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(HD) is essentially proportional to [D] so that the similarity of the curves of G(HD) and [D] (Fig. 1 and 6) demonstrate the self-consistency of the treatment in regard to saturation of G(HD).

For the second point it is easily shown from a steadystate treatment for CH_2D radicals that

$$\frac{[CH_3]}{[CH_2D]} = \frac{4}{3} \left[\frac{1}{2} + \frac{k_3[M]}{k_d} + \frac{2k_8^{1/2}R^\circ_{C_2H_6}^{1/2}}{k_2[D]} \left(1 + \frac{k_3[M]}{k_d} \right) \right]$$
(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 $[CH_2D]/[CH_3]$. 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

ISOTOPIC ETHANE DISTRIBUTION

Species	Calcd.	Obsd.	Species	Caled.	Obsd.
C ₂ H ₈	3.4	0.7	$C_2H_2D_4$	0.34	0.40
C₂H₅D	2.1	2.0	$C_2 H D_5$. 12	0.09
$C_2H_4D_2$	2.0	1.5	C_2D_6	.02	• •
$C_2H_3D_4$	1.0	1.0			

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 $G(CH_3D)/G$ - (CH_2D_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 $G(CH_2D_2)/G(CH_3D)$. 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 CH₃D as a primary product.

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

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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-(mbromobenzoyl)-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.

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

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

^{(1) (}a) Taken in part from a thesis by Gordon Engebretson 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.



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 Pca2₁. 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 Pca2₁, which the final structure confirms.

Intensity Data.—X-Ray intensity data were obtained using nickel-filtered, copper K α radiation, a G.E. single crystal orienter, scintillation counter, and θ -2 θ 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 $1e^{-}/Å$.² contour. Other contours $e^{-}/Å$.²

in streak corrections, etc. The weighting of reflections in least squares refinements was then $W_{\rm h} = 1/\sigma_{\rm h}^2$ where W is the weighting factor and $\sigma_{\rm h}^2$ 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 $\{h\bar{0}l\}$ 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 twodimensional 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).



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

Final Positional and Anisotropic Thermal Parameters and Their Standard Deviations $\times 10^5$

Atom	x/a	y/b	z /c	β_{11}	β 2 2	β33	β_{12}	β_{13}	β23
Ch	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
Oı	58081	2356	1947	114	12100	658	82	-7	-1152
	17	200	53	7	658	57	66	16	171
O2	66147	4761	6265	92	12585	721	49	15	-932
	19	213	54	6	734	53	61	15	186
Cı	44940	18084	9929	82	7955	722	70	-14	117
	25	273	77	8	845	73	68	20	223
C2	49365	12686	7181	89	7212	766	63	-42	796
	25	228	77	8	716	76	63	21	205
C3	52581	23767	15393	94	6680	544	-21	-14	384
	25	254	75	8	669	56	66	17	183
C4	51325	39178	26211	97	8237	683	-61	-20	-344
	25	238	83	9	778	64	66	21	217
Cs	46833	44041	28823	97	9158	773	-7	-7	-81
	26	274	86	9	843	79	76	23	230
C6	43521	32426	20746	75	8376	845	74	29	-38
	23	247	92	7	723	69	60	21	218
C7	57333	17847	12125	95	7256	569	9	3	-6
	25	260	75	9	726	59	66	20	186
Cs	60838	27812	19686	64	8699	585	28	7	184
	21	258	75	6	712	64	62	17	198
C,	65235	21088	16382	88	6074	614	150	-12	98
	23	233	71	7	643	59	62	17	181
C10	76557	48437	37647	116	832	791	-94	-67	211
	28	280	86	11	800	75	82	24	225
Cu	72238	55477	41867	83	9589	-113	-6	-6	535
	25	283	83	8	849	77	73	22	231
C12	68564	46246	34855	98	8183	702	-21	22	-71
	27	264	77	9	740	67	77	21	208
C18	61256	30733	23842	73	8016	559	- 33	-5	325
	22	225	67	7	692	61	62	18	175
C14	73303	22839	20002	88	8992	781	-55	-33	416
	23	275	88	7	787	74	70	21	236
Cıs	76998	31868	27006	67	8293	1096	66	2 6	491
	25	273	94	7	776	97	67	22	258
H_2	50300	-500	-1000	138	8433	1010			
H4	55600	47000	32500	138	8433	1010			
H	46000	55100	36800	138	8433	1010			
H.	39200	34300	22900	138	8433	1010			
H_8	60200	40300	28003	138	8433	1010			
H_{10}	79700	55400	42500	138	8433	1010			
\mathbf{H}_{11}	71800	67500	50400	138	8433	1010			
H_{12}	65300	50800	39700	138	8433	1010			
H_{14}	73700	9900	11700	138	8433	1010			
(H ₂ is	bonded	to C ₂ , et	tc.)						

independent atom to R = 13.8%, then to refinement cycles using anisotropic temperature factors using Busing and Levy's least squares program, ORXLS. 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 $|F_{\rm o} - F_{\rm c}|/\sigma(F_{\rm o}) > 6$. Fourteen reflections of this type were found. In every case $F_{\rm c}$ 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 $[\Sigma W(F_o - F_c)^2/(m - n)]^{1/2} = 1.86$, 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 $C_{13}\mathcal{-}C_{14}$ and $C_{10}\mathcal{-}C_{15}$. 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 C_3-C_7 and $C_9 C_{13}$ (1.492 and 1.482 Å.) are typical of C-C single bonds trigonally coordinated. In the enol ring the distances between C_7-C_8 and C_8-C_9 (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 II

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS BASED ON PARAMETERS LISTED IN TABLE I

The first column is the *l*-index; an asterisk after the *l*-index indicates an unobserved reflection. The second column is $10 |F_c|$ and the next columns are in order $10 |F_c|$. 10A, and 10B (the real and imaginary parts of F_c).

