

that the steady-state deuterium atom concentration depends on deuterium pressure as shown in the upper part of Fig. 6. Over the range of deuterium pressure covered, $G(\text{HD})$ is essentially proportional to $[\text{D}]$ so that the similarity of the curves of $G(\text{HD})$ and $[\text{D}]$ (Fig. 1 and 6) demonstrate the self-consistency of the treatment in regard to saturation of $G(\text{HD})$.

For the second point it is easily shown from a steady-state treatment for CH_2D radicals that

$$\frac{[\text{CH}_3]}{[\text{CH}_2\text{D}]} = \frac{4}{3} \left[\frac{1}{2} + \frac{k_3[\text{M}]}{k_d} + \frac{2k_3^{1/2}R^{\circ}\text{C}_2\text{H}_5^{1/2}}{k_2[\text{D}]} \left(1 + \frac{k_3[\text{M}]}{k_d} \right) \right] \quad (\text{E18})$$

Using E18 and E8 and our values for the pertinent rate constants, we have calculated the lower curve in Fig. 6 for the ratio $[\text{CH}_2\text{D}]/[\text{CH}_3]$. The agreement of the experimental points, particularly above 100 mm. where the treatment is expected to be more valid and where experimental error in determining the product CH_2D_2 is lessened, is evidence of the self-consistency of our treatment.

As a final check on the validity of our assumed mechanism we now consider the isotopic distribution of ethanes. As mentioned previously, we carried out a mass spectral analysis, using parent peaks, of the deuterated ethanes for the irradiations at 150 mm. of deuterium. Only analyses above ethane- d_0 are considered at all accurate because of sizable contributions from deuterated propane, the net result of which is to make the ethane d_0 value too small. The mass spectrometrically determined values normalized to unity

Species	Calcd.	Obsd.	Species	Calcd.	Obsd.
C_2H_6	3.4	0.7	$\text{C}_2\text{H}_2\text{D}_4$	0.34	0.40
$\text{C}_2\text{H}_5\text{D}$	2.1	2.0	C_2HD_5	.12	0.09
$\text{C}_2\text{H}_4\text{D}_2$	2.0	1.5	C_2D_6	.02	..
$\text{C}_2\text{H}_3\text{D}_3$	1.0	1.0			

[CONTRIBUTION No. 1265 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

The Crystal Structure of Bis-(*m*-chlorobenzoyl)-methane^{1a}

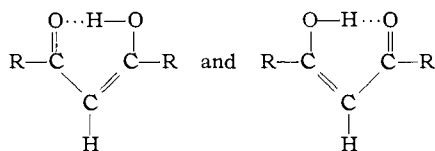
BY GORDON R. ENGBRETSON AND R. E. RUNDLE^{1b}

RECEIVED APRIL 17, 1963

The crystal structure of bis-(*m*-chlorobenzoyl)-methane has been determined by three-dimensional anisotropic least squares refinement of scintillation counter data. The molecule was found to be nearly planar with a maximum deviation from the least squares molecular plane of 0.068 Å. and an average deviation of 0.023 Å. Fourier transform techniques to locate phenyl rings provided the key to the structure determination. The intramolecular bond distances and thermal parameters of the oxygen atoms support a resonant, enol ring with a symmetric, intramolecular hydrogen bond. The structure confirms conclusions from the structure of bis-(*m*-bromobenzoyl)-methane where the symmetry of the molecule was forced by the crystal symmetry.

Introduction

Interest in short, strong, intramolecular hydrogen bonds has prompted structural investigations of β -diketones and other intramolecular, hydrogen-bonded compounds. It has been established that the β -diketones exist almost completely in the enol form, but the question has been whether the structure is a statistical distribution of the two enol forms



or a symmetric resonance hybrid of the two.

at ethane- d_3 are shown in column 3 of Table I. In column 2 of Table I, also normalized to unity at ethane- d_3 , are values calculated using eq. E8-E10, the assumption that all ethane arises by methyl recombination, and the assumption that the recombination rate constant for like radicals is one-half that for unlike. We consider the degree of agreement, for deuteration above d_0 , to be evidence of the validity of our mechanism.

We are somewhat at a loss to explain the discrepancies between this work and that of Firestone, *et al.*⁸ These authors, working at much higher deuterium pressures, found no ethane, so that we are limited in using our eq. E18 to calculate the theoretical $G(\text{CH}_3\text{D})/G(\text{CH}_2\text{D}_2)$. If we use their estimated upper limit to ethane formation and their estimate of the steady-state deuterium atom concentration in eq. E18, we calculate that they should have observed a minimum value of 0.23 for $G(\text{CH}_2\text{D}_2)/G(\text{CH}_3\text{D})$. As this should have been within their capability of detection, the much higher pressure of deuterium cannot be the explanation. The only explanation left to us at the moment is that Firestone, *et al.*,⁸ used no ionic scavenger and that hence a major part of their exchange may be due to ionic intermediates. The ionic paths, which are presumably absent in our work, lead by reasonable mechanistic schemes only to CH_3D as a primary product.

Acknowledgments.—We wish to thank Dr. R. H. Schuler and the staff of the Radiation Laboratories of the Mellon Institute for the use of their Van de Graaff accelerator and their assistance in conducting the irradiations. We are also pleased to acknowledge the assistance of the National Science Foundation in providing funds to aid in the purchase of the Bendix Model 14-101 mass spectrometer used in these studies. The work described herewith was supported by Contract No AF33(616)7716 with the Office of Aerospace Research.

