z_{C_5}	z_{C_6}	z_{C_7}	z_{C_8}
z_{Br_2}	1.00	+0.05	+0.06	+0.11	+0.16	+0.13	+0.22	+0.14	+0.14
z_{C_1}		1.00	+0.01	-.10	+0.02	+0.02	+0.16	+0.04	+0.01
z_{C_2}			1.00	+0.12	+0.08	+0.05	+0.10	-.08	+0.18
z_{C_3}				1.00	-.04	+0.10	-.15	+0.04	-.02
z_{C_4}					1.00	-.26	.00	+0.13	-.08
z_{C_5}						1.00	+0.12	+0.07	+0.02
z_{C_6}							1.00	+0.04	+0.20
z_{C_7}								1.00	+0.22
z_{C_8}									1.00

Comparison of the Refinement Methods

Table VI shows the coordinates, standard deviations, and final shifts for the best structures from the diagonal and full-matrix methods and the coordinates derived from the three-dimensional Fourier summation. The parameters from Cycles 9 and 24 show agreement within one standard deviation calculated from the full matrix for 25 out of the 40 cases. In eight other cases the difference is less than the sum of standard deviations of the two methods. The cases of larger discrepancy include only the scale factor and six temperature factors. The coordinates obtained from the electron-density calculations show agreement within one standard deviation of the values from Cycle 9 in 28 out of 30 cases. The two discrepancies do not exceed two standard deviations. This close agreement demonstrates that the final structure derived is not sensitive to the weighting scheme. The parameters from Cycle 9 are chosen as the final values for this structure determination because they give the lowest reliability factors. The standard deviations reported are those calculated from the complete least-squares matrix and are slightly larger than those given by the diagonal matrix.

Table VI

Final parameters for $C_8H_6Br_2$

- (a) Best parameters calculated on Cycle 9 (the final result)
 (b) Standard deviations in (a) from diagonal matrix
 (c) Shifts in (a) calculated on Cycle 10, using LS-II program
 (d) Result of refinement of (a) by six full-matrix cycles
 (e) Full-matrix standard deviations
 (f) Shifts on the 24th cycle (asterisk * indicates parameter oscillated on the 23rd and 24th cycles and $\Delta q_i = \frac{1}{2} \epsilon_i$)
 (g) Parameters from three-dimensional Fourier summation corrected for series-termination effects

	(a)	(b)	(c)	(d)	(e)	(f)	(g)
K	1.0000	.0015	-.0091	.9795	.0030	-.0070 *	
x_{Br_1}	.19340	.00025	-.00002	.19355	.00030	-.00001 *	.19323
y_{Br_1}	.18123	.00032	+.00005	.18103	.00038	+.00003 *	.18137
z_{Br_1}	.5000	.0024	-.0026	.5000	-	-	.4993
B_{Br_1}	$6.39A^2$.02	-.06	6.47	.03	-.08 *	-
x_{Br_2}	.33891	.00024	+.00005	.33898	.00029	+.00004 *	.33868
y_{Br_2}	-.02691	.00034	-.00005	-.02672	.00041	-.00002 *	-.02701
z_{Br_2}	.3794	.0023	+.0028	.3817	.0029	+.0013 *	.3801
B_{Br_2}	6.49	.02	-.05	6.51	.03	-.05 *	-
x_{C_1}	.3053	.0020	-.0002	.3074	.0024	-.0004 *	.3070
y_{C_1}	.1967	.0027	-.0019	.1929	.0034	-.0023	.1990
z_{C_1}	.677	.013	+.001	.679	.015	+.002 *	.668
B_{C_1}	5.08	.13	-.21	4.89	.14	-.20 *	-
x_{C_2}	.3722	.0023	+.0002	.3738	.0026	+.0003 *	.3701
y_{C_2}	.1077	.0029	+.0011	.1108	.0034	+.0009	.1084
z_{C_2}	.601	.011	-.0001	.597	.013	-.0002 *	.595
B_{C_2}	5.18	.13	-.20	4.82	.14	+.05 *	-

Table VI (concluded)

	(a)	(b)	(c)	(d)	(e)	(f)	(g)
x_{C_3}	.4135	.0024	+0.0004	.4168	.0029	+0.0004	.4157
y_{C_3}	.1956	.0030	+0.0017	.2021	.0036	+0.0003	.1988
z_{C_3}	.391	.013	+0.002	.397	.016	+0.0003	.393
B_{C_3}	6.26	.16	+0.61	7.40	.16	-.10	-
x_{C_4}	.3572	.0019	+0.0018	.3575	.0024	+0.0003	* .3567
y_{C_4}	.2748	.0028	+0.0008	.2771	.0033	-.0005	.2770
z_{C_4}	.469	.012	-.006	.467	.015	-.001	* .467
B_{C_4}	5.18	.12	-.08	5.37	.13	-.20	* -
x_{C_5}	.3693	.0020	+0.0001	.3680	.0023	-.0003	* .3690
y_{C_5}	.3860	.0027	+0.0010	.3904	.0032	-.0001	.3880
z_{C_5}	.347	.012	-.006	.348	.015	-.005	.342
B_{C_5}	4.92	.11	+0.07	5.19	.12	+0.04	* -
x_{C_6}	.4397	.0020	-.0008	.4394	.0024	-.0005	* .4391
y_{C_6}	.4143	.0028	+0.00003	.4117	.0033	+0.0009	* .4135
z_{C_6}	.183	.012	+0.0004	.179	.014	+0.004	.188
B_{C_6}	5.36	.13	-.21	4.88	.14	-.19	-
x_{C_7}	.4908	.0028	-.0017	.4911	.0033	-.0004	* .4920
y_{C_7}	.3203	.0029	+0.0007	.3222	.0038	+0.0013	.3191
z_{C_7}	.112	.014	-.003	.105	.018	+0.0006	.118
B_{C_7}	6.58	.18	+0.08	8.33	.19	-.42	* -
x_{C_8}	.4878	.0019	-.0004	.4869	.0023	-.0003	.4905
y_{C_8}	.2085	.0026	+0.0013	.2099	.0030	+0.0009	* .2146
z_{C_8}	.240	.0097	-.0009	.234	.012	-.001	.246
B_{C_8}	4.60	.11	-.26	4.72	.11	-.31	* -

The observed and calculated structure factors are listed in Table VII. Extinction effects for which no correction has been made represent a sizable portion of the error. The weighting scheme of Hughes reduces the effect of the large reflections on the refinement, which is desirable for the type of error involved. This same effect is probably the cause of the difficulty in the refinement of the temperature factors.

Figures 2 and 3 show the [001] electron-density projection and the $F_o - F_c$ difference projection based on the final parameters. These maps show the large anisotropic vibrations for the bromine atoms.

Discussion of the Structure

Figure 4 shows the distances and angles for the set of coordinates calculated on the 9th least-squares cycle. Table VIII lists the same distances and those derived from the full-matrix and Fourier structures. The standard deviations in the bond lengths have been calculated by using the full least-squares matrix. The effect of the z correlations on the errors in bond lengths have been taken into account.

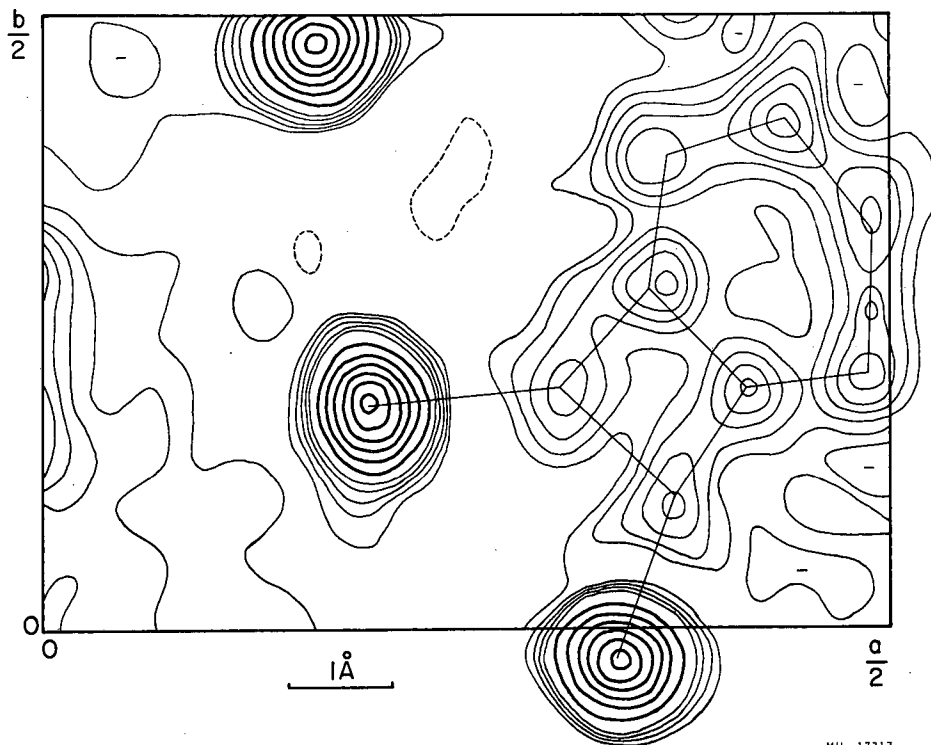
The bond distances of chemically equivalent bonds appear to be in much better agreement than the large standard deviations would lead one to expect. The large extinction effect may result in an underestimation of the accuracy of the intensities and correspondingly large standard deviations.

The bromine-bromine distance of 3.44A is somewhat shorter than twice the Van der Waals radius of 3.90A (Pauling 1948), but not so short as 3.16A, reported for the bromine-bromine distance in CBr_4 (Tables of Interatomic Distances, 1958). The carbon-bromine distance of $1.96 \pm 0.03A$ is in agreement with the usual aliphatic value of $1.937 \pm 0.003A$ from the above-mentioned tables.

The carbon-carbon single bonds of 1.54A are in agreement with the published values of $1.541 \pm 0.003A$ for the simple single bond and $1.52 \pm 0.03A$ for toluene. The average of the aromatic carbon-carbon bonds of 1.41 ± 0.03 is in agreement with the $1.397 \pm 0.005A$ for benzene and 1.395 ± 0.003 for other aromatic systems. The short distance of 1.35A for the bond shared by the four- and six-membered rings may be significant evidence of ring strain. Otherwise

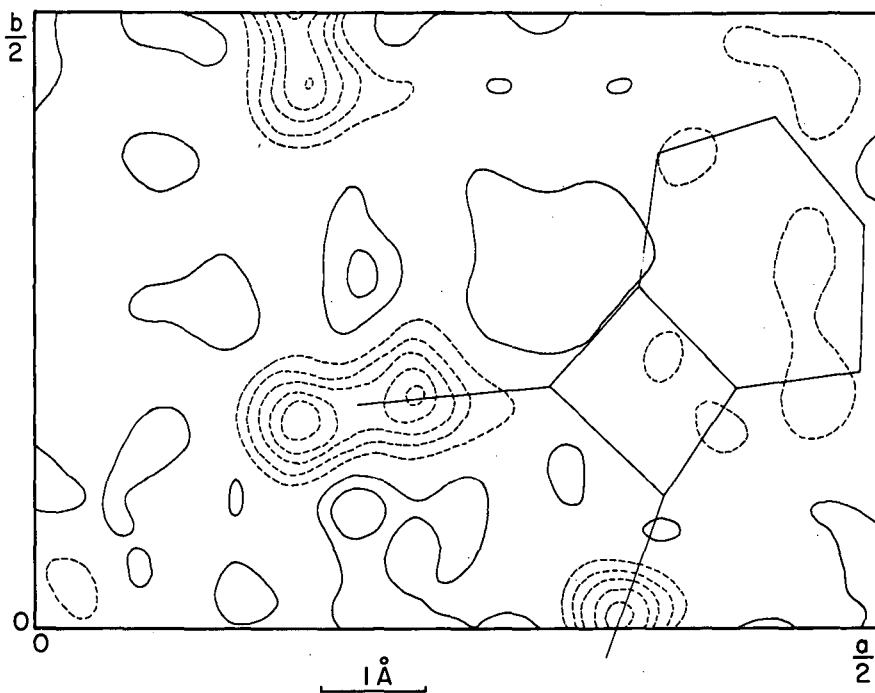
Table VII. Observed and calculated structure factors for C₈H₆Br₂ (*indicates minimum observable structure factor).