Ha	0 Kø	0			8 9 10	297 247 113	302 238 104	-48 -237 -67	-298 24 80	246	1532 468 316	1593 461 307	1190 409 286	1060 314 110	36. 9 04	K 28	1 31	-31 0	8 9 10	151 93 86	144 87 71	144 -86 -15	-12 -4 70		3* 39 4* 39	50 54	4	49 38
4	1114 715 477 203	1171 715 482 208	-671 694 33 200	-172 481	11*	36 92	57 89	-52 -89	-22 5	8 10 12	99 132 76	74 127 86	68 117 74	-29 50 -43	1 2 3	93 117 54	189 119 350	174 -72 115 28 -333 105	11 12*	67 24	56 29	52 29	-19 6		6* 38 7* 35 8 76	25 26 69	18	-20 19 69
10 12 14	157 81 89	146 74 99	146 65 98	12 34 -5	н∍ 0	18 K- 97 270	0 64 265	64	146	H.	1 K.	1	1101	0	4 5 6*	28	117 310 224	-64 -99 121 -286 217 -55	н. 0	18 K.	120	-120			H= 28 K	* 1	-	
Ha	2 K.	0			234	237 361 159	235 366 153	-197 -137 -148	130 340 -39	1 2 3	904 930 237	1014 982 264	765 -882 164	-666 431 207	8 9 10	93	1 80 84 11 3	-52 173 -58 -60 -34 -108	234	228 168 229	216 152 227	-202 -75 -151	79 132 170		0 75 1 133 2 174 10 10	106 - 136 180 -	90 179	0 103 -19 29
0 1 2	35 207 908	17 247 934	17 -233 625	0 -83 694	5 6 7	108 370 294	120 382 301	97 -341 17	-70 173 301	4 5 6	395 89 251	398 99 244	253 -89 -49	-307 42 239	11* 12* 13*	38 33 26	32 41 26	31 -2 41 2 -24 -11	5 6 7	185 170 158	196 172 151	66 -171 3	185 15 151		4 98 5* 38 6 105	97 45 103 -	-87 -9 101	-41 44 19
34	662 517 306	646 495 303	-587 112 139	-270 482 -269	8 9 10*	257 186 37	263 167 28	-241 -93 17	-104 139 -23	7 8 10+	103 88 42	98 79 42	-4 -2 -34	-98 -79 24	H= 1	0 K=	1		8 9 10	130 99 89	1 32 94 98	-122 -22 -84	-48 92 -50		7 115 8* 29 9 44	89 12 66	-67 -9 -58	59 8 51
8 8	474 228 163	481 224 166 250	-211 102	-420 -77 131 -217	12 H-	44 20 K-	56 0	-51	23	12+ 13+	34 29	30 10	-10 -26 2	-65 -15 -10	1 2	90 90 952	217 354 353	-143 -163 338 -105 300 185	12+ H-	22 19 K-	39	-32	-22	:	H= 29 K	- 1	03	
10 11 12+	110 118 37	99 117 47	88 79 35	-45 -86 32	0	324 220	317 207	-317 -127	0 163	H.= .0	2 K≖ 505	1 542	542	0	4 5 6	67 34 39	264 241 240	263 -13 233 58 236 42	0	235 175	230 177	230 158	-79		1 75 2 75 3* 38	90 83 63	-76 -78 62	49 29 -7
13 14*	71 22	84 18	-31 17	-79 7	2 3 4	340 191 188	356 200 198	352 23 -78	51 198 182	23	50 666 289	66 691 302	14 650 -212	65 -235 -215	7 8 9	57 42 62	66 147 55	63 18 138 52 -4 55	234	140 62 147	130 76 1 46	-123 -52 146	42 56 -4		4 130 5 62 6 60	116 47 68	76 -30 32	-88 35 60
9 0	4 K. (311	311	. 0	67	127 87 198	109 89 188	-49 83 57	-31 179	567	161 295 146	158 288 143	-158 -135 108	-254 94	10 1 11 12+	46 87 31	143 77 14	142 15 1 77 13 -3	5 6* 7	133 40 136 62	132 20 129	124 -19 16	-46 5 128		7 55 8 63	52 54	49 22	-19 -50
234	763 629 376	748 599 361	-601 364 -341	-446 -476 119	9 10 11	61 89 86	65 77 84	53 22 4	-38 -73 84	8 9 10*	157 189 42	156 195 54	156 -19 36	-8 -195 41	H= 1	∎. K≓	1	,, <u>,</u>	9 10* 11*	87 36 29	67 41 33	-66 40 22	-20 7 8 -25		0* 38 1* 38	= 1 56 68	-56 40	0 55
5* 6 7*	30 498 35	33 485 3	-19 -432 2	27 -220 2	12* H .	22 22 К=	75 0	74	12	11 12 13*	107 63 29	89 54 32	-38 53 14	-81 13 -29	0* 1 2 2 1	31 04 62	50 207 170	-50 0 -197 62 -168 -23	¥-	Z0 K=	1				2* 37 3 137 4* 36	17 124 53	17 -48 -40	0 115 35