In the one previous structural investigation of β -diketones the hydrogen atom was required to lie on a symmetry element.² There is the possibility, in such a case, that the observed symmetry results from averaging the results of two orientations of somewhat asymmetric molecules. The present investigation was undertaken to see if the apparent symmetry of a β -diketone persists in an asymmetric, crystalline environment.

Preparation and Properties of the Crystals.—Crystals of bis-*m*-(chlorobenzoyl)-methane were prepared

(1) (a) Taken in part from a thesis by Gordon Engbretson submitted November 7, 1962, to Iowa State University, Ames, Iowa, in partial fulfillment of the requirements for the Ph.D. degree. This work was performed under contract with the Atomic Energy Commission. (b) Deceased, October 9, 1963.

(2) D. Williams, R. Rundle, and W. Dumke, *Acta Cryst.*, **15**, 627 (1962).

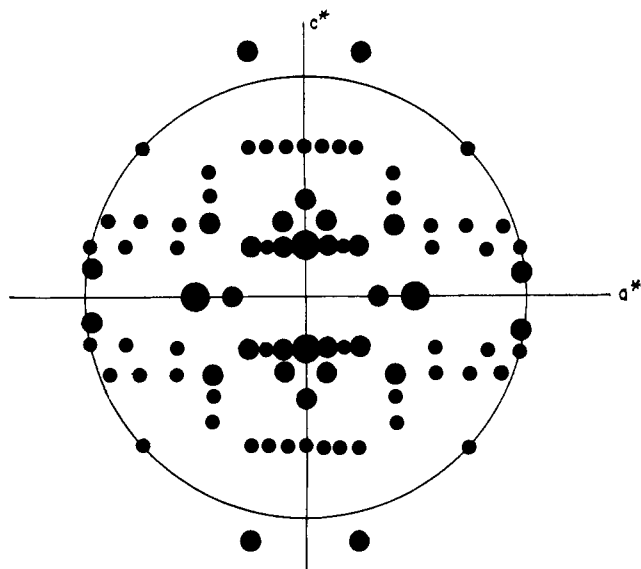


Fig. 1.—Weighted reciprocal lattice of the ($h0l$) zone of bis-(m -chlorobenzoyl)-methane.

by a basic condensation of m -chloroethyl benzoate and m -chloroacetophenone in the presence of sodium amide.³ Clear orthorhombic needles (m.p. 154–155°) were obtained by recrystallization from chloroform. These had a density of 1.50 g./cc. as determined by the flotation method.

X-Ray diagrams confirmed the orthorhombic symmetry. From back-reflection, Weissenberg, diffraction patterns lattice constants were obtained: $a = 30.082 \pm 0.002$, $b = 3.850 \pm 0.005$, $c = 11.123 \pm 0.002$ Å. The observed lattice constants and density require four molecules in a primitive, rhombic cell.

Systematic absences on diffraction patterns are $\{0kl\}$ if $l = 2n + 1$ and $\{h0l\}$ if $h = 2n + 1$, suggesting space groups $Pcam$ or $Pca2_1$. The fourfold positions in the former are special positions, either at centers of symmetry, which would require an impossible linear C–C–C bonding at the center of the molecule, or on mirror planes at $Z = 1/4, 3/4$.

If the molecules were to lie on the mirror planes the short axis, 3.85 Å., would have to accommodate the width of the molecule, which is not possible. If two halves of the molecule were related by a mirror plane the packing would become poor for this shape of unit cell. These considerations seem to require the space group $Pca2_1$, which the final structure confirms.

Intensity Data.—X-Ray intensity data were obtained using nickel-filtered, copper $K\alpha$ radiation, a G.E. single crystal orienter, scintillation counter, and θ - 2θ scan technique. The crystal used had a trapezoidal cross section with maximum dimensions of such size, 96.7 and 115 μ , that absorption corrections were necessary. These were made by carefully measuring the crystal and employing a program, ABCOR-I,^{4a} and the Iowa State Cyclone computer to make these corrections after the method of Busing and Levy.^{4b}

Unobserved reflections were assigned a most probable intensity and error depending upon the minimum observable intensity at the specified lattice point.⁵ The errors of the intensities of the observed reflections were obtained from the statistical counting errors in peak and background, analysis of errors from the reproducibility of standard reflections with time, estimated error

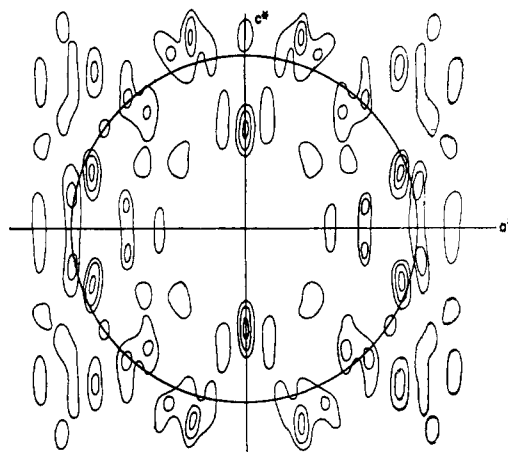


Fig. 2.—Fourier transform for the bis-(m -chlorobenzoyl)-methane molecule with the length of the molecule tilted 13° to the real space x -axis and the molecule tilted 24° out of the (010) plane. Circle is the "benzene circle."