h	k	l	F _o	F _o	h	k	l	F _o	F _o	h	k	l	F _o	F _o	h	k	l	F _o	F _o	h	k	l	F _o	F _o	h	k	l	F _o	F _o			
4	0	0	63	72	13	6	0	12*	6	6	2	1	31	31	3	9	1	12	9	3	5	2	48	44	7	1	3	17	16			
6	0	0	145	154	14	6	0	12*	5	7	2	1	20	20	4	9	1	18	13	4	5	2	35	34	8	1	3	18	19			
8	0	0	69	66	1	7	0	10*	8	8	2	1	35	42	5	9	1	13	6	5	5	2	38	37	9	1	3	14	11			
10	0	0	26	11	2	7	0	82	85	9	2	1	16	19	6	9	1	31	26	6	5	2	16	15	10	1	3	12	11			
12	0	0	12*	13	3	7	0	31	27	10	2	1	30	34	7	9	1	12*	12	7	5	2	25	26	11	1	3	15	21			
14	0	0	16*	3	4	7	0	72	78	11	2	1	17	17	8	9	1	20	17	8	5	2	21	20	12	1	3	10*	2			
16	0	0	17	6	5	7	0	10*	3	12	2	1	21	16	9	9	1	12*	8	9	5	2	12*	12	14	1	3	9*	1			
18	0	0	10*	5	6	7	0	12	13	13	2	1	18	13	10	9	1	13	8	10	5	2	12*	12	14	1	3	9*	1			
3	1	0	74	87	7	7	0	10*	7	14	2	1	12*	6	1	10	1	12*	8	11	5	2	12*	10	15	1	3	8*	5			
4	1	0	93	113	8	7	0	22	24	15	2	1	12*	6	2	10	1	12*	3	12	5	2	14	18	1	2	3	16	14			
5	1	0	11	9	9	7	0	19	17	16	2	1	11*	6	3	10	1	12*	5	5	6	2	17	13	3	2	3	19	18			
6	1	0	68	69	10	7	0	18	18	17	2	1	10*	3	4	10	1	12*	10	14	5	2	16	10	11	1	3	20	20			
7	1	0	68	72	11	7	0	13*	4	0	3	1	65	68	5	10	1	14	12	15	5	2	11*	11	4	2	3	24	20			
8	1	0	15	12	12	7	0	12*	2	1	0	1	59	72	6	10	1	12*	7	0	6	2	51	42	5	2	3	27	24			
9	1	0	39	43	13	7	0	12*	4	2	3	1	29	31	7	10	1	12*	21	21	1	6	2	27	24	7	2	23	24			
10	1	0	32	32	14	7	0	11*	5	3	3	1	38	42	8	10	1	12*	0	11	1	20	12	2	6	2	25	22	7	2	25	24
11	1	0	11*	1	0	8	0	25	39	4	3	1	18	19	1	11	1	12	16	3	6	2	15	15	8	2	3	28	27			
12	1	0	32	24	1	8	0	27	21	5	3	1	59	61	2	11	1	15	9	4	6	2	20	17	9	2	3	10*	1			
13	1	0	78	32	2	8	0	16	19	6	3	1	39	41	3	11	1	12*	5	5	6	2	17	13	10	2	3	10*	1			
14	1	0	24	16	3	8	0	12*	7	7	3	1	30	34	4	11	1	12*	10	6	6	2	18	15	10	2	3	10*	1			
15	1	0	23	23	4	8	0	17	22	8	3	1	30	29	5	11	1	12*	2	7	6	2	28	24	11	2	3	14	12			
16	1	0	12*	2	5	8	0	29	27	9	3	1	56	60	6	11	1	12*	11	8	6	2	26	24	13	2	3	12	10			
17	1	0	11*	1	6	8	0	11*	10	10	3	1	11*	8	7	11	1	11*	7	9	6	2	17	16	14	2	3	11	10			
18	1	0	10*	3	7	8	0	17	13	11	3	1	46	48	8	12	1	12*	9	10	6	2	14	12	15	2	3	10*	1			
1	2	0	52	61	8	8	0	26	28	12	3	1	15	15	3	12	1	19	17	11	6	2	17	14	15	2	3	10*	1			
2	2	0	7	4	9	8	0	14	12	13	3	1	12*	8	4	12	1	11*	7	12	6	2	12*	7	1	3	3	49	49			
3	2	0	51	95	10	8	0	10*	9	16	3	1	28	29	5	12	1	11*	12	13	6	2	12*	6	2	3	3	7	8			
4	2	0	73	84	11	8	0	12	14	15	3	1	12	12	6	12	1	11*	12	13	6	2	12*	6	2	3	3	7	14			
5	2	0	14	12	12	8	0	12*	4	16	3	1	11*	6	7	13	1	11*	19	17	11	6	2	17	14	10	3	3	12	10		
6	2	0	19	28	13	8	0	13	11	17	3	1	16	16	8	14	1	11*	17	12	6	2	11*	7	5	3	3	32	29			
7	2	0	24	21	14	8	0	10*	2	1	4	1	34	38	9	14	1	11*	22	2	7	2	41	36	6	3	3	8*	7			
8	2	0	16	14	15	9	0	12*	11	2	4	1	35	37	10	14	1	11*	22	4	7	2	17	16	7	3	3	28	28			
9	2	0	56	56	16	9	0	28	20	3	4	1	41	45	11	14	1	11*	22	6	7	2	14	11	8	3	3	16	16			
10	2	0	72	71	17	9	0	11*	12	4	4	1	50	53	12	14	1	11*	22	8	7	2	22	21	10	3	3	10	9			
11	2	0	43	40	18	9	0	12*	8	5	4	1	43	46	13	14	1	11*	22	9	7	2	22	21	10	3	3	10	9			
12	2	0	51	52	19	9	0	11*	9	6	4	1	43	46	14	14	1	11*	22	10	7	2	22	21	10	3	3	10	9			
13	2	0	12*	2	20	9	0	17	13	7	4	1	42	47	15	14	1	11*	22	11	8	2	22	21	10	3	3	10	9			
14	2	0	12*	1	21	9	0	15	8	8	4	1	28	35	16	14	1	11*	22	12	9	2	13	7	12	3	3	10*	7			
15	2	0	15	10	22	9	0	22	2	9	4	1	19	21	17	14	1	11*	22	13	10	2	13	7	12	3	3	10*	7			
16	2	0	16	18	23	9	0	12*	6	10	4	1	21	22	18	14	1	11*	22	14	11	2	13	7	12	3	3	10*	7			
17	2	0	16	14	24	9	0	12*	6	11	4	1	14	14	19	14	1	11*	22	15	12	2	13	7	12	3	3	10*	7			
18	2	0	14	12	25	9	0	12*	6	12	4	1	31	29	20	14	1	11*	22	16	13	2	13	7	12	3	3	10*	7			
1	3	0	78	80	12	9	0	13	10	13	4	1	12*	15	21	15	1	11*	22	17	14	2	13	7	12	3	3	10*	7			
2	3	0	14	15	13	9	0	13	12	14	4	1	32	17	22	15	1	11*	22	18	15	2	13	7	12	3	3	10*	7			
3	3	0	142	144	14	9	0	11*	6	15	4	1	22	2	23	16	1	11*	22	19	16	2	13	7	12	3	3	10*	7			
4	3	0	22	23	15	10	0	10	21	16	4	1	77	80	24	16	1	11*	22	20	17	2	13	7	12	3	3	10*	7			
5	3	0	97	102	16	10	0	12*	2	17	5	1	83	88	25	16	1	11*	22	21	18	2	13	7	12	3	3	10*	7			
6	3	0	16	13	17	10	0	12*	2	18	5	1	47	49	26	17	1	11*	22	22	19	2	13	7	12	3	3	10*	7			
7	3	0	26	33	18	10	0	12*	1	19	5	1	45	35	27	17	1	11*	22	23	20	2	13	7	12	3	3	10*	7			
8	3	0	39	44	19	10	0	28	28	20	5	1	26	26	28	18	1	11*	22	24	21	2	13	7	12	3	3	10*	7			
9	3	0	11*	11	20	10	0	12*	8	21	5	1	44	44	29	18	1	11*	22	25	22	2	13	7	12	3	3	10*	7			
10	3	0	11*	6	21	10	0	12*	8	22	5	1	50	49	30	19	1	11*	22	26	23	2	13	7	12	3	3	10*	7			
11	3	0	12*	4	22	10	0	12*	7	23	5	1	28	29	31	20	1	11*	22	27	24	2	13	7	12	3	3	10*	7			
12	3	0	22	23	23	10	0	12*	10	24	5	1	37	34	32	20	1	11*	22	28	25	2	13	7	12	3	3	10*	7			
13	3	0	12*	2	24	10	0	12*	10	25	5	1	12	11	33	21	1	11*	22	29	26	2	13	7	12	3	3	10*	7			
14	3	0	49	50	25	10	0	15	10	26	5	1	12*	8	34	22	1	11*	22	30	27	2	13	7	12	3	3	10*	7			
15	3	0	25	22	26	10	0	12*	1	27	5	1	12*	4	35	23	1	11*	22	31	28	2	13	7	12	3	3	10*	7			
16	3	0	28	25	27	10	0	12*	1	28	5	1	12*	4	36	24	1	11*	22	32	29	2	13	7	12	3	3	10*	7			
17	3	0	23	28	28	10	0	12*	4	29	5	1	29	28	37	25	1	11*	22	33	30	2	13	7	12	3	3	10*	7			
18	3	0	26	26	29	10	0	12*	4	30	5	1	19	22	38	26	1	11*	22	34	31											



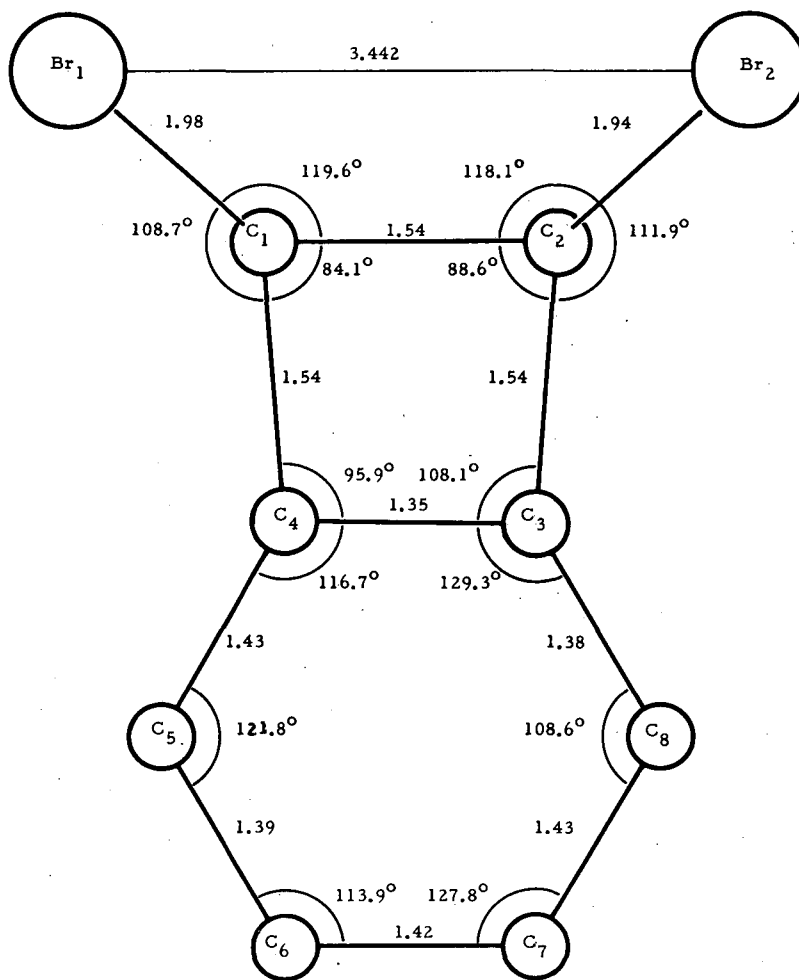
MU-17717

Fig. 2. [001] Projection of the F_0 synthesis of $C_8H_6Br_2$. Contours are drawn each electron/Å² except for the bromine atoms, where the contour interval is 5 electrons/Å² beginning with the 10-electron contour. Negative contours are dashed lines. The zero contour is omitted.



MU-17718

Fig. 3. [001] Projection of the $F_o - F_c$ synthesis of $C_8H_6Br_2$. Contours drawn every 0.5 electron/ \AA^2 ; zero contour omitted and negative contours dashed.



MU-17603

Fig. 4. Interatomic distances (Å) and bond angles in $C_8H_6Br_2$.

Table VIII

Interatomic distances (A) in $C_8H_6Cl_2$ at $25^\circ C$					
(a) Output of Cycle 9 - the final result					
(b) Coordinates from the three-dimensional Fourier summation					
(c) Output of Cycle 24 - the result of full-matrix refinement					
(d) Standard deviation of a single determination of a bond length					
(e) Standard deviation of the average of several determinations					
	(a)	(b)	(c)	(d)	(e)
$Br_1 - Br_2$	3.442	3.442	3.434	.008	
$C_1 - Br_1$	1.98	1.99	2.01		
$C_2 - Br_2$	1.94	1.97	1.96		
Average	1.96	1.98	1.98	.04	.03
$C_1 - C_4$	1.54	1.50	1.58		
$C_2 - C_3$	1.54	1.57	1.55		
$C_1 - C_2$	1.54	1.51	1.49		
Average	1.54	1.53	1.54	.07	.04
$C_3 - C_4$	1.34	1.37	1.34	.06	
$C_4 - C_5$	1.43	1.43	1.45		
$C_5 - C_6$	1.39	1.35	1.39		
$C_6 - C_7$	1.42	1.44	1.39		
$C_7 - C_8$	1.43	1.35	1.44		
$C_8 - C_3$	1.38	1.39	1.34		
Average	1.41	1.39	1.40	.07	.03

this determination does not detect any deviation in bond lengths from the generally accepted values for nonstrained systems quoted (Tables of Interatomic Distances, 1958).

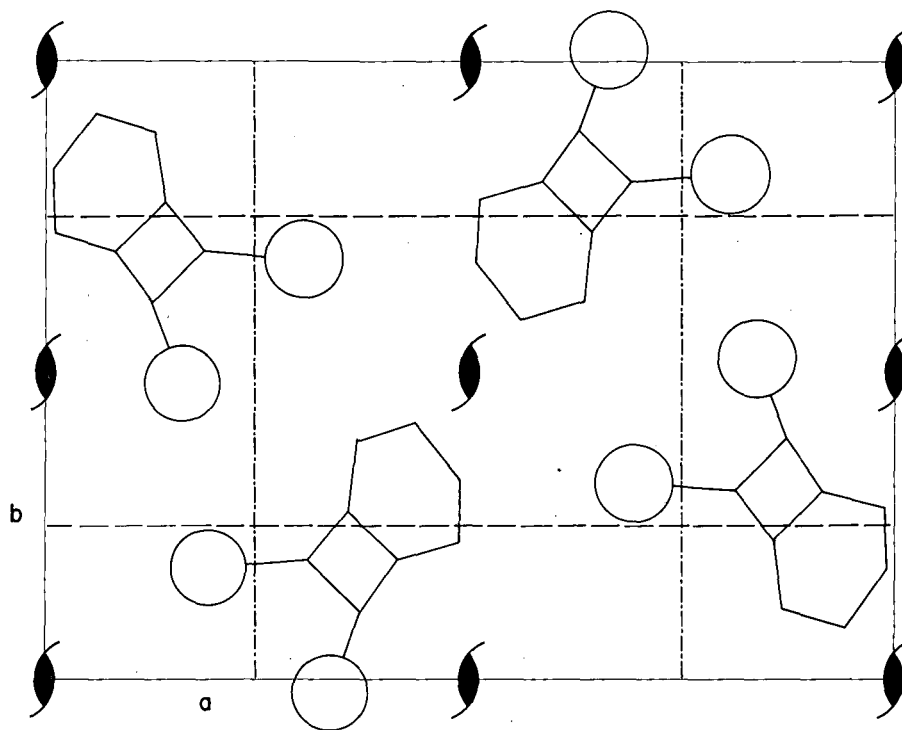
The equations of the planes of the four- and six-membered rings have been derived by substitution of the coordinates into the general linear equation. The calculated angle of 6° between the two planes is very near the limit of accuracy of the determination of this angle. This angle is such that the four-membered ring is on one side of the benzene plane and the halogen atoms on the opposite side. The four-membered ring appears twisted, so that a plane passed through C_2 , C_3 , and C_4 is 0.06A distant from C_1 . The plane including the bromine atoms and the outer edge of the four-membered ring makes an angle of 43° with the ring. Figure 5 is a c-axis projection of the unit cell showing the orientation of the molecules.

Structure Determination of $C_8H_6I_2$

The hk0 data were first used to determine the best x and y parameters for the iodine atoms. The first trial structure consisted of the two iodines in the isomorphous bromine positions, and a series of least-squares cycles refined these positions to an agreement of $R_1 = 0.174$. The carbon atoms were introduced at the carbon positions in the dibromo- derivative and were refined by least squares for two cycles, giving $R_1 = 0.129$. A c-axis Fourier projection was calculated by using the final phases, and the coordinates derived from it were refined by least squares for three further cycles with a final $R_1 = 0.118$. Figure 6 shows the [001] projection on which all the atoms appear resolved in spite of rather large diffraction and thermal vibration effects.