9 10	101 158 141	96 160 141	-40 -157 -91	-27 -107	0	414 248	399 249	399 -223	-109	H∎ 0	3 K.	1	- 171		4 1	35 34 54	414 133 137 53	135 -391 58 -120 58 124	2 3 4*	103 97 40	228 115 106 71	36 -91 -11	-70 105 71		5 133 6 49 7 126	129 37 118	46 -29 ; 2	121 22 117
12* 13 14*	36 53 21	31 49 6	-31 -2 -6	-100 -49 -2	34	463 309 75	471 292 82	449 291 -2	-141 -22 82	1 2 3	478 256 192	478 272 187	464 271 -133	-115 20 131	7 1 8* 9	92 39 92	187 35 83	-63 -177 -5 -34 69 47	5 6* 7*	142 41 41	139 17 22	39 1 -22	133 -17 -4	1	H= 31 K	24 2 1	- 2 3	•
R-	6 K= ()			6 7 8	113 84 200	105 76 201	35 23 163	99 -73 -117	4 5 6	339 175 170	332 180 172	-329 163 112	-43 75 -130	10* 11 12*	39 95 30	13 84 8	-3 -13 -71 -45 8 3	8 9 10	59 136 60	53 128 41	-4 20 26	53 127 -32		0* 37 1 108 2* 36	60 124 21	60 118 -13	-38 -16
1 2 2	177 389 942	151 385 938	-151 372 -902	-99 258	10 11	36 95 46	113 55	106 55	40 2	8 9+	153 154 41	146 130 58	-140 -18 -29	43 129 -50	13# H= 1	23 2 Ka	8 1	8 -1	H#	48 21 Ka	59 1	56	19		3 114 4* 36 5 129	116 - 55 123	54 67 -	45 -5 -103
456	297 163 466	271 168 473	-203 91 -462	180 142 98	Н∎ 0	24 K. 186	0 199	-199		11* 12* 13*	39 35 29	24 3 25	23 -2 -24	6 -3 -9	0	37 89 79	742 477 487	742 0 367 -304 457 166	0 1* 2	210 39 200	203 42 204	-203 25 182	0 -33 -92	t	7 69 H= 32 K	76	9	75
7 8 9	206 311 188	206 310 183	2 -295 -160	206 -93 90	1 2 3	611 426 102	600 433 99	287 433 -7	-527 20 99	H∎	4 K⊭	1			3 2 4 3	15 50 89	212 359 196	-62 -203 334 133 26 -195	3* 4 5 6	39 107 108	52 100 104	-17 -88 84	-49 49 -62		0* 35 1* 35	30 73	30 -26	68
11	131 123 11	356 121 144	106	-104 -58 -136	567	243 96 95	236 95 64	58 21 32	-228 -93	1 2 3	509 324 211	518 326 217	-299	-423 259	7 8*	70 40 16	152 79 59 122	13 78 43 40 105 -62	7 8 9	85 118 64	79 126 71	-38 -29 -28	69 122		2 78 3* 35 4 61 5* 32	92 48 66 14	91 33 63 29	36 19
14+ H=	17 8 K= (32	-4	31	8* 9 10*	37 164 30	27 162 36	27 4 31	3 -162 -19	4 5+ 6	317 31 74	299 31 68	-288 24 -60	-82 20 -31	10 11 12	83 76 48	83 74 50	82 17 -1 -74 45 -23	10 11+	67 25	69 28	-27 -17	-64 -22		48 7* 22	52 21	48 21	19 -5
0	648 472	661 489	-661 183	454	11+ H≠	22 26 K+	24 0	11	-21	7* 8 9	36 223 81	82 223 82	-52 -169 -76	-63 -146 31	13* H= 1	22 3 K≃	21 1	-1 -21	H= 0	22 K.	1	122	0	-	1# 33 K 1* 34 2 103	60 107	-60	9 -42
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6 7 8	135 228 303	147 236 312	-13 -33 -145	-146 233 276	3 4 5	240 181 200	237 162 193	218 -152 -190	-92 55 -33	H.	5 K.	1			3 1 4 2 5 1	50 71 22	151 269 128	86 125 103 -249 -62 -113	567	137 133 72	135 138 50	104 137 45	87 7 -21	2	ό 81 H= 34 ⊮	78 .+ 1	-11	- 77
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234	504 222 465	532 221 463	381 221 454	371 -7 90	6* 7 8	35 178 .67	41 172 62	-32 -22 -40	26 170 48	10 11 12	128 99 104	135 109 124	-100 -99 -77	-90 45 -97		89 86 04	191 178 114 296	161 60 140 111 -113 12 -257 147	6* 7 8	103 50 32	54 91 58	-13 -13 -18	-90 -34	I	-L= 0 K≥ 0≠ 33	47	47	0