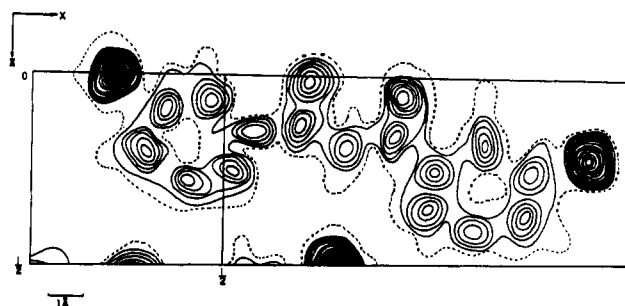


Fig. 3.—Final Fourier projected onto (010). Dashed line is $1e^{-}/\text{Å}^2$ contour. Other contours $e^{-}/\text{Å}^2$.

in streak corrections, etc. The weighting of reflections in least squares refinements was then $W_h = 1/\sigma_h^2$ where W is the weighting factor and σ_h^2 is the error in intensity for reflection (h).

Structural Investigations.—The Patterson projection onto (010) was calculated, but it was not readily interpretable, since the chlorine atom did not serve as a heavy atom in this structure.

It was then decided to calculate a Fourier transform, making use of the phenyl rings in the molecule to find the angular orientation of the molecule in the unit cell. A weighted reciprocal lattice was constructed using the $\{h0l\}$ data (Fig. 1). The circle indicated is the benzene circle, *i.e.*, the locus to which a benzene ring would transform. A study of the weighted reciprocal lattice showed twelve peaks on or near the benzene circle. Since there are four molecules in the unit cell which are parallel in projection in groups of two, one would expect two distinct angular orientations of the benzene rings, and hence twelve different peaks on the benzene circle. The peaks off the benzene circle near the c^* -axis indicated that the rings were rotated out of the plane of the benzene circle about an axis perpendicular to the line from the origin to the peaks. A measure of the amount of shift of the peaks off the benzene circle led to an out-of-plane tilt of 24°. The other peaks on the benzene circle near the a^* -axis led to an in-plane rotation of the benzene rings of 13°. Figure 2 shows the Fourier transform for one molecule using the indicated angles (the origin peak has been omitted for clarity). A re-examination of the two-dimensional Patterson projection using this information led to a satisfactory trial structure.

(3) W. Borduin, M.S. Thesis, Iowa State University Library, 1956.

(4) (a) D. Williams, Iowa State University, unpublished; (b) W. Busing and H. Levy, *Acta Cryst.*, **10**, 180 (1957).

(5) W. Hamilton, *ibid.*, **8**, 185 (1955).

[010] PROJECTION OF BIS (META-CHLOROBENZOYL) METHANE

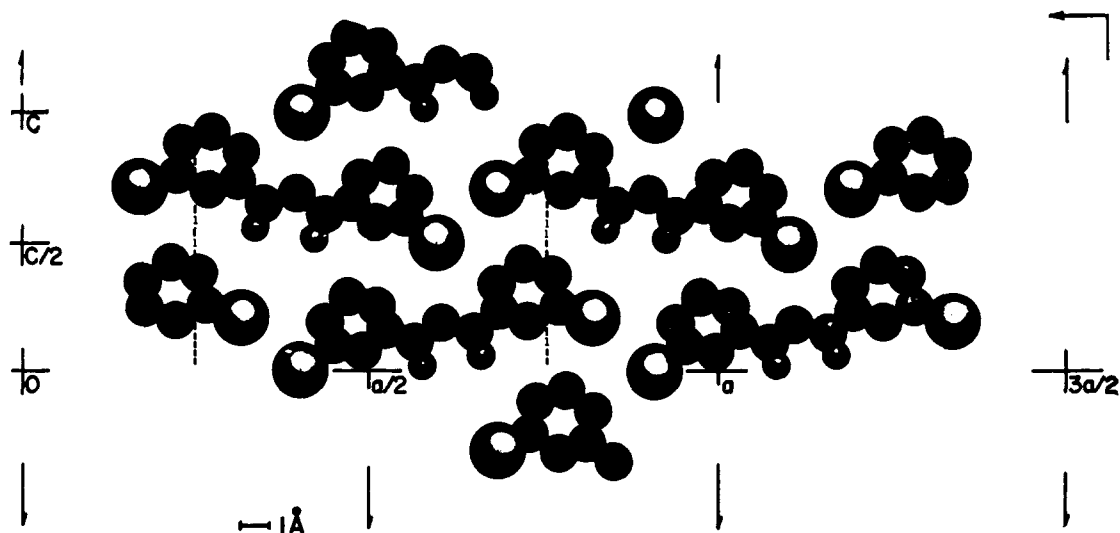


Fig. 4.—Molecular environment of a molecule of bis-(*m*-chlorobenzoyl)-methane projected onto the (010) plane with space group symmetry elements indicated.