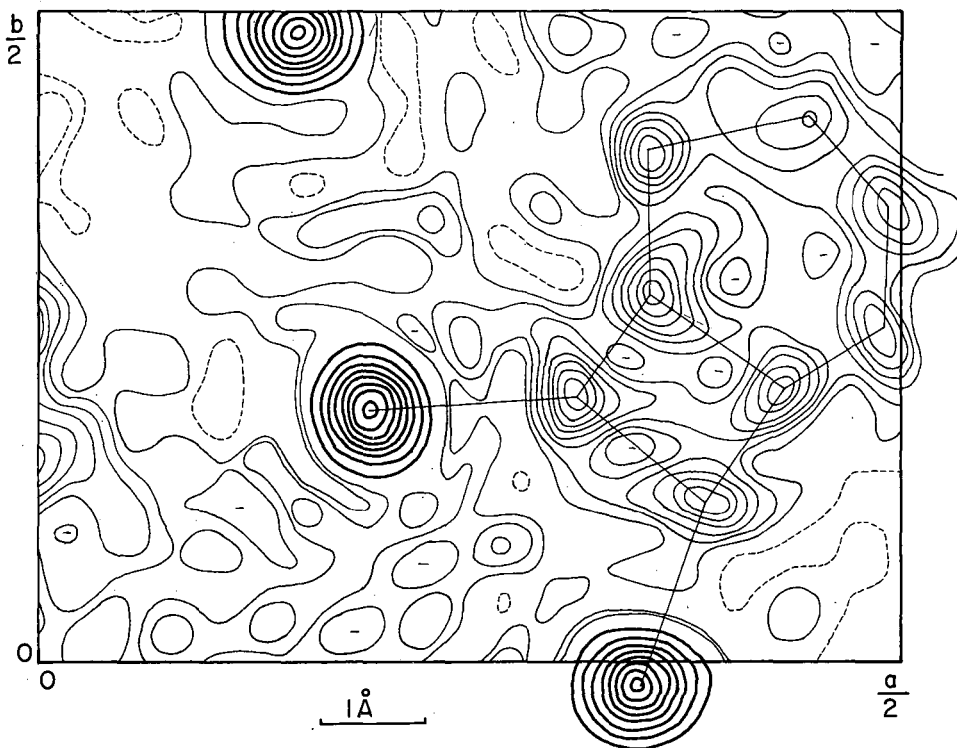
The MoK α data from the precession films were used to determine the best three-dimensional parameters for the iodine atoms. The [010] and [100] Fourier projections were not sufficiently resolved to locate the carbon atoms in the third dimension.

A cycle of three-dimensional least squares was calculated on the CuK α data by using the iodine positions from the MoK α data refinements as input along with the x and y coordinates for the carbons



MU-17719

Fig. 5. z-Axis projection of the unit cell of $C_8H_6Br_2$.



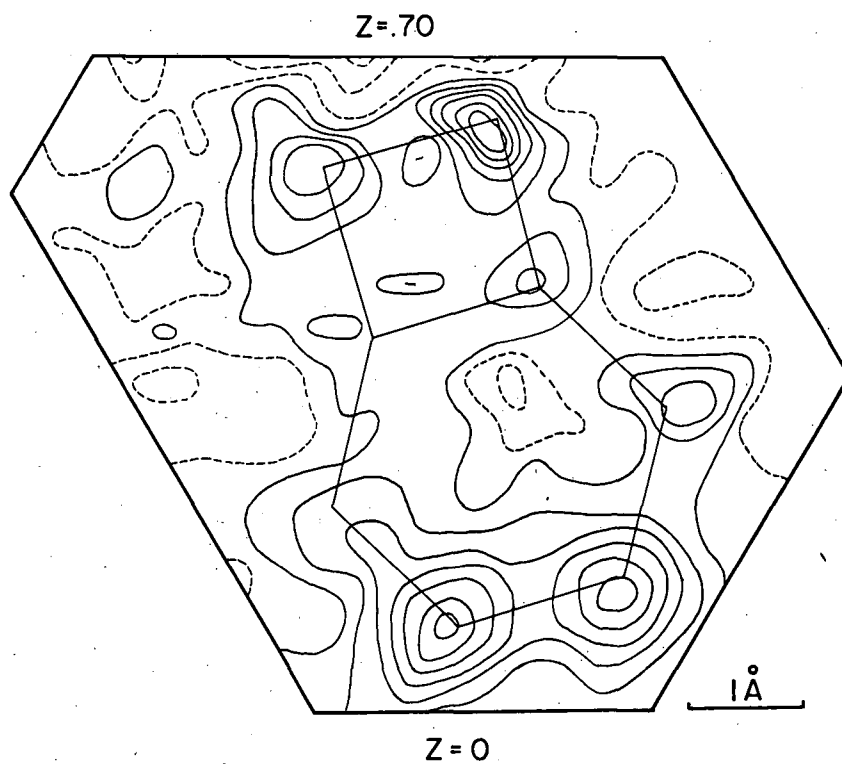
MU-17720

Fig. 6. [001] Projection of the F_0 synthesis of $C_8H_6I_2$. Contours are drawn each electron/ \AA^2 except for the heavy contours on the iodine atoms, where the contour interval is 10 electrons/ \AA^2 beginning with the 10-electron contour. Zero contour omitted and negative contours dashed.

from the [001] projection and z values of the carbon positions from $C_8H_6Br_2$. The R_1 for this cycle was 0.154. A three-dimensional Fourier summation was calculated by using the phases calculated on this first cycle. A portion of the electron-density map in the plane of the carbon rings is shown in Fig. 7. All except two of the carbon atoms are resolved in this plot, but the resolution was not so satisfactory as for the [001] projection.

Two further cycles of least squares resulted in a structure giving $R_1 = 0.144$. The refinements were concluded at this point because the carbon-carbon bond distance standard deviation was 0.11Å and it is doubtful that more accurate carbon parameters can be found from these X-ray data. A final structure-factor calculation was made, with average values for the iodine and carbon isotropic temperature factors used as input. The carbon atom positions were adjusted to give the same carbon-carbon bond distances as in the dibromo-derivative. Table IX lists the coordinates used in the final refinement and the resulting reliability factors and standard deviations. The list of observed and calculated structure factors is presented in Table X. Extinction is believed to be a large systematic part of the final discrepancy. A [001] $F_o - F_c$ difference map was calculated by using the final parameters; it is shown in Fig. 8. Strong anisotropic temperature vibrations of the iodine atoms are clearly shown. The small peaks at the carbon positions are an indication that the temperature factors used were too large.

The iodine-iodine distance determined in this structure is $3.517 \pm 0.008\text{Å}$, which is considerably less than twice the Van der Waals radius given by Pauling (1948) of 4.30Å. The plane containing the iodine atoms and their nearest carbon neighbors makes an angle of 25° with the plane of the four-membered ring. This is much flatter than the 43° found for the similar angle in $C_8H_6Br_2$, probably because of strain caused by repulsion of the iodine atoms.



MU-17721

Fig. 7. Three-dimensional F_0 Fourier synthesis of $C_8H_6I_2$. This section through the carbon rings is taken in the plane $1.382x + 0.746y + 0.655z = 1$. Contours are drawn every electron/Å³; zero contour omitted and negative contours dashed.

Table IX

Final parameters for $C_8H_6I_2$

	<u>x</u>	<u>y</u>	<u>z</u>	<u>σ_x</u>	<u>σ_y</u>	<u>σ_z</u>
I ₁	.34931	.98329	.9000	.00026	.00035	.0026
I ₂	.19241	.19401	.7566	.00026	.00034	.0025
C ₁	.316	.210	.612	.005	.006	.037
C ₂	.388	.125	.640	.005	.007	.027
C ₃	.420	.209	.400	.005	.006	.028
C ₄	.358	.291	.446	.005	.007	.032
C ₅	.360	.395	.315	.005	.007	.030
C ₆	.431	.417	.136	.005	.007	.028
C ₇	.498	.352	.085	.005	.006	.028
C ₈	.486	.252	.208	.005	.006	.026

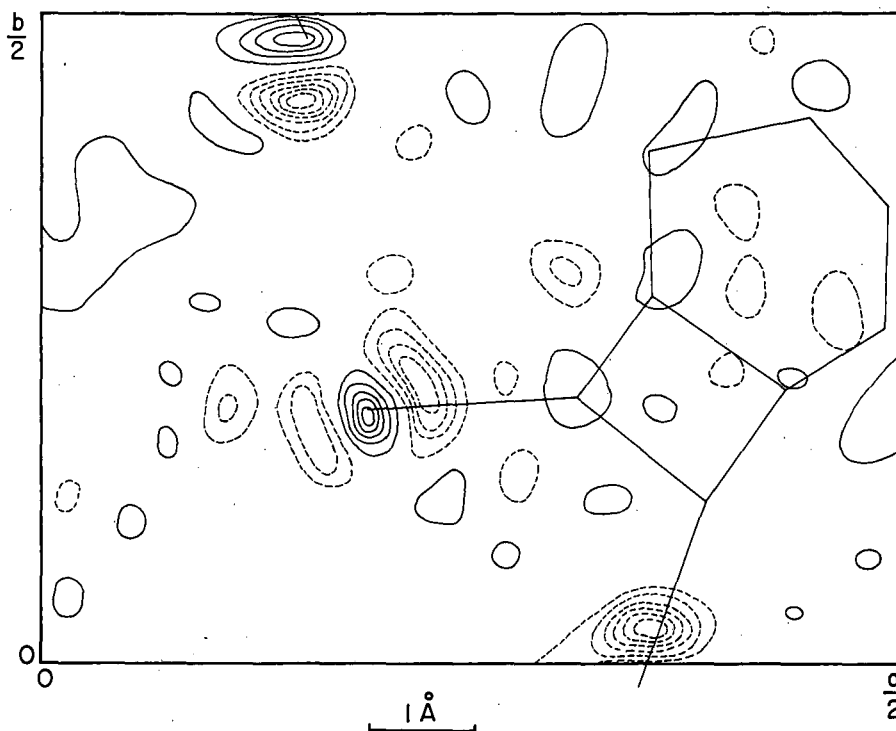
Average temperature factors of 5.25 and 5.95Å² were chosen for the iodine and carbon atoms respectively; also $R_1 = 0.148$, $R_2 = 0.172$, and $R_3 = 0.312$ for the three-dimensional data including the unobserved reflections

Table X. Observed and calculated structure factors for C₆H₆I₂ (* indicates minimum observable structure factor. ** indicates intensity measurement very uncertain. These ** reflections were omitted from the least squares and Fourier calculations.

Table with 16 columns: h, k, l, F_o, |F_c|, h, k, l, F_o, |F_c|, h, k, l, F_o, |F_c|, h, k, l, F_o, |F_c|. The table lists observed and calculated structure factors for C6H6I2, including reflections with minimum observable structure factors and intensity measurements that were very uncertain.

Table X. (concluded)