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2 3 4 5	613 619 225 147	567 619 233 150	-290 -195 -52	-547 128 -141	1 2 3*	49 32 166	117 59 10 156	48 -56 -9 126	-107 19 3 -92	10 11 12 13+	151 123 111 28	154 121 119 26	-135 -119 62 20	-18 -102 -18	2 2 3 1 4 2 5*	82 00 00 38	275 117 206 44	-267 -00 -39 -110 -195 -67 -1 44	10+ H#	23 26 Ka	30	-16	25		6 81 7* 42 8 124	64 74 98	-23 -13 -96	60 -73 15
6 7 8	194 189 132	197 178 131	-36 -144 -0	-193 -105 131	5	162 115	160 111	56 104	-150 40	H.	8 K.	1			6 2 7 8 1	51 97 38	264 102 138	-235 -120 -99 25 -132 39	0	160 118	119 128	-119	-125	1	9* 41 0* 40 1* 36	50 40 33	-14 7 -23	-48 40 -24
9 10+ 11 12=	151 39 81	158 39 88 23	65 -31 -5 21	-144 -24 -87	H= 1 2	216 104	210	170	-124	0 1 2+	248 291 30 255	242 281 117 257	-242 19 -94	280 -69 240	9 1 10* 11 12	UZ 36 92 71	68 15 85 6 P	-27 83 -14 -3 -71 -47 -68	2 3 4*	79 90 40	76 109 61 29	-5 -61 -21	-54 -54 19	1	29 H= 2 K:	2	- 4 1	-10
із н.	64 16 K=	77 · 0	-26	-73	34	99 36	102 45	-68 -31	-76 32	4 5 6	133 156 53	134 146 58	-132 -64 51	24 131 26	H= 1	, к.	1		6 7 8	70 141 81	51 120 76	-46 -49 -76	-21 -110 5		1 117 1 145 2 171	134 143 175 -	-67 - 166	0 126 54
2	303 540	262 536	-262	0 41	H= 0*	38 K= (3	-3		7 8 9	208 136 116	202 128 126	-49 -107 117	196 -71 46	0 1 1 2 2+	04 32 33	98 219 22	98 -213 51 20 -10	9* 10*	29 19 27 -	41 43	-23 -42	-34 -5		3 32 4 513 5 219 6 76	49 506 215 - 65	-42 505 188 - 39	-31 104 52
4 5 6	170 111 325	161 122 320	-142 -115 -277	-76 -42 160	He	21 0 K= 1	105	-103	-18	11 12+ 13	83 33 64	67 23 64	-01 58 19 36	34 -13 56	δ 1 6 1	37 10 22	41 116 126	-18 37 -14 115 -61 -111	00 10	40 59	48 19	-48 12	0 155		7 234 8* 41 9* 40	227 37 10	15 - 37 -4	-5
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 <t 3 H = 15 K+ 3 97 -77 -49 12 22 -27 -1 -11 -9 -61 -75 30 -14 -27 53 68 -5 -4 37 45 114 97 79 64 90 39 28 42 3 100 72 30 49 46 42 3 124 113 142 97 29 111 72 56 21 72 54 28 3 -124 73 -142 -85 11 35 -21 -50 -2 4 -54 5 -37 2 -113 47 78 -64 -69 29 -3 -16 2 45 11 85 -9 -2 58 26 -28 39 1 38 1 51 1 34 39 227 1 30 1 02 39 74 39 74 39 74 39 76 180 105 40 105 40 39 37 67 27 147 150 133 216 268 130 92 48 53 38 82 2 0 -131 90 -33 -167 -144 117 -83 -39 -51 37 -79 147 74 -97 28 136 -226 -57 39 -27 -13 7 21 67 241 282 97 220 76 121 41 97 63 38 50 30 5 K ≈ 79 239 265 108 212 77 106 46 59 69 22 40 49 0 1 2 3 4 5 6 7* 8 9 10* 11 12* H+ -79 217 -239 -41 -170 -9 -102 -27 -59 -33 -16 -37 -49 -101 -155 -100 -128 -77 27 -37 -4 -61 -15 -15 0 33 -40 112 -10 2 77 16 -17 18 -32 -55 -45 -4 -49 +27 -21 25 -48 -13 -141 32 -23 -23 -23 -23 -21 55 -21 54 1 49 -17 39 -100 56 -104 28 -32 -64 -27 -36 -30 -21 -45 -22 62 -72 -32 -13 33 35 -37 - 35 101 -70 -60 10 66 -7 -2 29 -8 6 5 35 119 72 6 51 115 31 128 43 51 11 128 43 11 11 15 3 188 56 422 22 174 33 121 21 21 2 . 