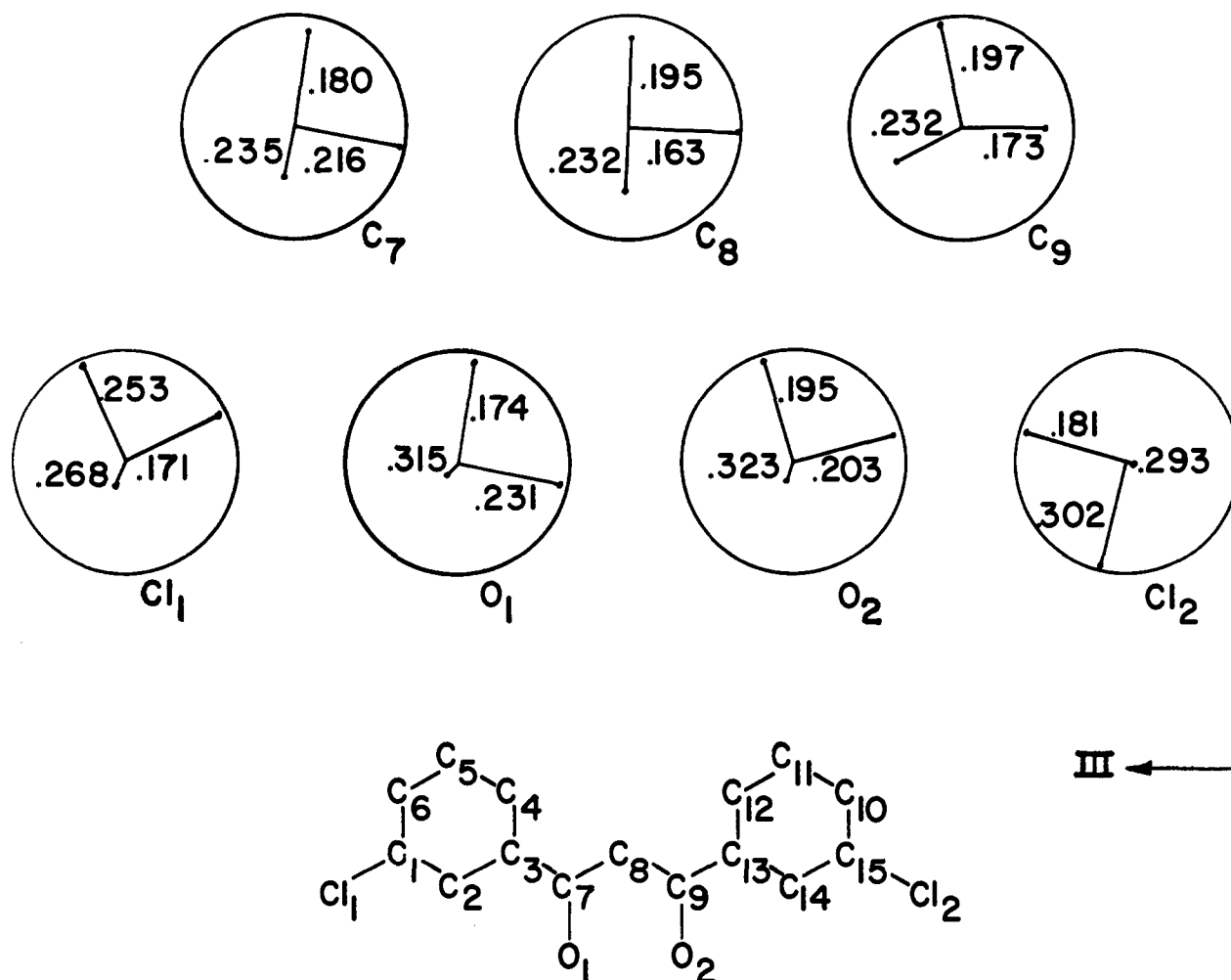


Fig. 5.—Anisotropic thermal stereograms for selected atoms in the bis-(*m*-chlorobenzoyl)-methane molecule. The plane of the paper is the molecular least squares plane and the stereograms are oriented in the same manner as the molecule at the bottom of the figure. The orientation of the reference coordinate system is also shown.

The IBM 704 least squares program of Busing and Levy⁶ (1959) was used to obtain a least squares refinement of the $\{h0l\}$ data, leading to an *R*-value of 5.6%.

(6) W. Busing and H. A. Levy, U.S.A.E.C. Report, ORNL 59-4-37 (1959).

A three-dimensional Patterson map was calculated and a trial structure was found based on this map and the Fourier transform alone.

Refinement proceeded through several cycles of least squares using isotropic temperature factors for each