h	k	l	F _o	[F _o]	h	k	l	F _o	[F _o]	h	k	l	F _o	[F _o]	h	k	l	F _o	[F _o]	
7 14	1	19	20	20	3 5	2	105	110	2 11	2	34	26	10 3	3	30	25	9 9	3	14	9
0 15	1	24	20	20	4 5	2	33	31	3 11	2	37	24	11 3	3	15*	12	10 9	3	41	29
1 15	1	9*	11	11	5 5	2	68	77	4 11	2	26	25	12 3	3	14*	10	11 9	3	11*	7
2 15	1	9*	9	9	6 5	2	18*	17	5 11	3	21*	18	13 3	3	14*	6	12 9	3	9*	9
3 15	1	9*	6	6	7 5	2	64	62	6 11	2	36	23	14 3	3	13*	8	1 10	3	2*	17
4 15	1	13	10	10	8 5	2	33	31	7 11	2	20*	9	15 3	3	12*	9	2 10	3	26	26
5 15	1	8*	2	2	9 5	2	33	26	8 11	2	30	19	16 3	3	10*	9	3 10	3	28	27
6 15	1	17	11	11	10 5	2	21*	4	9 11	2	16*	6	17 3	3	16	7	4 10	3	29	31
					11 5	2	41	36	10 11	2	17*	4	1 4	3	40	38	5 10	3	13*	8
2 0	2	135	94	**	12 5	2	31	17	11 11	2	15*	7	2 4	3	61	60	6 10	3	13*	12
4 0	2	109	108		13 5	2	46	37	12 11	2	26	16	3 4	3	70	80	7 10	3	18	12
6 0	2	78	81		14 5	2	20*	9	0 12	2	20*	13	4 4	3	41	42	8 10	3	12*	5
8 0	2	89	83		15 5	2	30	15	1 12	2	35	31	5 4	3	57	59	9 10	3	11*	10
10 0	2	94	100		0 6	2	74	68	2 12	2	20*	11	6 4	3	21	19	10 10	3	10*	7
12 0	2	37	27		1 6	2	78	85	3 12	2	22	11	7 4	3	14*	6	11 10	3	9*	3
14 0	2	34	35		2 6	2	33	35	4 12	2	19*	6	8 4	3	38	39	12 10	3	14	6
16 0	2	38	35		3 6	2	28	26	5 12	2	33	22	9 4	3	14*	13	0 11	3	37	35
18 0	2	25	15		4 6	2	52	47	6 12	2	22	8	10 4	3	15*	6	5 11	3	12*	5
1 1	2	77	81		5 6	2	40	51	7 12	2	18	16	11 4	3	23	16	2 11	3	22	17
2 1	2	64	78		6 6	2	42	37	8 12	2	22*	8	12 4	3	20	17	3 11	3	13*	9
3 1	2	122	114		7 6	2	54	47	9 12	2	17*	17	13 4	3	24	16	4 11	3	22	13
4 1	2	114	106		8 6	2	36	34	10 12	2	14*	6	14 4	3	12*	9	5 11	3	12*	5
5 1	2	98	93		9 6	2	48	39	11 12	2	14	11	15 4	3	20	12	6 11	3	32	19
6 1	2	94	74		10 6	2	54	43	12 12	2	8	2	0 5	3	22	15	7 11	3	11*	7
7 1	2	68	73		11 6	2	22*	25	1 13	2	18*	8	1 5	3	19	20	8 11	3	10*	7
8 1	2	24	23		12 6	2	22*	13	2 13	2	19	19	2 5	3	12*	8	9 11	3	14	12
9 1	2	46	48		13 6	2	21*	5	3 13	2	17*	16	3 5	3	34	35	1 12	3	11*	5
10 1	2	34	30		14 6	2	20*	17	4 13	2	17	10	4 5	3	24	29	2 12	3	11*	4
11 1	2	21*	26		15 6	2	18*	13	5 13	2	16	16	5 5	3	45	37	3 12	3	17	6
12 1	2	57	41		1 7	2	34	29	6 13	2	15	8	6 5	3	24	10	4 12	3	10*	5
13 1	2	64	62		2 7	2	50	49	7 13	2	14*	9	7 5	3	29	21	5 12	3	13	12
14 1	2	38	32		3 7	2	58	53	8 13	2	14	13	8 5	3	18	10	6 12	3	15	8
15 1	2	21*	7		4 7	2	52	52	9 13	2	11*	1	9 5	3	62	60	7 12	3	29	18
16 1	2	20*	10		5 7	2	43	40	0 14	2	14*	6	10 5	3	28	23	8 12	3	10	5
17 1	2	18*	18		6 7	2	51	44	1 14	2	18	15	11 5	3	38	37	0 13	3	20	10
18 1	2	16*	3		7 7	2	52	50	2 14	2	14*	2	12 5	3	14*	5	1 13	3	21	14
0 2	2	138	161		8 7	2	40	33	3 14	2	14*	8	13 5	3	13*	5	2 13	3	8*	4
1 2	2	72	79		9 7	2	27	18	4 14	2	13*	1	14 5	3	12*	7	3 13	3	8*	5
2 2	2	74	79		10 7	2	22*	11	5 14	2	12*	12	15 5	3	26	22	4 13	3	16	10
3 2	2	23	34		11 7	2	36	24	6 14	2	21	3	1 6	3	13*	10	5 13	3	8	5
4 2	2	79	70		12 7	2	36	31	7 14	2	14*	1	2 6	3	56	55				
5 2	2	41	41		13 7	2	32	25	8 14	2	13*	116	3 6	3	17	23				
6 2	2	101	105		14 7	2	26	19	9 14	2	26	14	4 6	3	37	45				
7 2	2	46	46		15 7	2	17*	9	10 14	2	15	15	5 6	3	40	39				
8 2	2	59	55		16 7	2	18	7	11 14	2	15	18	6 6	3	14*	11				
9 2	2	52	45		17 7	2	16	8	12 14	2	15	15	7 6	3	44	37				
10 2	2	57	51		0 8	2	85	68	13 14	2	15	12	8 6	3	26	22				
11 2	2	22	22		1 8	2	35	35	14 14	2	15	12	9 6	3	25	18				
12 2	2	26	17		2 8	2	44	47	0 1 3	3	102	83	10 6	3	14*	9				
13 2	2	22*	2		3 8	2	25	20	1 1 3	3	47	42	11 6	3	30	22				
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15 2	2	21*	11		5 8	2	37	29	3 1 3	3	41	34	13 6	3	34	27				
16 2	2	24	21		6 8	2	43	38	4 1 3	3	10*	9	14 6	3	11*	3				
17 2	2	18*	12		7 8	2	22*	12	5 1 3	3	61	61	15 6	3	16	10				
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1 3	2	89	77		9 8	2	34	23	7 1 3	3	18	9	1 7 3	3	52	50				
2 3	2	46	68		10 8	2	37	32	8 1 3	3	40	44	2 7 3	3	38	32				
3 3	2	104	128		11 8	2	26	21	9 1 3	3	53	50	3 7 3	3	14*	6				
4 3	2	60	58		12 8	2	20*	9	10 1 3	3	36	29	4 7 3	3	27	17				
5 3	2	89	77		13 8	2	19*	4	11 1 3	3	38	37	5 7 3	3	39	31				
6 3	2	36	31		14 8	2	17*	10	12 1 3	3	15*	7	6 7 3	3	39	37				
7 3	2	95	94		15 8	2	15	13	13 1 3	3	14*	7	7 7 3	3	28	23				
8 3	2	18*	14		16 8	2	12	11	14 1 3	3	14*	2	8 7 3	3	14	15				
9 3	2	41	39		1 9	2	21*	14	15 1 3	3	22	23	9 7 3	3	14*	7				
10 3	2	20*	15		2 9	2	62	56	16 1 3	3	21	12	10 7 3	3	14*	7				
11 3	2	56	48		3 9	2	26	21	17 1 3	3	19	9	11 7 3	3	13*	8				
12 3	2	38	21		4 9	2	54	52	1 2 3	3	15	18	12 7 3	3	12*	3				
13 3	2	38	50		5 9	2	22*	1	2 2 3	3	31	40	13 7 3	3	11*	3				
14 3	2	22*	16		6 9	2	38	35	3 2 3	3	23	27	14 7 3	3	10*	5				
15 3	2	27	17		7 9	2	22*	16	4 2 3	3	27	24	1 8 3	3	25	19				
16 3	2	19*	7		8 9	2	31	25	5 2 3	3	49	43	2 8 3	3	21	8				
17 3	2	17*	16		9 9	2	21*	12	6 2 3	3	79	73	3 8 3	3	44	39				
0 4	2	98	101		10 9	2	20*	12	7 2 3	3	38	27	4 8 3	3	23	23				
1 4	2	75	94		11 9	2	20*	7	8 2 3	3	62	53	5 8 3	3	15	11				
2 4	2	14*	20		12 9	2	26	22	9 2 3	3	14*	5	6 8 3	3	42	36				
3 4	2	55	47		13 9	2	17*	11	10 2 3	3	27	14	7 8 3	3	14*	16				
4 4	2	68	77		14 9	2	18	15	11 2 3	3	26	22	8 8 3	3	28	23				
5 4	2	33	36		0 10	2	38	39	12 2 3	3	55	51	9 8 3	3	23	13				
6 4	2	69	51		1 10	2	35	31	13 2 3	3	24	21	10 8 3	3	13*	9				
7 4	2	59	57		2 10	2	22*	25	14 2 3	3	33	29	11 8 3	3	12*	5				
8 4	2	33	22		3 10	2	22*	15	15 2 3	3	12	10	12 8 3	3	36	24				
9 4	2	86	62		4 10	2	22*	15	16 2 3	3	11	4	13 8 3	3	10*	5				
10 4	2	52	50		5 10	2	41	30	0 3 3	3	15	20								



MU-17722

Fig. 8. $[001]$ Projection of $F_o - F_c$ synthesis of $C_8H_6I_2$. Contours drawn every electron/ \AA^2 ; zero contour omitted and negative contours dashed.

THE CRYSTAL STRUCTURE OF $C_8H_6Cl_2$ AT $25^\circ C$

After the crystal-structure determinations of the dibromo- and diiodo- cis-1, 2-dihalobenzocyclobutenes was well under way, the dichloro- derivative was prepared (by Jensen and Coleman) and found to crystallize in the monoclinic space group $P2_1/c$. The bond lengths should be more accurately determined in the latter case because the X-ray scattering is less concentrated in the heavy atoms and the structure refinement should be more direct in the centrosymmetric space group.

Experimental Procedure

The sample was recrystallized several times from a hexane-ether mixture by slow evaporation at room temperature in order to grow crystals of sufficient size for diffraction experiments. The crystals form flat plates perpendicular to the [100] direction. A piece cut from a plate was sealed in a thin-walled glass capillary and aligned about the [011] direction. Multiple-film Weissenberg photographs were taken through the twelfth layer on the newer "improved" Kodak medical no-screen X-ray film with $CuK\alpha$ X-rays at room temperature. A flat plate crystal was aligned about the [010] axis and a zero-level Weissenberg photograph was taken, and in addition a 0kl precession photograph was made of this crystal with $MoK\alpha$ X-rays.

The intensities of the reflections on the [011]-axis Weissenberg films were measured by visual comparison with an intensity standard. The usual corrections for Lorentz and polarization effects were made and the relative scale factors were determined by comparison of equivalent reflections on the different layers. No absorption correction was made.

Unit Cell and Space Group

The quartz-calibrated b-axis rotation photograph was used to determine the length of the b axis. The other unit-cell parameters were determined from the calibrated h0l film. The cell dimensions for $C_8H_6Cl_2$ at $25^\circ C$ are

$$\underline{a} = 8.597 \pm 0.024\text{A},$$

$$\underline{b} = 11.061 \pm 0.048\text{A},$$

$$\underline{c} = 8.782 \pm 0.016\text{A},$$

$$\beta = 110^{\circ} 29' \pm 13',$$

With a cell volume of 782.3A^3 the calculated density is 1.475, assuming four molecules per unit cell. There were 844 observed reflections and 303 unobserved in the portion of the reciprocal lattice photographed.

The systematic absences suggest $P2_1/c$ as a probable space group, and the structure analysis was carried out on this assumption. The general fourfold positions of this group are

$$x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, 1/2+y, 1/2-z; \text{ and } x, 1/2-y, 1/2+z.$$

Determination of the Atomic Parameters

All the observed reflections were included in a three-dimensional Patterson summation using the Fourier program of Dodge (1958). The chlorine-chlorine vectors were well resolved. A two-atom trial structure with the chlorine atoms at (0.08, 0.25, 0.06) and (0.16, 0.01, 0.29) was found to be consistent with the vectors.

The LS-II program was used, with alteration, for the refinement of the atomic coordinates and temperature factors in this structure. Table XI lists the reliability factors for the various least-squares cycles.

Cycle 1

The structure factors were calculated on the basis of the chlorine parameters and arbitrarily chosen scale and temperature factors. The signs of the calculated structure factors were used in a three-dimensional F_0 Fourier summation. The positions of the eight carbon atoms were all resolved by this calculation.

Cycle 2

The atomic parameters from the first F_0 Fourier summation were the input for this cycle with improved scale and temperature factors. Another three-dimensional Fourier summation was made with the signs based on all the atomic positions.

Cycles 3-8

The parameters from the second Fourier summations were the input for Cycle 3. The input for each of the later cycles was that

Table XI

Least-squares refinement of $C_8H_6Cl_2$ at $25^\circ C$				
Cycle	R_1	R_2	R_3^a	
1	.541	.607		Chlorine atom positions only from three-dimensional Patterson function
2	.349	.342	.650	Chlorine and carbon atom positions from a three-dimensional Fourier summation
3	.296	.313	.401	Input based on further Fourier refinement
4	.271	.286		
5	.297	.339		Unobserved reflections included
6	.260	.284		
7	.235	.247		
8	.225	.238		Only one atomic coordinate shift exceeded the standard deviation
9	.219	.234		Hydrogen atoms included in structure-factor calculations
10	.211	.225		
11	.211	.226		All shifts smaller than the standard deviations
12	.209	.225	.338	Hughes weighting factors introduced
13	.208	.226	.327	Shifts all smaller than 1/2 the standard deviations
14	.213	.232	.339	Normal benzene distances imposed on the ring

^aWhen Hughes weighting factors were used.

calculated from the previous least-squares cycles. The unobserved reflections were introduced into the calculations on the 5th and subsequent cycles. Only one of the atomic-parameter shifts exceeded the standard deviation on the 7th and 8th cycles. The reflections were given unit weighting factors.

Cycle 9

The positions of the hydrogen atoms were estimated from geometrical considerations. The benzene-ring hydrogen atoms were placed in the plane of the ring at a distance of 1.08A from the neighboring carbon atoms. The unsaturated ring hydrogens were given the same hydrogen-carbon distance and the bond angles were assumed symmetrical with the carbon-chlorine bonds. Table XII lists the coordinates of the hydrogen atoms with the temperature factor B equal to 2.38A.

Table XII

Hydrogen parameters for $C_8H_6Cl_2$ at 25°C			
	<u>x</u>	<u>y</u>	<u>z</u>
H ₁	.190	.371	.382
H ₂	.248	.591	.615
H ₃	.609	.575	.841
H ₄	.825	.418	.816
H ₅	.783	.253	.672
H ₆	.481	.182	.481

These parameters were included in the structure-factor calculations for subsequent cycles, but were not refined by least squares.

Cycles 10 and 11

The coordinate shifts were all smaller than their respective standard deviations. Several of the bond lengths differed from the expected values by many standard deviations. The agreement between observed and calculated structure factors was not as good as had been expected.

Cycles 12 and 13

These cycles were calculated by weighting the individual reflections according to the variable scale described in the section on least squares. On the 13th cycle the shifts remained smaller than one-half the corresponding standard deviations. The output parameters of Cycle 12 are listed in Table XIII.

Cycle 14

Several of the bond distances still varied from the expected values by many standard deviations. A set of structure parameters was derived by imposing the expected values on the bond distances, which constituted the input for this cycle. The reliability factors were higher and the shifts tended to move the atoms in the direction of the previously refined coordinates. The observed and calculated structure factors listed in Table XIV are from this cycle. The fogginess of the films severely limited the measurement of weak intensities.

Discussion of the Structure

The atomic parameters calculated on Cycle 12 and the reliability factors and standard deviations from Cycle 13 are presented as the final results of the least-squares refinement of the structure of $C_8H_6Cl_2$ at room temperature.

The interatomic distances and angles are shown in Fig. 9 and the interatomic distances are listed in Table XV. The standard deviations of bond lengths were calculated from the diagonal least-squares matrix elements by using the corrections of Templeton (1959) for the x- and z-axis correlation and assuming a spherical standard deviation surface.

The chlorine-chlorine distance of 3.175Å is much shorter than twice the Van der Waals radius of 3.60Å suggested by Pauling (1948), but longer than the chlorine-chlorine distance in CCl_4 of 2.887Å. The carbon-chlorine distance of 1.802 ± 0.019 Å is in agreement with the value for 1, 2-dichloroethane of 1.78 ± 0.01 Å. All published values of interatomic distances are from the Tables of Interatomic Distances (1958) unless otherwise noted.

Table XIII

Final parameters for $C_8H_6Cl_2$ at 25°C

	x	y	z	B(A ²)	σ_x	σ_y	σ_z	σ_B
C1 ₁	.16393	.01843	.28912	4.693	.00054	.00047	.00052	.014
C1 ₂	.08509	.25302	.06669	5.936	.00073	.00053	.00065	.019
C ₁	.2458	.4830	.6256	5.05	.0024	.0019	.0023	.06
C ₂	.2033	.3625	.5125	4.59	.0022	.0018	.0021	.05
C ₃	.3869	.3377	.5755	4.38	.0021	.0017	.0020	.05
C ₄	.4262	.4404	.6745	3.86	.0019	.0017	.0018	.05
C ₅	.4170	.5213	.2355	5.31	.0025	.0020	.0024	.07
C ₆	.2964	.6010	.2511	5.14	.0024	.0020	.0023	.06
C ₇	.3188	.6939	.3355	5.00	.0023	.0022	.0022	.06
C ₈	.4852	.7338	.4368	6.76	.0034	.0024	.0031	.09

$R_1 = 0.208$, $R_2 = 0.226$, and $R_3 = 0.327$ for the three-dimensional data including the unobserved reflections.

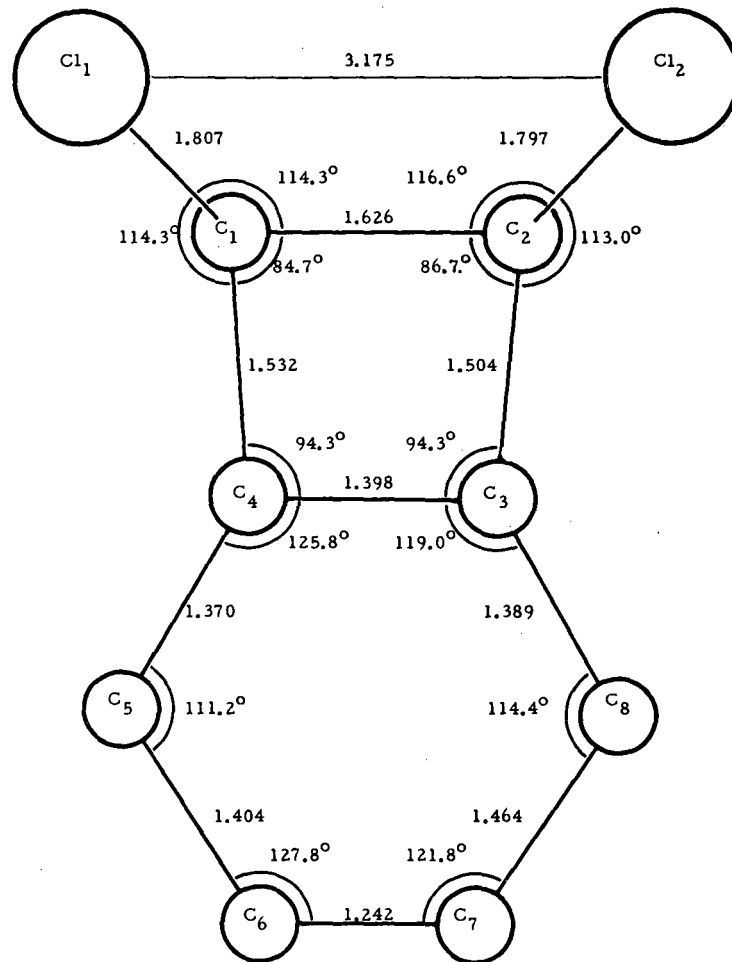
Obsolete see corrected page

Table XIV. Observed and calculated structure factors for $C_8H_6Cl_2$ at 25°C (* indicates minimum observable structure factor).