17 39 58 79 172 110 35 39 29 30 42 25 25 0 16 10 12 105 -33 37 22 5 39 18 -17 -36 55 37 -172 -33 10 -14 -18 -30 -15 17 -48 -21 5 -42 12 38 -71 26 -13 0 -31 -25 -45 34 -111 -25 15 20 141 68 172 95 107 89 143 43 130 69 34 29 140 77 232 101 100 64 135 6 140 69 36 32 -103 -24 195 -50 11 54 78 -2 -85 32 -10 -30 95 -73 126 -87 99 -34 110 5 112 61 35 12 1234567890 112* -11 99 27 -57 1 71 -16 -21 58 67 52 106 61 35 52 26 58 3 58 59 -27 -6 39 4 35 4 16 38 30 -45 106 -47 41 3 51 21 44 -61 -24 38 -15 9 21 54 -29 6 0 -5 7 -37 -10 -8 -39 -21 35 -188 .-25 -12 -1 -171 -33 -113 31 1 -16 -28 3 н, 6 K = 2 0 -79 -28 60 -21 67 -64 -32 51 -41 -51 29 -286 118 -45 -243 30 51 -101 -62 -4 -115 -79 -159 -8 -50 -80 -77 1 -42 -20 0 7 -42 86 51 9 -73 55 315 88 178 35 301 127 192 41 185 90 39 36 76 316 104 175 18 292 123 196 29 190 93 63 40 83 012345678901112 -316 -75 -175 6 -239 -41 -176 -18 -176 44 -42 -15 -76 0 72 12 17 168 116 -85 -23 -73 81 -48 38 34 0 41 -4 40 -7 96 -21 18 16 0 59 43 82 47 59 22 92 19 41 25 3 -59 -14 -82 25 -51 -27 8 -4 -38 -25 -68 -57 -31 20 -42 -59 -10 41 -38 0 -8 -7 20 1 25 -9 -17 39 -36 5 11 39 1 37 -6 -58 -14 86 -33 -20 -21 0 87 71 -16 -43 199 -22 15 -27 86 35 -2 33 -11 3 -43 45 -12 21 11 85 136 38 46 119 42 88 28 31 35 3 11 60 130 23 28 106 33 -29 7 -19 34 $\begin{array}{c} 0 \\ 60 \\ -39 \\ 311 \\ 377 \\ 5263 \\ -27 \\ -28 \\ -27 \\ -581 \\ -24 \\ 482 \\ 0 \\ -148 \\ 23 \\ 0 \\ -19 \\ -59 \\ -59 \\ -59 \\ -79 \\ -56 \\ 18 \\ 23 \\ 0 \\ -71 \\ -58 \\ -29 \\ -59 \\ -59 \\ -59 \\ -59 \\ -59 \\ -59 \\ -59 \\ -59 \\ -59 \\ -59 \\ -58 \\ -9 \\ -56 \\ 18 \\ -28$ 7 K= 2 -22 -47 15 101 -27 35 85 -21 42 -18 84 2 ,н = 1* 2* 3 4 5* 6 7 8* 9 10* 11 12* 33 96 178 38 110 224 42 76 38 81 28 43 50 105 167 20 99 218 35 76 47 67 47 -10 33 -53 -4 51 186 31 73 -2 56 -27 -42 -37 35 158 20 85 113 -17 -21 47 -37 -39 H= 0+ 1+ 2+ 3+ 5+ 6+ 7+ 8+ H= 0+ 1+ 2+ 3+ 5+ 6+ 7+ 8+ H= 2+ 3+ 5+ 6+ 7+ 8+ 7+ 8+ 7+ 4 K -37 39 38 38 39 34 32 30 22 4 19 455 66 18 56 3 64 32 72 52 21 33 37 34 3 19 -41 51 56 14 56 15 50 0 -19 -18 9 39 24 -35 10 26 44 12 33 34 60 15 11 19 12 -44 -12 -18 4 -49 -14 11 -6 11 0 -4 -28 -34 -35 -0 -18 4 99 28 25 15 86 7 22 -72 -74 20 -30 -75 -7 59 16 46 3 22 128 75 72 34 75 58 72 29 66 23 3 -178 -154 -8 171 -183 -53 -95 -54 -43 -19 -101 6 н. 8 K= 2 4 106 -2 54 2 163 -39 53 58 73 2 33 5 K = 36 40 39 78 35 32 29 19 6 K = 38 36 62 36 37 31 27 0 -12 1 -21 -3 -32 -13 20 -29 -27 24 12 10 -10 31 61 -13 67 -46 -17 32 35 -15 92 230 188 127 105 185 193 165 96 175 62 73 53 94 222 186 132 103 179 186 169 114 171 66 90 27 92 -62 -176 14 32 -67 -188 74 67 57 8 -46 -31 -3 29 40 -10 6 47 37 25 45 37 68 5 36 26 44 18 25 2 -35 14 -2 25 -12 -20 -8 221 67 127 -100 172 40 -148 -70 165 62 56 -43 45 -11 67 5 25 -23 39 16 5 6 7 8 9 10 11 12* 18 10 38 6 0 -29 -11 -29 -3 30 97 61 64 112 68 50 78 83 46 38 38 30 -77 59 28 112 -12 -41 -25 62 42 28 46 2 -46 62 38 4 86 -6 -40 39 82 -34 -44 17 25 H = 0* 1* 2* 4* 5* 6* 7* 86 41 54 85 48 47 57 26 0 -41 -14 -37 -20 -34 -16 -55 -7 83 66 32 54 79 41 13 33 -5 44 34 20 60 16 52 11 28 14 -31 31 -4 -97 23 63 78 -65 17 69 -34 -2 -57 -16 -42 11 8 -12 20 18 4 -32 0 -27 7 H * 0* 1 2 3 4 5 6 7* 8* 9 10* 11* 12* 9K-2 32 105 108 98 58 168 139 42 43 70 38 32 26 0 42 -74 -38 13 -134 -11 32 31 -37 -19 -2 -27 8 118 108 48 149 117 36 32 53 24 5 37 8 111 79 -80 47 65 117 17 8 -38 -14 -5 26 -18 -43 24 4 -35 3 7 K * 37 36 83 37 56 76 31 27 134 32 49 83 60 106 62 25 85 23 31 3 134 32 42 -62 52 103 61 16 77 6 29 0 55 55 -30 -22 -12 19 36 23 11 31 9 74 40 55 37 98 72 3 -31 8 73 -40 50 9 59 72 0 -4 -13 -2 24 -36 -79 -6 0* 1* 2 3* 4 5 6* 7* 2 21 72 29 50 77 26 29 2 •16 72 25 20 3 2 -6 -31 -27 84 39 19 112 -21 -69 -15 113 -39 17 64 45 27 1 100 90 108 -59 73 46 48 -24 27 38 - 37 - 38 -60 н. 10 K - 2 н∍ 4 8 K= 184 346 183 150 82 134 198 257 122 39 37 64 55 183 355 194 146 86 124 198 246 104 42 52 71 0 -50 51 113 -8 -123 -52 208 43 33 20 14 41 183 351 187 -92 86 13 191 132 95 7 37 50 58 37 38 36 38 68 33 31 26 45 134 62 67 66 97 63 24 3 -45 92 -52 -57 -62 -20 6 24 0 -97 -34 35 22 -95 -62 5 0* 1* 2* 3* 4 5* 6* 27 38 4 50 51 44 19 28 -27 -4 -49 -32 43 19 -5 60 165 51 56 23 133 21 8 42 50 11 3 -38 94 295 52 33 17 -60 123 -44 9 6 18 -11 2 34 -9 -16 5 135 135 135 147 74 -69 221 25 33 0 -109 -26 -56 -22 -132 -19 -8 -24 -49 -2 0 -33 34 25 10 -73 -75 161 -20 -25 7 -28 -22 -33 5 6 7 8 9 10 11 12 -85 -40 -46 6 -36 -8 -16 11 0 -19 28 70 -21 -19 17 83 18 12 -43 -20 90 103 170 0 103 170 0 199 970 12 20 H = 4 0 1* 15 2* -24 3 -113 4* -7 5 -54 6* 5 7* 12 63 77 113 39 56 65 36 37 77 35 57 29 26 22 26 77 38 46 21 39 12 -61 73 11 -39 12 64 -13 -8 -21 27 1 -15 -38 -18 24 74 26 -46 14 5 -200 20 -49 -103 115 -5 -32 4 1 -41 -5 н 11 K = 2 315 181 219 63 45 94 98 30 33 20 21 5 -186 -165 -174 25 -14 -91 -81 27 -18 -11 -19 -4 324 182 219 62 41 111 111 42 36 35 31 23 -255 75 132 -59 -43 21 56 -13 -28 16 9 -4 39 165 136 211 95 72 57 27 42 37 33 3 0 -44 42 -42 -168 -28 63 -8 -1 -0 -20 -151 59 20 -23 -17 33 -17 33 -14 -5 H= 4 0 5 -19 -33 22 -17 27 103 54 42 22 27 3 17 56 79 45 57 3 43 43 34 15 27 -40 -93 51 -26 -2 -20 0* 1* 2* 3* 5* 6* 7* 37 38 35 36 34 32 29 24 6 48 21 42 31 25 35 12 -6 -25 19 15 29 7 34 -7 40 -9 -39 -10 24 7 71 -30 1 34 53 -111 104 18 6 15 24 -10 0 -35 -95 -49 -118 -37 131 -106 9 -22 12 -20 H= 12 K = 2 156 -23 376 34 102 122 123 15 84 -21 27 -4 H • 1* 2* 3 4 5 6 7* 8 9 23 K + 41 40 60 151 82 75 36 52 54 54 24 K + -17 -29 -56 -77 45 8 156 155 376 101 176 122 127 158 21 36 11 48 140 169 379 74 167 128 131 169 39 36 30 24 11 K = 37 133 56 37 34 32 27 22 4 -153 21 -95 143 -7 33 -157 25 1 -23 -10 2 H+ 1 2 3+ 4+ 7+ -9 1 -16 -1 -56 145 107 80 49 91 48 72 23 24 11 40 -145 -40 16 7 -73 48 -68 -21 -18 11 -40 46 42 78 139 57 29 63 45 45 3 -27 15 -33 42 -30 -25 -60 -30 -48 -32 -77 -135 -41 48 -14 -18 -34 0 -99 -79 -48 -1 -26 -1 -26 -9 19 -1 -29 19 -1 57 110 61 50 55 3 0249949494 92499494 94994 57 61 -57 -60 -1 38 3 -1 43 -14 -34 -5