TABLE I

FINAL POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS $\times 10^6$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl ₁	40885	4084	0	88	9627	879	-25	-95	-139
	7	70	0	2	206	18	18	6	71
Cl ₂	83345	20930	21959	73	11668	1463	45	36	134
	6	89	36	2	265	30	21	7	87
O ₁	58081	2356	1947	114	12100	658	82	-7	-1152
	17	200	53	7	658	57	66	16	171
O ₂	66147	4761	6265	92	12585	721	49	15	-932
	19	213	54	6	734	53	61	15	186
C ₁	44940	18084	9929	82	7955	722	70	-14	117
	25	273	77	8	845	73	68	20	223
C ₂	49365	12686	7181	89	7212	766	63	-42	796
	25	228	77	8	716	76	63	21	205
C ₃	52581	23767	15393	94	6680	544	-21	-14	384
	25	254	75	8	669	56	66	17	183
C ₄	51325	39178	26211	97	8237	683	-61	-20	-344
	25	238	83	9	778	64	66	21	217
C ₅	46833	44041	28823	97	9158	773	-7	-7	-81
	26	274	86	9	843	79	76	23	230
C ₆	43521	32426	20746	75	8376	845	74	29	-38
	23	247	92	7	723	69	60	21	218
C ₇	57333	17847	12125	95	7256	569	9	3	-6
	25	260	75	9	726	59	66	20	186
C ₈	60838	27812	19686	64	8699	585	28	7	184
	21	258	75	6	712	64	62	17	198
C ₉	65235	21088	16382	88	6074	614	150	-12	98
	23	233	71	7	643	59	62	17	181
C ₁₀	76557	48437	37647	116	832	791	-94	-67	211
	28	280	86	11	800	75	82	24	225
C ₁₁	72238	55477	41867	83	9589	-113	-6	-6	535
	25	283	83	8	849	77	73	22	231
C ₁₂	68564	46246	34855	98	8183	702	-21	22	-71
	27	264	77	9	740	67	77	21	208
C ₁₃	61256	30733	23842	73	8016	559	-33	-5	325
	22	225	67	7	692	61	62	18	175
C ₁₄	73303	22839	20002	88	8992	781	-55	-33	416
	23	275	88	7	787	74	70	21	236
C ₁₅	76998	31868	27006	67	8293	1096	66	26	491
	25	273	94	7	776	97	67	22	258
H ₁	50300	-500	-1000	138	8433	1010			
H ₂	55600	47000	32500	138	8433	1010			
H ₃	46000	55100	36800	138	8433	1010			
H ₄	39200	34300	22900	138	8433	1010			
H ₅	60200	40300	28003	138	8433	1010			
H ₁₀	79700	55400	42500	138	8433	1010			
H ₁₁	71800	67500	50400	138	8433	1010			
H ₁₂	65300	50800	39700	138	8433	1010			
H ₁₄	73700	9900	11700	138	8433	1010			

(H₁ is bonded to C₂, etc.)

independent atom to $R = 13.8\%$, then to refinement cycles using anisotropic temperature factors using Busing and Levy's least squares program, ORXLS.⁶ Near the end of the refinement two rejection tests were made. The first gave zero weight in the refinement to unobserved reflections where $F_c < F_o$ and where F_o had been assigned a value by Hamilton's method.⁵ The second test gave zero weight to reflections where $|F_o - F_c|/\sigma(F_o) > 6$. Fourteen reflections of this type were found. In every case F_c was greater than F_o , and a remeasurement of these reflections showed that an error had been made, presumably in hand setting counter and/or crystal angles for the measurement. Remeasured structure factors were reinserted into the final refinement cycles. Toward the end, all the hydrogens but the enolic hydrogen were inserted assuming C-H = 1.07 Å. and using estimated temperature factors for hydrogen atoms. Certain carbon positions changed by more than one standard deviation in the next cycle, so new, consistent, hydrogen positions were reinserted. (Hydrogen parameters were held constant during least squares refinement.) The final R -value was 5.8% for observed data, 10.2% over all, and $[\sum W(F_o - F_c)^2/(m - n)]^{1/2} = 1.86$, indicating a reasonable weighting scheme.

Since for some of the most intense reflections extinction seems to be 5% or less, extinction effects were ignored in the refinement.

Figure 3 shows the final Fourier projection onto (010). For atomic designations see Fig. 5.

Table I lists the final positional and anisotropic thermal parameters with their respective standard errors for bis-(*m*-chlorobenzoyl)-methane.

Table II lists a comparison of the observed and calculated structure factors based on the parameters listed in Table I.

Discussion of the Structure

The molecules were found to be nearly parallel to the (010) plane. The chlorine atoms tend to pack in zig-zag chains in the y -direction. It can be seen that the two nonequivalent chlorine atoms have different atomic environments. One chlorine atom "sees" the oxygen side of the carbonyl groups while the other chlorine atom "sees" the carbon side of the carbonyl groups.

Least squares planes were calculated for the entire molecule and several subgroups within the molecule. The IBM 650 program of Stewart (1960) was used. Least squares planes were calculated for the Cl₁ atom and its attached phenyl group (plane 1), Cl₂ and its attached phenyl group (plane 2), the enol subgroup (plane 3), and the entire molecule (plane 4). The planes were of the form

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

The coefficients are listed in Table III.

The molecule was found to be planar with a maximum deviation of 0.068 Å. from the plane and an average deviation of 0.023 Å. The distance of each atom (excluding the hydrogen atoms) from the molecular least squares plane is listed in Table IV.

The C-C bond distances in the benzene rings were near the accepted experimental value of 1.397 Å. except for two shorter bonds between C₁₃-C₁₄ and C₁₀-C₁₅. The average C-C bond distances for the two phenyl rings were 1.395 and 1.382 Å, the latter ring containing the two short bonds. (We presume these two short bonds are the result of some systematic error.) The bond distances between C₃-C₇ and C₉-C₁₃ (1.492 and 1.482 Å.) are typical of C-C single bonds trigonally coordinated. In the enol ring the distances between C₇-C₈ and C₈-C₉ (1.399 Å.) are indicative of 50% double bond character. This supports the hypothesis that these bond distances are determined by resonance between the two enol forms. The two CO bonds (1.31 Å.) are longer than typical CO double bonds (1.23 Å.), shorter than typical single CO bonds (1.43 Å.), and rather closer to the former, again supporting resonance in the enol ring. Table V compares the intramolecular bond distances and errors within a molecule of bis-(*m*-chlorobenzoyl)-methane to the equivalent distances in bis-(*m*-bromobenzoyl)-methane.² Similarly, Table VI compares bond angles between the two derivatives.