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
0	0	4	20	19	1	3	5	26	26	2	9	2	10	3	3	6	2	24	28	
0	0	6	17	15	1	3	5	7	6	2	9	2	10	3	3	6	2	12	6	
0	0	7	70	82	1	3	6	18	23	2	9	3	10	3	3	6	3	8	11	
0	1	3	17	17	1	3	6	5*	5*	2	5	4	5*	6	3	6	3	10	6	
0	1	4	36	40	1	3	7	4*	3	2	10	0	9	10	3	5	4	8	4	
0	1	5	21	24	1	3	7	6*	3	2	10	2	5	5	3	6	4	18	23	
0	1	6	10	10	1	3	7	1*	0	2	10	2	10	2	0	0	6	5	6	14
0	1	7	16	19	1	3	8	7	1	2	11	1	6	5	3	6	5	0	1	2
0	1	8	4	2	1	3	8	6	1	2	11	1	5*	4	3	6	6	6*	6*	2
0	2	2	80	111	1	3	9	4	1	2	11	1	5*	4	3	6	7	0	0	0
0	2	4	21	23	1	3	9	4*	5	2	11	1	5*	4	3	6	8	2	2	0
0	2	5	8	7	1	4	0	29	36	2	2	3	3*	4*	3	6	8	5*	3	3
0	2	6	17	9	1	4	1	4	3	2	2	4	13	13	3	6	9	5	3	3
0	2	7	4*	2*	1	4	2	3*	2	2	2	4	7	8	3	6	10	15	15	15
0	2	8	7	8	1	4	2	4*	1	2	2	5	6	3	3	6	11	7	6	6
0	2	9	1	0	1	4	4	14	20	2	2	6	14	13	3	6	12	15	17	17
0	3	1	32	35	1	4	5	12	9	2	2	6	21	27	3	6	13	3	7	7
0	3	2	10	10	1	4	5	6	1	2	2	7	8	9	3	6	14	10	10	10
0	3	3	6	10	1	4	5	18	10	2	2	7	6	7	3	6	15	5	2	2
0	3	4	23	22	1	4	6	8	4	2	2	8	12	12	3	6	16	6	6	6
0	3	5	24	24	1	4	7	9	7	2	2	8	4*	3	3	6	17	5	9	9
0	3	6	13	15	1	4	7	5	5	2	2	9	5*	3	3	6	18	11	10	10
0	3	7	15	13	1	4	8	7	9	2	2	9	28	3	3	6	19	7	8	8
0	3	8	5	6	1	4	8	7	9	2	2	9	43	3	1	2	13	11	9	3
0	3	9	3*	4*	1	4	8	4*	3*	2	2	9	31	28	3	1	2	17	16	16
0	4	0	84	85	1	4	9	3	3	2	3	2	39	37	3	1	3	32	13	13
0	4	1	31	32	1	4	9	4*	1	2	3	2	18	22	3	1	3	17	11	11
0	4	2	15	16	1	5	0	19	21	2	3	3	24	20	3	1	4	7	5	6
0	4	3	25	28	1	5	1	11	12	2	3	3	6	10	3	1	4	11	11	6
0	4	4	4	1	1	5	1	34	36	2	3	4	46	49	3	1	5	18	16	13
0	4	5	5*	4	1	5	2	6	3	2	3	4	7	3	3	7	5	10	12	7
0	4	6	10	13	1	5	2	18	21	2	3	5	32	36	3	1	6	13	14	14
0	4	7	8	1	1	5	3	17	17	2	3	5	1*	0	3	1	6	11	9	5
0	4	8	5	8	1	5	4	14	16	2	3	6	6	5	3	1	7	7	9	9
0	4	9	3*	0	1	5	4	23	31	2	3	6	6*	1	3	1	7	11	9	7
0	5	2	17	17	1	5	5	7	10	2	3	7	11	7	3	1	7	9	11	8
0	5	3	10	4	1	5	6	11	3	2	3	8	7	10	3	1	9	7	11	8
0	5	4	16	21	1	5	7	8	1	2	3	9	4	4	3	2	0	37	34	5
0	5	5	6	14	1	5	7	6	1	2	3	9	6*	4	3	2	1	9	4	4
0	5	6	6	8	1	5	8	6	8	2	4	0	19	17	3	2	1	4*	4*	4
0	5	7	8	9	1	5	8	6*	4	2	4	1	10	9	3	2	2	10	8	6
0	5	8	6	4	1	5	8	4*	5	2	4	2	39	39	3	2	2	54	52	5
0	5	9	3	4	1	5	9	4*	3	2	4	2	9	11	3	2	3	15	13	9
0	6	0	23	33	1	6	0	9	9	2	4	3	14	20	3	2	3	10	5	5
0	6	1	8	12	1	6	1	4	6	2	4	3	18	21	3	2	4	38	39	4
0	6	2	3	8	1	6	1	14	14	2	4	4	51	51	3	2	4	15	14	0
0	6	3	6	4	1	6	2	22	32	2	4	4	18	22	3	2	5	4*	1	27
0	6	4	6	4	1	6	2	9	8	2	4	5	13	10	3	2	5	4*	1	26
0	6	5	6	7	1	6	3	3*	4	2	4	5	16	18	3	2	6	5	7	1
0	6	6	6	2	1	6	4	4*	4	2	4	6	16	14	3	2	6	4	1	6
0	6	7	5*	4	1	6	5	22	12	2	4	6	8	1	3	2	7	4	3	9
0	6	8	4	2	1	6	6	15	17	2	4	7	13	3	3	2	8	8	7	27
0	6	9	3	2	1	6	6	7*	3	2	4	8	4*	3	3	2	8	4	1	6
0	7	0	12	18	1	6	7	6*	6	2	4	8	4*	4	3	2	9	0	2*	4*
0	7	1	10	11	1	6	8	5*	6	2	4	9	6*	1	3	2	9	2*	22	10
0	7	2	5	10	1	6	8	5*	1	2	4	10	5	11	3	3	1	14	0	6*
0	7	3	5*	3	1	6	9	3	2	2	5	0	33	40	3	3	1	17	13	34
0	7	4	0	0	1	6	9	4*	1	2	5	1	29	27	3	3	2	36	35	4
0	7	5	0	0	1	6	9	3	1	2	5	2	19	26	3	3	2	19	18	3
0	7	6	0	0	1	6	9	3	1	2	5	2	13	14	3	3	2	20	18	2
0	7	7	0	0	1	7	1	15	14	2	5	2	18	17	3	3	3	5*	2	8
0	7	8	0	0	1	7	2	24	33	2	5	3	18	20	3	3	4	4*	1	14
0	7	9	0	0	1	7	2	23	33	2	5	3	9	11	3	3	4	4*	2	3
0	8	0	4	3	1	7	3	3*	1	2	5	4	6	7	3	3	5	2	20	9
0	8	1	4	3	1	7	3	3*	1	2	5	4	1*	0	3	3	5	14	15	4
0	8	2	6	14	1	7	3	6*	3	2	5	5	10	5	3	3	6	7	5	11
0	8	3	6	14	1	7	4	13	3	2	5	5	8	31	3	3	6	7	5	8
0	8	4	5	1	1	7	4	8	5	2	5	6	5	5	3	3	7	9	10	16
0	8	5	1	5	1	7	5	5	5	2	5	6	5	5	3	3	7	6	10	8
0	8	6	49	53	1	7	5	5	5	2	5	7	7	3	3	3	8	6	9	7
0	8	7	15	16	1	7	7	6*	3	2	5	7	6	5	3	4	0	3*	9	4
0	8	8	7	2	1	7	9	4	2	2	5	8	6	4	3	4	0	3*	34	8
0	8	9	2	2	1	8	0	17	23	2	5	9	2*	0	3	4	1	15	15	12
0	9	0	10	10	1	8	1	10	11	2	6	0	27	28	3	4	1	17	18	3
0	9	1	40	45	1	8	3	23	9	2	6	1	6	11	3	4	2	32	37	11
0	9	2	38	39	1	8	3	10	4	2	6	1	6*	2	3	4	2	16	13	6
0	9	3	27	29	1	8	4	10	9	2	6	2	27	30	3	4	3	6	6	15
0	9	4	20	19	1	8	4	4	10	2	6	2	12	11	3	4	3	4*	1	16
0	9	5	14	16	1	8	8	6	1	2	6	3	9	6	3	4	4	16	16	22
0	9	6	17	19	1	9	0	21	27	2	6	4	10	12	3	4	4	6*	5	2
0	9	7	14	13	1	9	2	4*	9	2	6	4	7	6	3	4	5	6*	2	4
0	9	8	6	7	1	9	2	4*	1	2	6	5	21	6	3	4	5	5*	7	4
0	9	9	8	11	1	9	3	8	2	2	6	6	15	16	3	4	6	18	22	7
0	10	0	4*	1	1	9	3	3	6	2	6	6	7	9	3	4	6	7	1	8
0	10	1	4	1	1	9	4	6	4	2	6	7	8	5	3	4	6	6*	1	7
0	10	2	12	12	1	10	1	7	6	2	6	8	5	3	3	4	7	5	1	4
0	10	3	5*	4	1	10	1	9	4	2	6	9	4*	4	3	4	7	5*	5	3
0	10	4	49	49	1	10	2	5*	13	2	7	1	20	19	3	4	8	6	5	4
0	10	5	26	26	1	10	2	5*	7	2	7	1	4	6	3	4	8	2	3	4
0	10	6	8	8	1	11	1	5	1	2	7	2	14	1						

Table XIV. (concluded)