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32 -13 68 -5 -5

8 -75 -7 -7 -4

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31 31 28 25 17 K = 1* 2* 3* 4* 5* H≂

0* 32 1* 30 2* 29 3 63 4* 27 5* 22 H = 18 K = 0* 30 1* 30 2* 29 3* 27 4* 24 H* 19 K = 0* 28 1* 27 2 87 3* 27 4* 24 4* 22

H= 21 K= 4

H= 22 K= 4

22 16 20 23 0* 1*

0* 1* 2* 3

0* 1* 2* 24 24 22 17 26 18

41

13 H+ 12 K+

4

14 K=

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31 30 33 31 21 -31 21 -31 -19 -7 22 -11 24 -20

4

Plane	А	В	С
1	-0.05307	-2.09875	1.02959
2	05034	-0.99214	0.50857
3	05874	-0.92279	. 49278
4	06002	-1.41053	.71061

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 C_7 to O_1 . Axis II: the vector cross-product of Axis I into the vector from C_7 to C_8 . 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]	LV .
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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.
Cl1	0.0237	C1	-0.0165	C_5	0.0234	C,	-0.0256	C13	-0.0299
Cl_2	.0686	C_2	.0012	C_6	.0476	C10	0206	C11	.0100
Oı	0197	C_3	— .0199	C7	0387	C_{11}	0038	C15	.0010
O_2	.0313	C₄	.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

m-Ch	loro derivative——	m-Bromo derivative						
Bond	Distance, Å.	Bond	Distance, Å.					
Cl_1-C_1 Cl_2-C_{15}	1.731 ± 0.008 $1.727 \pm .008$	Br-C ₁	1.901 ± 0.007					
$O_2 - O_1$	$2.475 \pm .008$	$O_1 - O_1'$	$2.464 \pm .015$					
C ₁ C ₈ C ₁₀ C ₁₅	$1.391 \pm .012$ $1.351 \pm .014$	C1-C6	$1.375 \pm .009$					
$C_6 - C_5$ $C_{10} - C_{11}$	$1.414 \pm .011$ $1.407 \pm .011$	$C_6 - C_5$	$1.397 \pm .010$					
$C_5 - C_4$ $C_{11} - C_{12}$	$1.395 \pm .010$ $1.398 \pm .010$	C ₅ -C ₄	$1.389 \pm .010$					
$C_4 - C_3$ $C_{12} - C_{13}$	$1.394 \pm .011$ $1.373 \pm .011$	C4-C3	$1.410 \pm .008$					
$C_3 - C_2$ $C_{13} - C_{14}$	$1.381 \pm .010$ $1.362 \pm .010$	$C_{3} - C_{2}$	$1.400 \pm .009$					
$C_1 - C_2$ $C_{14} - C_{15}$	$1.397 \pm .011$	$C_1 - C_2$	$1.392 \pm .009$					
$C_3 - C_7$ $C_9 - C_{13}$	$1.492 \pm .010$ $1.482 \pm .010$	C ₃ C ₇	$1.457 \pm .009$					
$C_7 - C_8$ $C_8 - C_9$	$1.402 \pm .011$	C7~C8	$1.393 \pm .008$					
$C_{7} - O_1$ $C_{9} - O_2$	$1.299 \pm .010$ $1.318 \pm .009$	C ₇ –O	$1.306 \pm .008$					

^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 C_7 -O₁-O₂ and C_9 -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 $C_3-C_7-C_8$ and $C_8-C_9-C_{13}$ indicate that these angles open to relieve the strain caused by the close approach of H_8 to both H_4 and H_{12} (H_4H_8 contact distance of 2.02 Å., $H_{12}H_8$ contact distance of 1.95 Å.). This was also observed in the bromo derivative ($H_4'H_8'$ 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

Table VI

A Comparison of Bond Angles within Molecules of Bis-(*m*-chlorobenzoyl)-methane and Bis-(*m*-bromobenzoyl)-methane^a