No significant deviations from symmetry can be detected in the *m*-chloro derivative, nor do there appear to be any significant differences between *m*-bromo and *m*-chloro derivatives except in $\angle C_3C_7C_8$ which is considerably larger in the bromo derivative. The reason for this is not clear. (The 99% confidence level is three times the standard deviations quoted.)

The largest thermal amplitudes of the oxygen atoms are normal to the C-O bond and hence did not affect the accuracy of this bond distance seriously. The average chlorine-carbon distance of 1.729 Å. agrees quite well with that observed for *o*-dichlorobenzene (1.735 Å.)⁷ but is longer than the average accepted distance.⁸

(7) L. O. Brockway and K. J. Palmer, *J. Am. Chem. Soc.*, **59**, 2181 (1937).

(8) "Tables of Interatomic Distances," L. E. Sutton, Ed., The Chemical Society, London, 1958.

TABLE III
LEAST SQUARES PLANE COEFFICIENTS FOR
BIS-(*m*-CHLOROBENZOYL)-METHANE

Plane	A	B	C
1	-0.05307	-2.09875	1.02959
2	-.05034	-0.99214	0.50857
3	-.05874	-0.92279	.49278
4	-.06002	-1.41053	.71061

TABLE IV

DEVIATIONS OF ATOMS IN Å. FROM THE MOLECULAR LEAST SQUARES PLANE (PLANE 4 OF TABLE III)

Atom	$D,^a$ Å.	Atom	$D,^a$ Å.	Atom	$D,^a$ Å.	Atom	$D,^a$ Å.	Atom	$D,^a$ Å.
Cl ₁	0.0237	C ₁	-0.0165	C ₅	0.0234	C ₉	-0.0256	C ₁₃	-0.0299
Cl ₂	.0686	C ₂	.0012	C ₆	.0476	C ₁₀	-.0206	C ₁₄	.0100
O ₁	-.0197	C ₃	-.0199	C ₇	-.0387	C ₁₁	-.0038	C ₁₅	.0010
O ₂	.0313	C ₄	.0077	C ₈	-.0461	C ₁₂	.0061		

^a Distance from least squares plane.

TABLE V
A COMPARISON OF INTRAMOLECULAR BOND DISTANCES IN
BIS-(*m*-CHLOROBENZOYL)-METHANE AND
BIS-(*m*-BROMOBENZOYL)-METHANE^a

<i>m</i> -Chloro derivative		<i>m</i> -Bromo derivative	
Bond	Distance, Å.	Bond	Distance, Å.
Cl ₁ -C ₁	1.731 ± 0.008	Br-C ₁	1.901 ± 0.007
Cl ₂ -C ₁₅	1.727 ± .008	O ₁ -O ₁ '	2.464 ± .015
O ₂ -O ₁	2.475 ± .008	C ₁ -C ₆	1.375 ± .009
C ₇ -C ₈	1.391 ± .012	C ₆ -C ₅	1.397 ± .010
C ₁₀ -C ₁₅	1.351 ± .014	C ₅ -C ₄	1.389 ± .010
C ₉ -C ₅	1.414 ± .011	C ₄ -C ₃	1.410 ± .008
C ₁₀ -C ₁₁	1.407 ± .011	C ₃ -C ₂	1.400 ± .009
C ₅ -C ₄	1.395 ± .010	C ₁ -C ₂	1.392 ± .009
C ₁₁ -C ₁₂	1.398 ± .010	C ₃ -C ₇	1.457 ± .009
C ₄ -C ₃	1.394 ± .011	C ₇ -C ₈	1.393 ± .008
C ₁₂ -C ₁₃	1.373 ± .011	C ₇ -O	1.306 ± .008
C ₃ -C ₂	1.381 ± .010		
C ₁₃ -C ₁₄	1.362 ± .010		
C ₁ -C ₂	1.397 ± .011		
C ₁₄ -C ₁₅	1.401 ± .010		
C ₃ -C ₇	1.492 ± .010		
C ₉ -C ₁₃	1.482 ± .010		
C ₇ -C ₈	1.402 ± .011		
C ₈ -C ₉	1.397 ± .009		
C ₇ -O ₁	1.299 ± .010		
C ₉ -O ₂	1.318 ± .009		

^a The bromo derivative has twofold symmetry in the molecule, hence only half of the atoms in the molecule are listed. Standard deviations in bond lengths are given.

The observed O-H-O distance of 2.475 Å. confirms the existence of a strong intramolecular hydrogen bond. The angles C₇-O₁-O₂ and C₉-O₂-O₁ are both less than 90° and show that the two oxygen atoms are being forced apart somewhat by steric repulsions. If the hydrogen atom is placed on the line of centers of the two oxygen atoms, an improbably small C-O-H angle (<90°), at least 15° less than normal, results. It seems likely that the hydrogen atom lies off the line of centers of the two oxygen atoms. Presumably the large out-of-plane thermal parameters of the oxygens are due to opposite displacements of the oxygens from the molecular plane as in the bromo derivative.²

The larger than normal angles C₃-C₇-C₈ and C₈-C₉-C₁₃ indicate that these angles open to relieve the strain caused by the close approach of H₈ to both H₄ and H₁₂ (H₄H₈ contact distance of 2.02 Å., H₁₂H₈ contact distance of 1.95 Å.). This was also observed in the bromo derivative (H₄H₈' distance of 2.01 Å.). (Hydrogen atoms are given the same number as the carbon to which they are bonded in Fig. 5.)