h	k	z	F ₀	F _c	h	k	z	F ₀	F _c	h	k	z	F ₀	F _c	h	k	z	F ₀	F _c	h	k	z	F ₀	F _c
4	4	1	4*	2	5	2	4	26	21-	6	1-	4	19	16-	7	1	5	4*	2-	8	-	2	8	0
4	4	2	35	33	5	2	4	26	21-	6	1-	4	19	16-	7	1	5	4*	2-	8	-	2	8	0
4	4	3	13	11-	5	2	5	5*	4-	6	1	5	11	7-	7	1	6	15	12-	8	-	3	8	0
4	4	4	6*	4-	5	2	6	6*	3-	6	1	5	5	5	7	1	7	9	8	8	-	3	8	0
4	4	5	9	7-	5	2	6	6*	3-	6	1	6	5	6	7	2	0	27	22	8	-	3	3	15
4	4	6	11	12-	5	2	6	5*	6-	6	1	7	9	6	7	2	1-	11	9	8	-	3	4	6*
4	4	7	7	7	5	2	6	5*	6-	6	1	9	5*	2-	7	2	1	5*	2-	8	-	3	5	8
4	4	8	8	1-	5	2	7	4*	3-	6	2	0	18	15	7	2	2	7	4-	8	-	3	6	6
4	4	9	5	2	5	2	8	8	17-	6	2	1-	10	6	7	2	2	4*	3-	8	-	3	7	5
4	4	10	19	20	5	2	9	5*	3-	6	2	1-	9	8	7	2	3	19	12	8	-	3	8	4
4	4	11	12-	1-	5	2	10	5	4	6	2	2	4	3-	7	2	3	3*	1	8	-	3	9	3
4	4	12	5	2	5	3	1	10	13	10-	2	3	0	9	7	2	4	27	22	8	-	4	0	4
4	4	13	4*	3-	5	3	1	10	13	10-	2	3	0	9	7	2	5	5*	2	8	-	4	1	5
4	4	14	5	2	5	3	1	7	7	6	2	4	10	9	7	2	5	6*	1	8	-	4	2	5
4	4	15	4*	3-	5	3	2	16	14-	6	2	4	6*	6	7	2	6	16	10-	8	-	4	2	5
4	4	16	14	13	5	3	2	17	18	6	2	5	5	1-	7	2	7	4*	3-	8	-	4	3	6
4	4	17	1*	4-	5	3	3	19	18	6	2	5	6*	2	7	2	8	4*	1-	8	-	4	3	6
4	4	18	4*	4-	5	3	3	12	15-	6	2	6	5	6*	7	2	10	5	5-	8	-	4	5	6*
4	4	19	22	23	5	3	4	28	22-	6	2	6	5	3-	7	3	0	27	9	8	-	4	6	7
4	4	20	23	23	5	3	4	5	5*	6	2	7	12	0	7	3	1	14	13	8	-	4	7	5*
4	4	21	21	23	5	3	5	15	13-	6	2	8	2	11-	7	3	1	16	8-	8	-	4	8	10
4	4	22	8	9-	5	3	5	5	5	6	2	9	2	6	7	3	2	9	6	9	-	4	9	4
4	4	23	5*	6-	5	3	6	5	1-	6	2	10	6	5	7	3	2	9	6-	9	-	4	9	0
4	4	24	5*	4	5	3	6	5*	1-	6	3	0	18	14	7	3	3	7	7	8	-	5	0	9
4	4	25	5*	4	5	3	7	7	5	6	3	1	7*	3	7	3	3	9	7	7	-	5	1	8
4	4	26	5*	4	5	4	0	13	11-	6	3	2	1	0	7	3	5	7	1	8	-	5	2	4*
4	4	27	10	9-	5	4	0	13	11-	6	3	2	1	0	7	3	6	6	6	8	-	5	3	7
4	4	28	5	3	5	4	1	5	1	6	3	3	14	13	7	3	7	10	8	8	-	5	4	7
4	4	29	7	9-	5	4	1	10	3	6	3	4	9	3	7	3	8	11	7	8	-	5	5	8
4	4	30	7	9-	5	4	2	16	14-	6	3	4	16	14-	7	3	9	8	7	8	-	5	6	9
4	4	31	34	34	5	4	2	34	34	6	3	4	7	11-	7	4	0	6*	1	8	-	5	7	5
4	4	32	10	7	5	4	3	10	7	6	3	5	18	16-	7	4	1-	7	8-	8	-	5	8	4*
4	4	33	3	4-	5	4	3	5*	2-	6	3	6	7	4-	7	4	2-	25	20-	8	-	5	9	2
4	4	34	4	7	5	4	4	7	4	6	3	6	7	4*	7	4	2-	8	1	8	-	5	10	3
4	4	35	1*	0	5	4	4	1*	0	6	3	7	4*	3	7	4	3-	8	6	8	-	5	11	4
4	4	36	13	14	5	4	5	14	13	6	3	8	4	4	7	4	3-	6	6	8	-	5	12	5
4	4	37	3*	5	5	4	5	4	4	6	4	0	5	2-	7	4	5	7	6-	8	-	5	13	6
4	4	38	6	6-	5	4	6	6	3	6	4	1	11	6	7	4	6	7	2-	8	-	5	14	7
4	4	39	13	10-	5	4	7	11	11-	6	4	1	4	3	7	4	7	2*	0	8	-	5	15	8
4	4	40	8	8	5	4	7	3	3	6	4	2	18	16-	7	4	8	8	7	8	-	5	16	9
4	4	41	26	29-	5	4	8	4*	1-	6	4	3	6*	6	7	4	9	3*	2	8	-	5	17	10
4	4	42	5	2	5	5	0	5	1	6	4	3	7	3	7	5	0	0	0	9	-	5	18	11
4	4	43	7	4	5	5	1	12	15-	6	4	5	6*	7	7	5	1	4*	3	9	-	5	19	12
4	4	44	6	7	5	5	2	26	25	6	4	6	6	8	7	5	2-	6	4	9	-	5	20	13
4	4	45	8	7	5	5	2	6*	1	6	4	7	6	4	7	5	3-	6	4	9	-	5	21	14
4	4	46	10	20-	5	5	3	20	19	6	4	8	7	3	7	5	4-	8	8	9	-	5	22	15
4	4	47	18	20-	5	5	4	10	8	6	4	10	2	5	7	5	6	7	5	9	-	5	23	16
4	4	48	4*	1	5	5	4	13	13	6	5	0	7	6-	7	5	7	3	9	1	-	5	24	17
4	4	49	8	7-	5	5	5	19	19-	6	5	1	4*	3-	7	5	8	6	5	9	-	5	25	18
4	4	50	4*	4	5	5	5	9	2	6	5	2	3*	3	10	6	0	0	9	1	-	5	26	19
4	4	51	3*	6-	5	5	6	4*	4-	6	5	3	2	10	12	7	6	1-	9	1	-	5	27	20
4	4	52	6*	6-	5	5	7	0*	4-	6	5	3	12	11	7	6	1-	6*	2	9	-	5	28	21
4	4	53	6*	6-	5	5	8	6	6-	6	5	3	14	0	7	6	2-	4*	3-	9	-	5	29	22
4	4	54	3	6*	5	5	9	2	4	6	5	4	5*	5	7	6	3-	5*	3	9	-	5	30	23
4	4	55	4	0	5	5	6	0	24	23	6	5	4	5*	2	7	6	3-	10	9	-	5	31	24
4	4	56	6	11	5	5	6	1	15	9	6	5	5	0	9	7	6	3-	6	1	-	5	32	25
4	4	57	4	4	5	5	6	1	4*	2-	6	5	6	7	6	7	6	4-	10	9	-	5	33	26
4	4	58	8	3-	5	5	6	2	5*	1	6	5	7	7	6	7	6	4	7	7	-	5	34	27
4	4	59	8	8	5	5	6	3	5	2	6	5	8	5	1-	7	6	7	4*	1-	-	5	35	28
4	4	60	13	17	5	5	6	3	5	5	6	6	0	13	14	7	7	0	6*	4	-	5	36	29
4	4	61	9	9-	5	5	6	4	9	6	6	6	1	14	7	7	1-	5*	1	9	-	5	37	30
4	4	62	7	9	5	5	6	5	5*	4	6	6	2	4*	2	7	7	2	5	6	-	5	38	31
4	4	63	7	9	5	5	6	6	8	10	6	6	2	6*	5	7	7	3	3-	9	-	5	39	32
4	4	64	4	6-	5	5	6	6	8	10	6	6	2	6*	5	7	7	3	3-	9	-	5	40	33
4	4	65	10	1-	5	5	6	7	5*	2-	6	6	3	6*	3	7	7	5	4-	9	-	5	41	34
4	4	66	10	1-	5	5	7	0*	2-	6	6	4	3	6*	3	7	8	0	5	4	-	5	42	35
4	4	67	3	6*	5	5	8	6	6	2	6	6	4	3	3	7	8	0	5	4	-	5	43	36
4	4	68	3	6*	5	5	9	4*	3	3	6	6	4	5*	2	7	8	0	5	4	-	5	44	37
4	4	69	5	5	5	5	10	2*	3	3	6	6	4	7*	3	7	8	1-	6	5	-	5	45	38
4	4	70	2	0	5	5	10	8	9	6	6	6	6	2	2	7	8	2-	9	8	-	5	46	39
4	4	71	4*	3	5	5	11	9	6-	6	6	7	5*	3	7	8	3	5	7	9	-	5	47	40
4	4	72	7	1-	5	5	12	10	11	6	6	7	9	4*	2	7	8	4	3*	1	-	5	48	41
4	4	73	4	3	5	5	13	11	3	6	7	0	5*	1-	7	8	4	3*	4	9	-	5	49	42
4	4	74	7	4	5	5	14	15	15	6	7	1	8	5-	7	9	4	5	5	9	-	5	50	43
4	4	75	4	5	5	5	15	15	15	6	7	2	8	2	7	9	5	5*	1-	9	-	5	51	44
4	4	76	1	9	5	5	16	10	11	6	7	3	5	7	9	5	5	7	9	4	-	5	52	45
5	0	0	5	1-	5	7																		



MU-17604

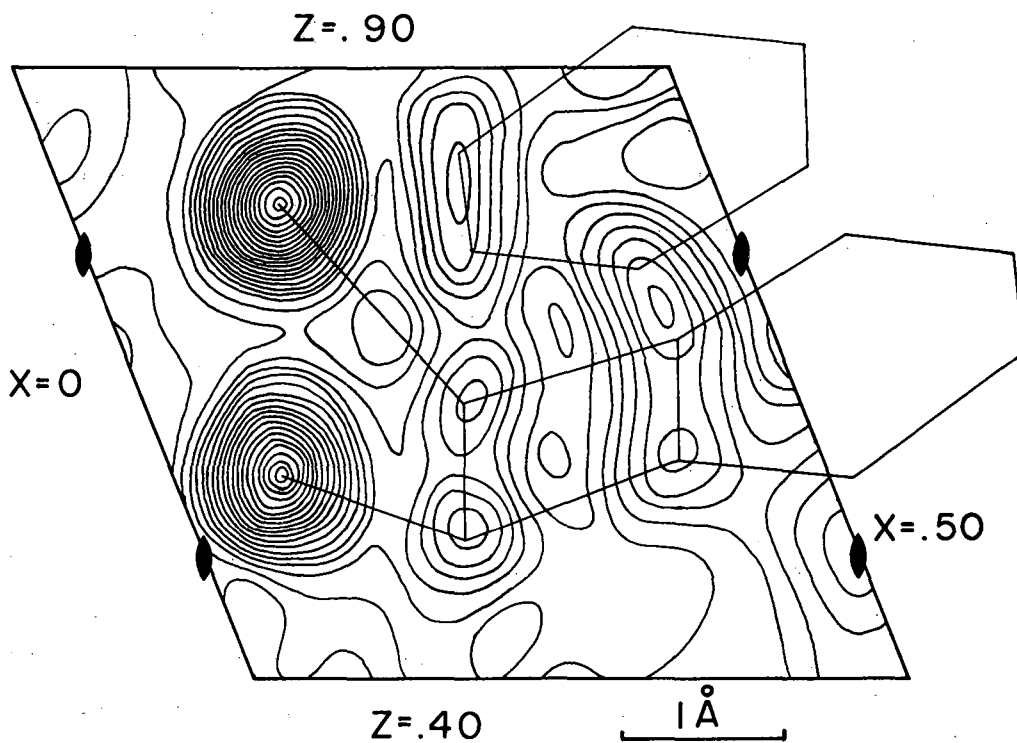
Fig. 9. Interatomic distances (Å) and angles in $C_8H_6Cl_2$ at 25°C.

Table XV

Interatomic distances (A) in $C_8H_6Cl_2$ at $25^\circ C$			
(a)	Distance calculated from the final coordinates		
(b)	Standard deviation of a single determination of the bond distance		
(c)	Standard deviation of the average of several determinations		
	(a)	(b)	(c)
$Cl_1 - Cl_2$	3.175	.013	
$C_1 - Cl_1$	1.807		
$C_2 - Cl_2$	1.797		
Average	1.802	.024	.019
$C_1 - C_2$	1.626	.029	
$C_1 - C_4$	1.532		
$C_2 - C_3$	1.504		
Average	1.518	.029	.021
$C_3 - C_4$	1.398		
$C_4 - C_5$	1.370		
$C_5 - C_6$	1.404		
$C_6 - C_7$	1.242		
$C_7 - C_8$	1.464		
$C_8 - C_3$	1.389		
Average	1.378	.029	.012

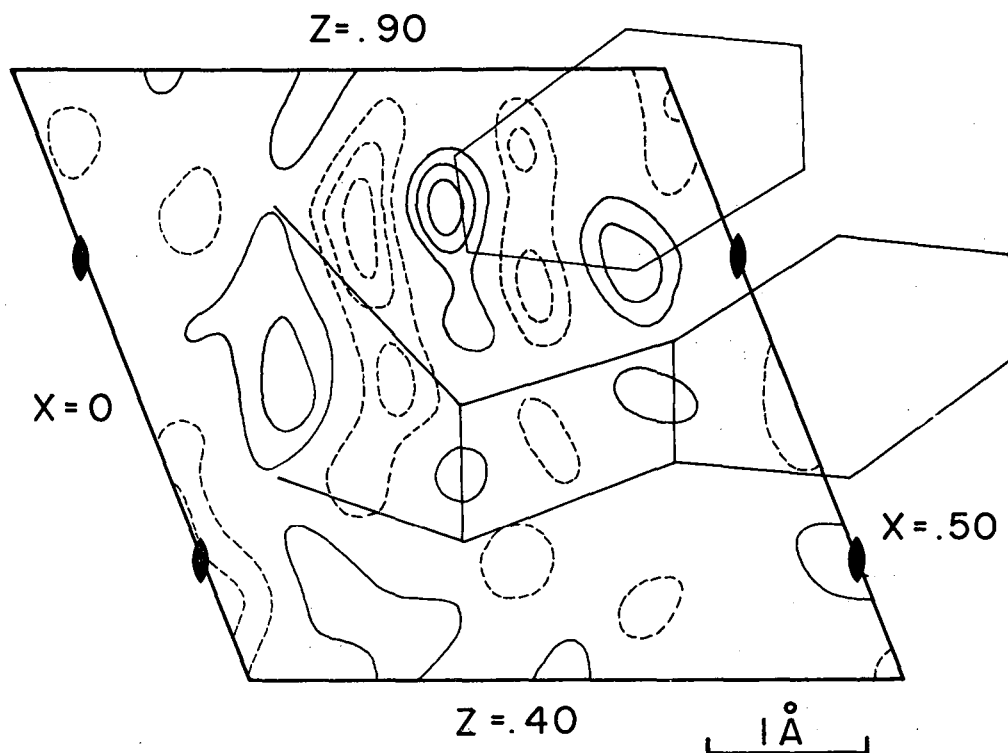
The $C_1 - C_2$ distance of 1.626A is much longer than any carbon-carbon single bond reported. The other aliphatic bond lengths are in satisfactory agreement with the value of 1.52A reported for toluene. The benzene ring has the very short bond of 1.242A, which is unexpected. This bond is the one farthest from the weight center of the molecules. The packing of the molecules favors in-plane torsional vibrations, which have the largest amplitude on this $C_6 - C_7$ bond. The use of isotropic temperature factor fails to account for this motion and resulting overlap of electron density and appearance of a shorter bond. Thus on the average the centers of electron density appear to be at a shorter separation than the expected instantaneous value.

Figure 10 is a plot of the F_o Fourier projection [010], showing anisotropic vibration of the chlorine atoms and resolution of some individual carbon atoms. Figure 11 is a difference map based on the structure parameters used in the 14th cycle imposing expected bond-distance values on the structure. The large peak on the difference map between atoms C_6 and C_7 is the most striking feature. The anisotropic motion of the chlorine atoms is also evident. The present computing programs did not make anisotropic temperature-factor refinement practical. The only alternative, to improve the reliability of the determination, was to gather a new set of data at a lower temperature.



MU-17723

Fig. 10. [010] Projection of F_o synthesis of $C_8H_6Cl_2$ at $25^\circ C$. Contours drawn each electron/ Å^2 , zero contour omitted.



MU-17724

Fig. 11. [010] Projection of $F_o - F_c$ synthesis of $C_8H_6Cl_2$ at $25^\circ C$. Contours drawn each 0.5 electron/ Å^2 ; zero contour omitted and negative contours dashed.

THE CRYSTAL STRUCTURE OF $C_8H_6Cl_2$ AT $-195^\circ C$

Experimental Procedure

Some crystals of $C_8H_6Cl_2$ were sealed in a thin-walled glass capillary of diameter 0.2 mm. The sample was melted and recrystallized very slowly in a hot air stream and several cylindrical single crystals longer than the diameter of the X-ray beam were prepared in the capillary. One of these was aligned about the a axis.

The X-ray exposures at liquid nitrogen temperature were taken, using the equipment described by Olovsson and Templeton (1959). Gaseous dry nitrogen was obtained from a 100-liter Dewar flask of liquid N_2 by a constant input of electrical heating. The gas was recooled to liquid nitrogen temperature by passage through a copper coil in another Dewar of liquid nitrogen, and finally the cold gas was transferred through a Dewar tube onto the capillary. The temperature was measured with a copper-constantan thermocouple and did not vary more than $4^\circ C$ from the lower limit of $-195^\circ C$.

No phase transition was observed on cooling, and multiple-film Weissenberg photographs were taken through the 6kl layer with CuK α X-rays. Ilford Industrial G film was used.

The intensities were measured by visual comparison with an intensity standard. The data were corrected in the usual way for Lorentz and polarization effects. No absorption correction was made. No relative scale factors between layers were determined experimentally, therefore these were determined in the least-squares refinements. In all, 972 independent reflections were observed and measured, and there were 209 reflections too weak to be observed in the photographs taken. The 18% unobserved of the total reflections is to be compared to the 26% for the room-temperature data.