Bis-(m-chlorob	enzoyl)-methane	Bis-(m-bromobenzoyl)-methane					
Atoms	Bond angle, deg.	Atoms	Bond angle, deg.				
$Cl_1C_1C_6$	117.3 ± 0.6	BrC.C.	110.5 ± 0.6				
$Cl_2C_{15}C_{10}$	119.3 ± .7∫	DICICS	119.0 - 0.0				
$Cl_1C_1C_2$	$119.4 \pm .7$	BrC C	117 8 - 5				
$Cl_2C_{15}C_{14}$	118.9 ± .8∫	BIC_1C_2	117.0 ± .0				
$C_8C_1C_2$	$123.1 \pm .8)$	000	199 7 - 7				
$C_{10}C_{15}C_{14}$	121.7 ± .8∫	$C_6C_1C_2$	122.1 ± .1				
$C_1C_8C_5$	$117.3 \pm .7$	000	117 0 - 7				
$C_{15}C_{10}C_{11}$	118.3 ± .8∫		$117.0 \pm .7$				
$C_6C_5C_4$	$120.5 \pm .8$	000	191 G - G				
$C_{10}C_{11}C_{12}$	119.6 ± .8∫		$121.0 \pm .0$				
$C_5C_4C_3$	$120.0 \pm .7$	000	110 6 - 7				
$C_{11}C_{12}C_{13}$	$120.7 \pm .5$	$C_5C_4C_3$	$119.0 \pm .7$				
$C_4C_3C_2$	$120.4 \pm .7$	000	110 2 - 6				
$C_{12}C_{13}C_{14}$	119.4 ± .6∫	$C_4C_3C_2$	119.2 ± .0				
$C_3C_2C_1$	$118.4 \pm .8$	000	110 1 - 6				
$C_{13}C_{14}C_{15}$	120.1 ± .8∫	$C_3C_2C_1$	119.10				
$C_4C_3C_7$	$122.3 \pm .7$	000	191 6 ± 6				
$C_{12}C_{13}C_{9}$	$120.7 \pm .6$	$C_4C_3C_7$	121.0 ± .0				
$C_2C_3C_7$	$117.2 \pm .7$	000	110 2 - 6				
$C_{14}C_{13}C_{9}$	$119.8 \pm .7$	$C_2C_3C_7$	119.00				
$C_3C_7C_8$	$122.2 \pm .7$	C.C.C.	195 O + 6				
$C_{13}C_{9}C_{8}$	$123.6 \pm .7$	C3C7C8	120.00				
$C_3C_7O_1$	$116.6 \pm .7$	0.0.0	115 G + G				
$C_{13}C_9O_2$	$115.7 \pm .6$	C3C70	110.00				
$O_1C_7C_8$	$121.2 \pm .6$	00-0	110.4 ± 7				
$O_2C_9C_8$	$120.7 \pm .7$	00708	110.41				
$C_7C_8C_9$	$120.2 \pm .7$	$C_7C_8C_7'$	$122.2 \pm .8$				
$C_7O_1O_2$	$89.0 \pm .7$	C•00′	895+8				
$C_9O_2O_1$	$88.8 \pm .6$	2,00	50.0 - .0				

^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 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

	Principal				•		Principal				
Atom	axis	cos a	$\cos \beta$	$\cos \gamma$	Length, Å.	Atom	axis	cos a	$\cos \beta$	$\cos \gamma$	Length, Å
Cl_1	1	-0.369	0 153	-0.940	0.171	C _s	3	. 419	. 889	0.183	0.247
	2	902	. 192	. 386	. 253	C7	1	885	. 452	— .111	. 180
	3	. 236	.969	. 069	.268		2	. 139	. 030	— . 990	.216
Cl_2	1	230	.051	. 959	. 181		3	. 444	. 891	. 090	.235
	2	.013	. 999	049	. 293	C_8	1	, 024	.003	-1.000	.163
	3	.960	.001	. 280	. 302		2	812	. 583	017	. 195
O_1	1	.986	. 082	143	.174		3	. 582	. 813	.016	.259
	2	. 148	. 059	987	. 231	C,	1	006	. 655	756	. 173
	3	- 072	. 995	071	. 315		2	— .956	. 219	. 197	. 197
O_2	1	940	. 124	. 317	. 195		3	. 294	. 723	. 625	. 232
	2	313	. 054	948	. 203	C10	1	— . 553	. 320	769	. 203
	3	. 135	. 991	.012	. 323		2	— .155	. 868	.472	. 236
Cı	1	013	.274	962	. 183		3	.818	. 381	431	. 259
	2	843	. 515	. 158	. 215	C_{11}	1	145	.267	. 953	. 181
	3	. 538	. 812	. 224	268		2	— . 589	. 750	300	. 212
C_2	1	242	.744	- 623	, 168		3	.795	. 605	048	. 287
	2	287	. 558	. 779	. 197	C_{12}	1	777	.359	. 518	. 203
	3	927	. 367	079	. 273		2	504	. 139	852	. 223
C:	1	601	. 748	280	. 175		3	.378	. 923	— .07 3	. 237
	2	085	.275	. 956	. 207	C_{11}	1	560	. 524	642	. 173
	3	. 792	. 604	— .089	. 237		2	479	.427	. 767	. 189
C₄	1	739	.054	672	. 200		3	, 676	.737	.012	. 245
	2	647	. 220	. 730	.210	C14	1	142	. 124	982	. 174
	3	. 188	. 974	128	.247		2	604	.775	. 185	. 207
C,	1	104	.059	— , 993	. 200		3	. 784	. 620	035	. 283
	2	917	. 382	. 119	.238	C15	1	. 111	.175	978	.167
	3	. 386	. 922	.015	.257		2	173	. 973	. 154	. 233
C ₆	1	— .439	.022	. 898	. 183		3	.979	152	. 138	. 281
	2	795	. 457	— .399	.223	was o	calculat	ed for each	of the	compounds	. This

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-(mchlorobenzoyl)-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 Å.³ larger than the chloro compound while only 53 Å.³ 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.

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The Fragmentation of Some Boron Hydrides by Electron Impact¹

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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).