Table VII lists the lengths of the principal axes of the anisotropic thermal vibrations and the direction

cosines of these axes for all the atoms. The reference coordinate system for these direction cosines is defined by the following: Axis I: the vector from C₇ to O₁. Axis II: the vector cross-product of Axis I into the vector from C₇ to C₈. Axis III: the vector cross-product of axis I into axis II. The anisotropic thermal stereograms for selected atoms are represented in Fig. 5. The length of each thermal axis is listed in Å. The plane of the paper is the molecular least squares plane and

TABLE VI
A COMPARISON OF BOND ANGLES WITHIN MOLECULES OF
BIS-(*m*-CHLOROBENZOYL)-METHANE AND
BIS-(*m*-BROMOBENZOYL)-METHANE^a

Bis-(<i>m</i> -chlorobenzoyl)-methane		Bis-(<i>m</i> -bromobenzoyl)-methane	
Atoms	Bond angle, deg.	Atoms	Bond angle, deg.
Cl ₁ C ₁ C ₆	117.3 ± 0.6	BrC ₁ C ₆	119.5 ± 0.6
Cl ₂ C ₁₅ C ₁₀	119.3 ± .7	BrC ₁ C ₂	117.8 ± .5
Cl ₁ C ₁ C ₂	119.4 ± .7	C ₆ C ₁ C ₂	122.7 ± .7
Cl ₂ C ₁₅ C ₁₄	118.9 ± .8	C ₁ C ₆ C ₈	117.8 ± .7
C ₈ C ₁ C ₂	123.1 ± .8	C ₆ C ₅ C ₄	121.6 ± .6
C ₁₀ C ₁₅ C ₁₄	121.7 ± .8	C ₅ C ₄ C ₃	119.6 ± .7
C ₁ C ₆ C ₅	117.3 ± .7	C ₄ C ₃ C ₂	119.2 ± .6
C ₁₅ C ₁₀ C ₁₁	118.3 ± .8	C ₃ C ₂ C ₁	119.1 ± .6
C ₈ C ₅ C ₄	120.5 ± .8	C ₁ C ₆ C ₇	121.6 ± .6
C ₁₀ C ₁ C ₁₂	119.6 ± .8	C ₂ C ₈ C ₇	119.3 ± .6
C ₅ C ₄ C ₃	120.0 ± .7	C ₃ C ₇ C ₈	125.0 ± .6
C ₁₁ C ₁₂ C ₁₃	120.7 ± .5	C ₃ C ₇ O	115.6 ± .6
C ₄ C ₃ C ₂	120.4 ± .7	OC ₇ C ₈	119.4 ± .7
C ₁₂ C ₁₃ C ₁₄	119.4 ± .6	C ₇ C ₈ C ₇ '	122.2 ± .8
C ₃ C ₂ C ₁	118.4 ± .8	C ₇ O ₁ O ₂	89.0 ± .7
C ₁₃ C ₁ C ₁₅	120.1 ± .8	C ₉ O ₂ O ₁	88.8 ± .6
C ₄ C ₃ C ₇	122.3 ± .7		
C ₁₂ C ₁₃ C ₉	120.7 ± .6		
C ₃ C ₂ C ₇	117.2 ± .7		
C ₁₄ C ₁₃ C ₉	119.8 ± .7		
C ₃ C ₇ C ₈	122.2 ± .7		
C ₁₃ C ₂ C ₈	123.6 ± .7		
C ₃ C ₇ O ₁	116.6 ± .7		
C ₈ C ₉ O ₂	115.7 ± .6		
O ₁ C ₇ C ₈	121.2 ± .6		
O ₂ C ₉ C ₈	120.7 ± .7		
C ₇ C ₈ C ₉	120.2 ± .7		
C ₇ O ₁ O ₂	89.0 ± .7		
C ₉ O ₂ O ₁	88.8 ± .6		

^a The central atom is the vertex. Standard deviations are given for bond angles.

the stereograms are in the same orientation as the molecule shown at the bottom of the figure. It is evident that the chlorine atoms have their shortest thermal amplitude nearly parallel to the Cl-C bond and their largest amplitudes normal to this bond, as expected. The carbon atoms in the enol ring have their greatest thermal amplitude nearly perpendicular to the molecular least square plane. This is also true for the carbon atoms in the benzene rings. Hence it can be concluded that the molecule oscillates as a whole perpendicular to the molecular least squares plane. The two oxygen atoms have their lowest thermal amplitude nearly parallel to the C-O bond. This gives some confidence to the hypothesis that the intramolecular hydrogen bond is the symmetrical type, for if it were not the thermal amplitude