Unit-Cell Parameters

The a rotation axis and the b and c* axes were measured from a quartz-calibrated combination rotation and 0kl Weissenberg photograph. The angle β was determined from the upper-layer Weissenberg photographs by the method of angular lag (Buerger 1942). The dimensions are

$$\begin{array}{ll} \underline{a} = 8.479 \pm 0.014\text{A}, & \underline{b} = 10.954 \pm 0.018\text{A}, \\ \underline{c} = 8.561 \pm 0.016\text{A}, & \beta = 110^{\circ} 56' \pm 4', \end{array}$$

The cell volume is 742.4A^3 and the calculated density is 1.554, assuming four molecules per unit cell. By comparison with the cell dimensions at room temperature the average coefficient of volume expansion is calculated to be $2.37 \times 10^{-4}/^{\circ}\text{C}$ and the linear expansion coefficients for the a, b, and c axes respectively are $0.628 \times 10^{-4}/^{\circ}\text{C}$, $0.442 \times 10^{-4}/^{\circ}\text{C}$, and $1.158 \times 10^{-4}/^{\circ}\text{C}$. It is significant that the largest of these axis expansions is nearly perpendicular to the plane of the benzene rings.

Least-Squares Refinement

The best parameters for atomic positions from the higher-temperature structure and suitable temperature and scale factors were refined by least squares, using the 0kl data. The reliability factors R_1 for the six cycles were 0.295, 0.236, 0.183, 0.120, 0.094, and 0.085.

The three-dimensional least-squares refinements were carried out by using the LS-II program altered in one respect. If a variable shifted in opposite directions on two successive cycles, one-half the usual partial-shift factor p was used. The reliability factors for all the three-dimensional cycles are listed in Table XVI.

Cycles 1-6

The input parameters for the first cycle were the temperature factors from the 0kl data refinements and the best atomic parameters calculated from the high-temperature data. The input to subsequent cycles was the output from the previous cycle in each case. The reliability factors leveled off rapidly after initial adjustment of the

Table XVI

Least-squares refinement of $C_8H_6Cl_2$ at $-195^\circ C$				
Cycle	R_1	R_2	R_3^a	
1	.261	.258		Input the best parameters at $25^\circ C$
2	.180	.186		
3	.130	.147		
4	.123	.141		
5	(.118	.131)		Part of the higher-order reflections not included in this cycle
6	.122	.139		Largest shift $< 0.5 \sigma$
7	.122	.139	.151	Hughes weights introduced
8	.122	.139	.150	Largest coordinate shift $< 0.3 \sigma$
9	.118	.135	.146	Hydrogen atoms in the structure factors
10	.114	.123	.146	
11	.113	.123	.144	
12	.113	.123	.144	Shifts all less than 0.5σ final agreement
13	(.102	.112	.127)	Program altered to set $F_o - F_c = F_{min} - F_c$ rather than $F_o - F_c = -F_c$ for unobserved reflections with $F_c > F_{min}$

^a when Hughes weights were used.

scale factors for the different layers. Unit weighting factors for the individual reflections were used. The atomic-parameter shifts calculated on the sixth cycle were all less than half their standard deviations.

Cycles 7 and 8

The Hughes (1941) system of weights was introduced. This resulted in several large coordinate shifts on Cycle 7. The shifts on Cycle 8 were all less than 0.3 the standard deviations.

Cycle 9

The hydrogen atoms were introduced into the structure-factor calculations on this and subsequent cycles. The positions of the four benzene hydrogen atoms were derived from geometrical considerations. They were placed in the plane of the ring at 1.08Å from the neighboring carbon atoms. A complete three-dimensional $F_o - F_c$ Fourier summation was made by using the carbon and chlorine atoms in the structure-factor calculations. Peaks of about 0.5 electron/Å³ were the prominent features at the expected positions of the hydrogens. The positions of the hydrogen atoms in the unsaturated ring were determined by use of the Fourier map alone. Table XVII shows the hydrogen parameters used.

Table XVII

Hydrogen parameters for $C_8H_6Cl_2$ at $-195^\circ C$			
	<u>x</u>	<u>y</u>	<u>z</u>
H ₁	.16	.39	.37
H ₂	.19	.55	.55
H ₃	.609	.572	.841
H ₄	.841	.435	.821
H ₅	.775	.249	.646
H ₆	.490	.181	.483

Refinement of the isotropic temperature factors for the hydrogen atoms on the ninth cycle showed that 4.40\AA^2 was a more suitable average value than the 4.17\AA^2 used previously. These parameters were held constant on the later cycles.

Cycles 10-12

The coordinate shifts became more reduced and on the twelfth cycle the largest shift was less than half the standard deviation and the average coordinate shift was less than 0.09σ . The shifts in temperature factors were also less than the standard deviations. The coordinates calculated on Cycle 11 are accepted as the final result and are listed in Table XVIII with their standard deviations and reliability factors.

Cycle 13

Since for 75 of the unobserved reflections $|F_c|$ was weaker than $|F_{\min}|$, a cycle of least squares was calculated, using the final parameters as input, allowing $|F_o| - |F_c| = |F_{\min}| - |F_c|$ instead of the usual LS-II value of $-|F_c|$. All the shifts remained smaller than the corresponding standard deviations, and the average shift was 0.2σ . The reliability factors calculated for this cycle are not believed to be as true a measure of the accuracy as the usual LS-II procedure results.

Table XIX shows the final list of observed and calculated structure factors for $\text{C}_8\text{H}_6\text{Cl}_2$ at -195°C . The limit of minimum observation is much lower than in the high-temperature data. Extinction or other systematic errors are not evident.

Three-dimensional Fourier summations were calculated, after the 10th cycle of both the F_o and $F_o - F_c$ types, based on structure-factor calculations with all the atoms. The equation of the average plane of the carbon atoms was calculated from the atomic parameters. Figure 12 shows the F_o map exhibiting the well-resolved carbon peaks. Figure 13 shows the difference Fourier summation in the same plane with no peaks exceeding ± 0.5 electron/ \AA^3 . Figure 14 shows the packing of the molecules in the unit cell.

Table XVIII

Final parameters for $C_8H_6Cl_2$ at $-195^\circ C$

	<u>x</u>	<u>y</u>	<u>z</u>	<u>B(A²)</u>	<u>σ_x</u>	<u>σ_y</u>	<u>σ_z</u>	<u>σ_B</u>
Cl ₁	.16773	.01815	.29189	2.466	.00033	.00018	.00026	.018
Cl ₂	.07966	.25573	.06028	2.711	.00033	.00020	.00027	.020
C ₁	.2450	.4778	.6220	2.58	.0013	.0007	.0011	.08
C ₂	.2035	.3600	.5120	2.88	.0014	.0008	.0011	.08
C ₃	.3871	.3400	.5736	2.58	.0013	.0008	.0011	.08
C ₄	.4186	.4456	.6669	2.39	.0013	.0007	.0010	.07
C ₅	.4171	.5158	.2389	2.53	.0013	.0007	.0011	.08
C ₆	.2886	.5921	.2501	3.15	.0014	.0009	.0012	.09
C ₇	.3230	.6962	.3478	3.05	.0014	.0008	.0012	.09
C ₈	.4841	.7357	.4408	3.10	.0014	.0009	.0012	.09

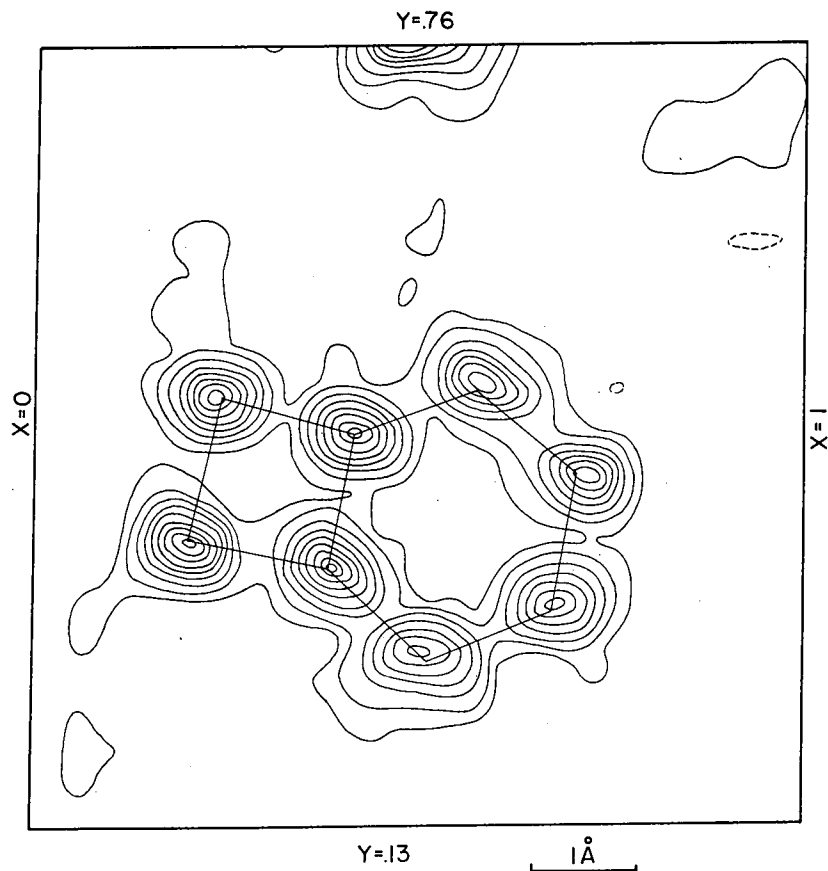
$R_1 = 0.113$, $R_2 = 0.123$, and $R_3 = 0.144$ for the three-dimensional data, including the unobserved reflections. For the observed reflections alone $R_1 = 0.0997$, $R_2 = 0.110$, and $R_3 = 0.121$.

Table XIX. Observed and calculated structure factors for C₈H₆Cl₂ at -195°C (* indicates minimum observable structure factor).

Table with multiple columns (h, k, l, F_o, F_c) listing observed and calculated structure factors for C8H6Cl2 at -195°C. The table is organized into several groups of columns, each representing different hkl reflections. Asterisks indicate minimum observable values.

Table XIX. (concluded)

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	P _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
3 3 5 6	8	8	8	8	4 1 5	7	7	7	7	4 10 0	0	5	5	4	5 6 0	0	34	39	6 3 2	2	7	6	6	
3 3 5 7	6	3	11	11	4 1 6	16	14	3	3	4 10 1	1	3*	2	2	5 6 1	1	17	15	6 3 3	2	6	17	17	
3 3 5 8	6	8	11	11	4 1 7	2*	3	3	3	4 10 2	2	9*	8	0	5 6 2	2	8	8	6 3 4	2	8	20	19	
3 3 5 9	5	3	11	11	4 1 10	12	12	2	2	4 10 3	3	2*	0	0	5 6 3	3	8	8	6 3 5	2	17	21	21	
3 3 5 10	13	11	11	11	4 2 1	11	13	2	2	4 10 4	4	18	18	2	5 6 4	4	18	20	6 3 6	2	21	21	21	
3 3 6 0	20	18	12	12	4 2 2	11	18	18	18	4 10 5	5	2*	0	0	5 6 5	5	20	20	6 3 7	2	6	7	7	
3 3 6 1	19	18	12	12	4 2 2	23	25	25	25	4 10 6	6	5	9	9	5 6 6	6	28	25	6 3 8	2	6	9	9	
3 3 6 2	5	5	5	5	4 2 3	3	3	3	3	4 10 7	7	5	5	5	5 6 7	7	6	6	6 3 9	2	6	6	6	
3 3 6 3	28	36	12	12	4 2 5	4	1	1	1	4 10 8	8	4	4	4	5 6 8	8	12	12	6 4 0	2	6	6	6	
3 3 6 4	32	34	12	12	4 2 7	7	6	6	6	4 10 9	9	4	4	4	5 6 9	9	17	17	6 4 1	2	6	6	6	
3 3 6 5	21	21	1	1	4 2 10	5	5	5	5	4 11 0	0	19	18	18	5 6 10	10	12	12	6 4 2	2	6	6	6	
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3 3 6 9	5	4	4	4	4 3 3	2	1	1	1	4 11 4	4	7*	1	1	5 6 14	14	11	10	6 4 6	2	6	6	6	
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3 3 8 5	12	13	13	13	4 4 9	2	30	30	30	4 11 20	20	9	9	9	5 6 30	30	7	7	6 6 2	2	6	6	6	
3 3 8 6	20	18	18	18	4 4 10	14	36	36	36	4 11 21	21	9	9	9	5 6 31	31	7	7	6 6 3	2	6	6	6	
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3 3 8 9	5	5	5	5	4 4 13	16	14	14	14	4 11 24	24	9	9	9	5 6 34	34	7	7	6 6 6	2	6	6	6	
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3 3 10 2	26	28	28	28	4 4 25	18	20	20	20	4 11 36	36	9	9	9	5 6 46	46	7	7	6 7 8	2	6	6	6	
3 3 10 3	9	9	9	9	4 4 26	5	5	5	5	4 11 37	37	9	9	9	5 6 47	47	7	7	6 7 9	2	6	6	6	
3 3 10 4	17	17	17	17	4 4 27	6	6	6	6	4 11 38	38	9	9	9	5 6 48	48	7	7	6 8 0	2	6	6	6	
3 3 10 5	7	8	8	8	4 4 28	11	35	35	35	4 11 39	39	9	9	9	5 6 49	49	7	7	6 8 1	2	6	6	6	
3 3 10 6	1*	1	1	1	4 4 29	6	6	6	6	4 11 40	40	9	9	9	5 6 50	50	7	7	6 8 2	2	6	6	6	
3 3 10 7	2*	4	4	4	4 4 30	2	13	13	13	4 11 41	41	9	9	9	5 6 51	51	7	7	6 8 3	2	6	6	6	
3 3 10 8	21	21	21	21	4 4 31	6	6	6	6	4 11 42	42	9	9	9	5 6 52	52	7	7	6 8 4	2	6	6	6	
3 3 10 9	7	7	7	7	4 4 32	6	6	6	6	4 11 43	43	9	9	9	5 6 53	53	7	7	6 8 5	2	6	6	6	
3 3 11 0	5	6	6	6	4 4 33	9	8	8	8	4 11 44	44	9	9	9	5 6 54	54	7	7	6 8 6	2	6	6	6	
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3 3 12 0	5	6	6	6	4 4 43	17	16	16	16	4 11 54	54	9	9	9	5 6 64	64	7	7	6 9 6	2	6	6	6	
3 3 12 1	7	10	10	10	4 4 44	14	14	14	14	4 11 55	55	9	9	9	5 6 65	65	7	7	6 9 7	2	6	6	6	
3 3 12 2	3	4	4	4	4 4 45	17	14	14	14	4 11 56	56	9	9	9										



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Fig. 12. Three-dimensional F_0 Fourier synthesis of $C_8H_6Cl_2$ at $-195^\circ C$. This section through the plane of the carbon rings is taken in the plane $-2.559x - 5.199y + 6.571z = 1$. Contours drawn each electron/ \AA^3 ; zero contour omitted and negative contours dashed.

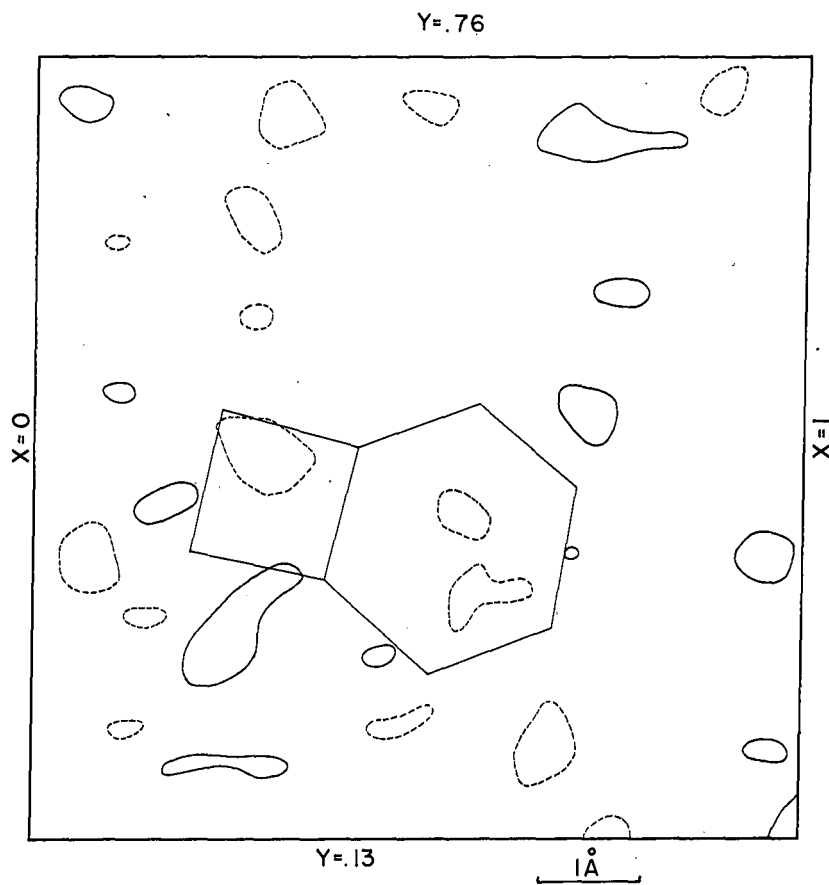
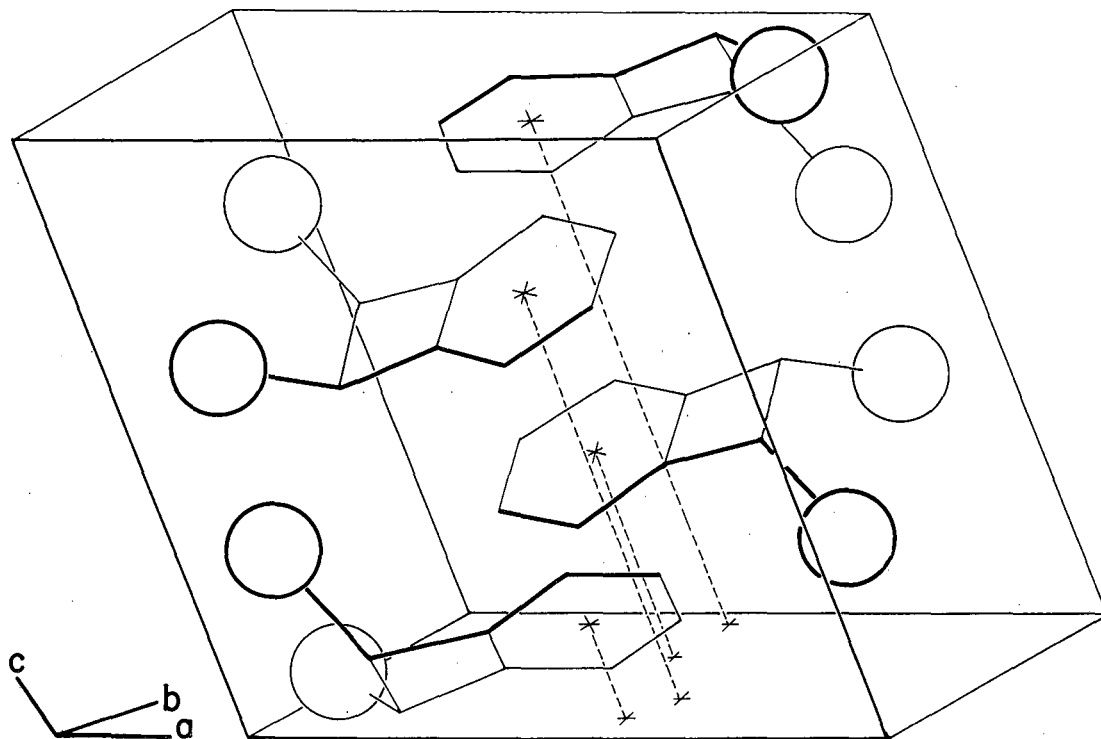


Fig. 13. Three-dimensional F_0-F_c Fourier synthesis of $C_8H_6Cl_2$ at $-195^\circ C$. Taken in the same plane as Fig. 12; 0.25 contour at $+0.25$ electron/ \AA^3 in solid lines and contour at -0.25 electron/ \AA^3 in dashed lines.



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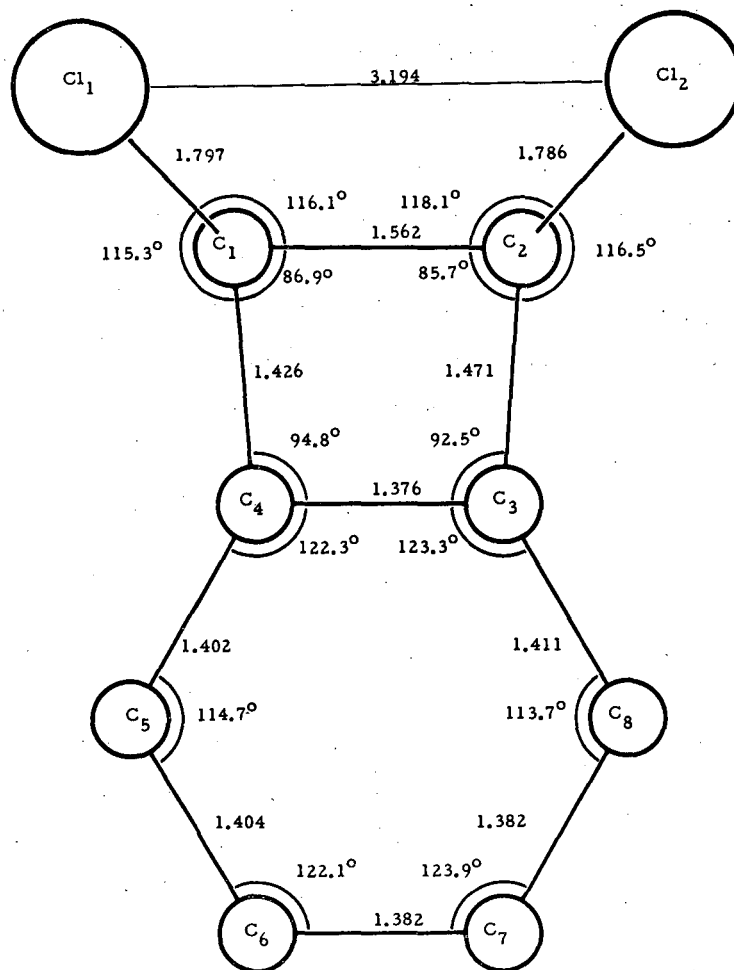
Fig. 14. The unit cell of $C_8H_6Cl_2$.

The ratio of the squares of the average temperature factors for the high- and low-temperature determinations is 3.4, while the ratio of the absolute temperatures is 3.9. This is a good indication that these factors are a real measure of thermal motion and not due to other errors such as absorption or extinction.

Discussion of the Structure

Figure 15 shows the interatomic distances and angles calculated from the final parameters of Cycle 11. Table XX lists the distances for the structures calculated on cycles 6, 8, and 11. The standard deviations were calculated by using the x-z cross terms for the same atom in the least-squares matrix. The first columns show structures calculated by least squares, not taking into account the hydrogen atoms with unit and Hughes-type weighting schemes. As expected, the structure appears to be independent of the weighting methods well within the standard deviations. The X-ray method tends to locate the carbon atoms at the centers of electron density between the carbon and hydrogen atoms when the latter are not included in the structure-factor calculations. The effect is clearly shown in the shortening of the C₁-C₂ distance by more than a standard deviation on inclusion of the hydrogen atoms. The shortening of the average of carbon-carbon distances in the benzene ring by more than a standard deviation can be explained by the same effect.

The chlorine-chlorine distance of $3.194 \pm 0.005\text{A}$ is much less than the 3.60A predicted by the Van der Waals radius given by Pauling (1948) or the 3.63A closest approach of the chlorine atoms in two different molecules in this structure. This distance is somewhat longer than the $2.887 \pm 0.004\text{A}$ for the Cl-Cl closest approach in CCl₄ (Tables of Interatomic Distances, 1958). The average carbon-chlorine distance of $1.792 \pm 0.008\text{A}$ of this is in agreement with the value of $1.78 \pm 0.01\text{A}$ quoted in the above published tables for the C-Cl bonds in 1, 2-dichloroethane. This bond is longer than the average of aliphatic carbon-chlorine bonds of $1.767 \pm 0.002\text{A}$.



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Fig. 15. Interatomic distances (A) and angles in $C_8H_6Cl_2$ at $-195^\circ C$.

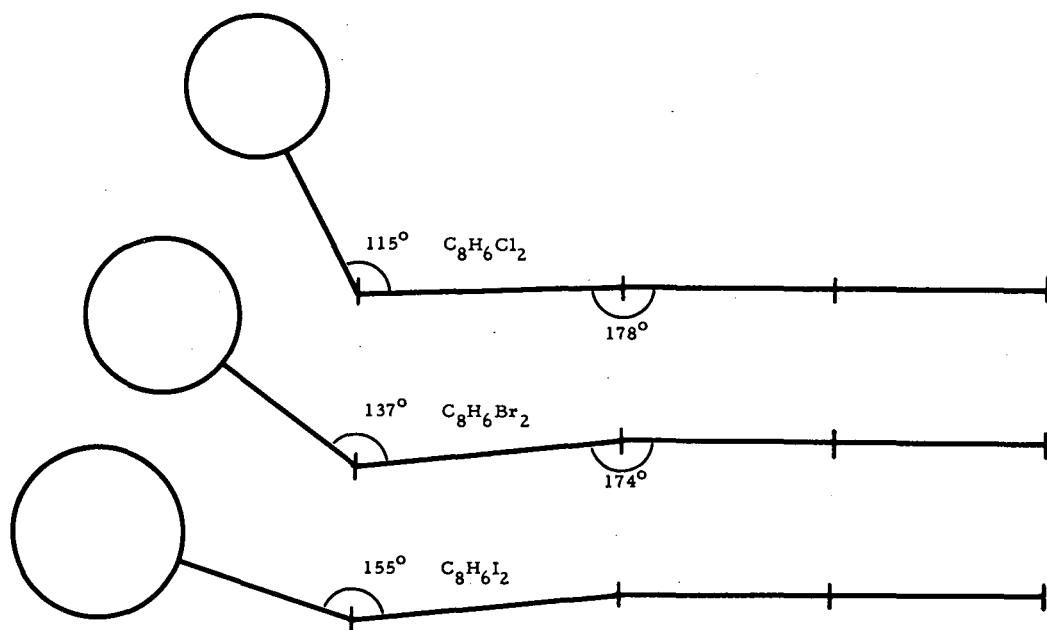
Table XX

Interatomic distances (A) in $C_8H_6Cl_2$ at $-195^\circ C$					
(a)	Cycle 6 output - unit weights, hydrogen atoms excluded				
(b)	Cycle 8 output - Hughes weights, hydrogens excluded				
(c)	Cycle 11 output - final parameters, Hughes weights, and hydrogen atoms included				
(d)	Standard deviation of a single determination of a bond distance				
(e)	Standard deviation of the average of several equivalent distances				
	(a)	(b)	(c)	(d)	(e)
$Cl_1 - Cl_2$	3.196	3.197	3.194	.005	
$C_1 - Cl_1$	1.806	1.807	1.797		
$C_2 - Cl_2$	1.792	1.791	1.786		
Average	1.799	1.799	1.792	.012	.008
$C_1 - C_2$	1.584	1.579	1.562	.014	
$C_1 - C_4$	1.442	1.425	1.426		
$C_2 - C_3$	1.450	1.457	1.471		
Average	1.446	1.442	1.448	.014	.010
$C_3 - C_4$	1.386	1.398	1.376	.014	
$C_4 - C_5$	1.401	1.419	1.402		
$C_5 - C_6$	1.419	1.417	1.404		
$C_6 - C_7$	1.395	1.396	1.382		
$C_7 - C_8$	1.398	1.397	1.382		
$C_8 - C_3$	1.417	1.409	1.411		
Average	1.406	1.408	1.396	.014	.006

Chlorine substitution on polyatomic carbon molecules can decrease or increase the carbon-carbon bond distances, depending on whether or not the tendency towards resonance shortening is overcome by steric hindrance. The 1.49A carbon-carbon distance in 1,2-dichloroethane is an example of shortening, while the 1.59A average carbon-carbon distance in octachlorocyclobutane shows the effect of steric strain. The result of this research shows a C_1-C_2 bond distance of $1.562 \pm 0.014A$, where the chlorine-chlorine distance indicates steric strain. The average bond on the side of the four-membered ring of 1.448 ± 0.010 is shorter than either the bonds of 1.49A in 1,2-dichloroethane or 1.52A in toluene, but in agreement with the $1.46 \pm 0.05A$ single bonds between the two benzene rings of diphenylene. The common bond between the four- and six-membered rings of $1.376 \pm 0.014A$ is somewhat shorter than the usual benzene value because of ring strain. The average carbon-carbon distance in the benzene ring of 1.396 ± 0.006 is in excellent agreement with the published value of $1.397 \pm 0.005A$ for benzene.

A plane determined by atoms C_3 , C_4 , and C_1 is separated from C_2 by 0.06A. This same amount of twist was observed in cis-1,2-dibromobenzocyclobutene. A least-squares plane comes within 0.015A of each atom. The best plane of the benzene ring averages distances of 0.014A from the atoms, with most of the discrepancy consisting of a twist of 0.04A at the C_3-C_4 bond.

In summary, Fig. 16 shows that the effect of an increase in size of the halogens is to twist the unsaturated ring, putting the halogens closer to the planes of the carbon skeleton and increasing the slight angle between the rings. The effects of halogen atoms on the shortening of the carbon-carbon bond distances are well marked in cis-1,2-dichlorobenzocyclobutene. In this case the carbon-carbon bonds in the four-membered ring are not twisted by steric repulsion of the halogens. The structure determination of $C_8H_6Br_2$, on the other hand, shows more deviation from tetrahedral arrangement about the carbon atoms bonded to the bromines and a larger angle between the planes of the four-membered ring and the benzene ring.



MU-17606

Fig. 16. Steric strain in the cis-1,2-dihalobenzocyclobutenes. The angle between the four- and six-membered rings in $C_8H_6I_2$ was not experimentally determined.

Bond-shortening effects as large as those observed for $C_8H_6Cl_2$ were not evident, probably because of steric hinderance of resonance. The structure determination of $C_8H_6Br_2$ was precise enough to show such effects if they were present.

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