TABLE VII: TABLE OF DIRECTION COSINES OF PRINCIPAL AXES FOR ANISOTROPIC THERMAL ELLIPSOIDS OF EACH ATOM

Atom	Principal axis				Length, Å.	Atom	Principal axis				Length, Å.	
	axis	cos α	cos β	cos γ			axis	cos α	cos β	cos γ		
Cl ₁	1	-0.369	0.153	-0.940	0.171	C ₈	3	.419	.889	0.183	0.247	
	2	.902	.192	.386	.253		C ₇	1	-.885	.452	-.111	.180
	3	.236	.969	.069	.268			2	.139	.030	-.990	.216
Cl ₂	1	-.230	.051	.959	.181	C ₈	3	.444	.891	.090	.235	
	2	.013	.999	-.049	.293		1	.024	.003	-1.000	.163	
	3	.960	.001	.280	.302		2	-.812	.583	-.017	.195	
O ₁	1	.986	.082	-.143	.174	C ₉	3	.582	.813	.016	.259	
	2	.148	.059	-.987	.231		1	-.006	.655	-.756	.173	
	3	-.072	.995	-.071	.315		2	-.956	.219	.197	.197	
O ₂	1	-.940	.124	.317	.195	C ₁₀	3	.294	.723	.625	.232	
	2	-.313	.054	-.948	.203		1	-.553	.320	-.769	.203	
	3	.135	.991	.012	.323		2	-.155	.868	.472	.236	
C ₁	1	-.013	.274	-.962	.183	C ₁₁	3	.818	.381	-.431	.259	
	2	-.843	.515	.158	.215		1	-.145	.267	.953	.181	
	3	.538	.812	.224	.268		2	-.589	.750	-.300	.212	
C ₂	1	-.242	.744	-.623	.168	C ₁₂	3	.795	.605	-.048	.287	
	2	-.287	.558	.779	.197		1	-.777	.359	.518	.203	
	3	-.927	.367	-.079	.273		2	-.504	.139	-.852	.223	
C ₃	1	-.601	.748	-.280	.175	C ₁₁	3	.378	.923	-.073	.237	
	2	-.085	.275	.956	.207		1	-.560	.524	-.642	.173	
	3	.792	.604	-.089	.237		2	-.479	.427	.767	.189	
C ₄	1	-.739	.054	-.672	.200	C ₁₄	3	.676	.737	.012	.245	
	2	-.647	.220	.730	.210		1	-.142	.124	-.982	.174	
	3	.188	.974	-.128	.247		2	-.604	.775	.185	.207	
C ₅	1	-.104	.059	-.993	.200	C ₁₄	3	.784	.620	-.035	.283	
	2	-.917	.382	.119	.238		1	.111	.175	-.978	.167	
	3	.386	.922	.015	.257		2	-.173	.973	.154	.233	
C ₆	1	-.439	.022	.898	.183	C ₁₄	3	.979	.152	.138	.281	
	2	-.795	.457	-.399	.223							

of each oxygen atom parallel to the C-O bond would be increased by a distribution between longer and shorter C-O bonds of the asymmetric molecule.

The asymmetric environment of the oxygen atoms, as seen from Fig. 4, would lead one to expect asymmetry of the two carbonyl groups. But the symmetry of the two halves of the molecule in both positional and thermal parameters is quite good. Since this symmetry persists even though the two halves of the molecule do not have a symmetry environment, this is good evidence that the molecular symmetry is real, and that the hydrogen bond is symmetric although probably not linear. Of course, this structure does not preclude the possibility that the hydrogen distribution is split into two in a symmetrical double well.

A comparison was made between the packing efficiencies of the nonisostructural compounds bis-(*m*-chlorobenzoyl)-methane and bis-(*m*-bromobenzoyl)-methane. The packing coefficient of Kitaigorodskii⁹

was calculated for each of the compounds. This packing coefficient represents the ratio of the volume of the unit cell occupied by the molecules in the unit cell to the volume of the unit cell. The coefficient of the bromo derivative was 0.686 and that of the chloro derivative was 0.691. If the chloro derivative were assumed to be isostructural with the bromo derivative, the packing coefficient would be 0.648. The unit cell volume of the bromo compound is 87 Å³ larger than the chloro compound while only 53 Å³ would be required for bromine instead of chlorine atoms. Evidently the chloro derivative packs more efficiently than the bromo derivative. The bromine atoms in bis-(*m*-bromobenzoyl)-methane tend to pack in sheets while the chlorine atoms in bis-(*m*-chlorobenzoyl)-methane tend to pack in zig-zag chains. The large congregation of bromine atoms may in some way compensate for the loss in packing efficiency.

(9) A. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1955.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MD.]

The Fragmentation of Some Boron Hydrides by Electron Impact¹

BY T. P. FEHLNER AND W. S. KOSKI

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The fragmentation of isotopically labeled volatile boron hydrides by electron impact has been studied. Monoisotopic spectra, appearance potentials of selected fragments, and metastable transitions are reported both for protonated and deuterated compounds. Ionization potentials are given for diborane, tetraborane, pentaborane-9 and -11, and hexaborane. Heats of formation are calculated for the various fragment ions produced and are used in determining the decomposition paths for the parent ions. Structures of several fragment ions are postulated from data on isotopically labeled hydrides; ionization potentials are calculated from the corresponding appearance potentials.

Introduction

In a previous paper the fragmentation of tetraborane was studied utilizing measured appearance potentials and the observed metastable transitions in the spectra

of monoisotopic and isotopically labeled tetraboranes.² Since then, this approach has been extended to the rest

(1) This work was done under the auspices of the United States Atomic Energy Commission.

(2) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 1905 (1963).