

THE CRYSTAL STRUCTURE  
of  
DIGLYCINE HYDROBROMIDE



by

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## Introduction

Due to the possibilities of the use of diglycine compounds in glycine separations and identifications and their usefulness as therapeutic agents it would seem desirable to obtain information on the structure of one such compound. By X-ray analysis the arrangement of the atoms in the crystal unit may be determined and the properties of the crystal may be accounted for in terms of this arrangement. A crystal such as diglycine hydrobromide affords an excellent example of the use of a heavy atom in determining the phase constants which cannot be ascertained from experimental observations.

Briefly the steps in the structure determination consisted of the following:

1. Determination of the unit cell and space group.
2. Determination of the atomic positions.

## Literature and History of the Problem

As far as is known no previous work has been done on the crystal structure of diglycine hydrobromide. The method of preparation of diglycine hydrobromide, diglycine hydrochloride

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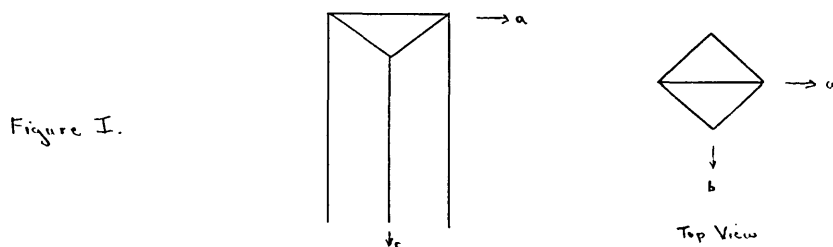
(I) Refers to two glycine molecules, not glycylglycine.

and diglycine hydrobromide has been reported by Walter S. Frost.<sup>2</sup> Previous to this diglycine hydrochloride was reported by K. Kraut<sup>3</sup> and F. Hartmann.

#### Material

Crystals and powder of diglycine hydrobromide ( $C_4H_{11}BrN_2O_4$ ) were presented by Dr. W. S. Frost of the Burnham Soluble Iodine Co, Auburndale, Mass. The material had been made by evaporation of water solutions of glycine and monoglycine hydrobromide and glycine and hydrobromic acid in theoretical quantities. Suitable crystals for x-ray work could not be found in this material so that crystals were grown by evaporation of a water solution of the diglycine hydrobromide powder. The crystals are stable in the dry condition, very soluble in water yielding free hydrobromic acid on dissolving in water and are insoluble in alcohol and ether. The average melting point is  $163^\circ - 165^\circ$ .

The orthorhombic crystals are elongated parallel to the c axis and are almost equidimensional in cross section. The typical habit of the crystals is shown in Figure I.



(2) Walter S. Frost. Bis (Amino-Acid) Derivatives. I. Diglycine Halogen Addition Products. J.A.C.S. 64 (1942) 1286.

(3) K. Kraut and F. Hartmann. Ann 133 (1865) 101.

### Experimental Method of Investigation

The colorless crystals of diglycine hydrobromide were investigated by means of the De Jong, Weissenberg, precession and rotation x-ray methods. X-ray work with the De Jong method was done by M. J. Buerger. For the determination of parameters the Weissenberg method was used for the hko and hol reflections using  $\text{CuK}\alpha$  radiation. The precession method was used for the okl reflections using  $\text{MoK}\alpha$  radiation. The Dawton<sup>4,4c</sup> method was used to determine the intensities.

### The Unit Cell

A c-axis rotation photograph gave  $c = 5.40 \text{ \AA}$ . Measurements from a c-axis Weissenberg photograph gave  $a = 8.21 \text{ \AA}$  and  $b = 18.42 \text{ \AA}$ .

The number of molecules per cell is 4 and may be calculated as,

$$Z = \frac{\text{Volume (density)}}{\text{Formula weight ( } 1.66 \times 10^{-24} \text{ )}}$$

$$= \frac{(5.40)(18.42)(8.21) \times 10^{-24} (1.941)}{231.02 ( 1.66 \times 10^{-24} )}$$

$$= 4.12$$

---

(4) Dawton, R.H.V.N. The Integration of Large Numbers of X-ray Crystal Reflections. Proc. Phys. Soc. 50 (1938) 919-925.

(4)<sub>2</sub> Klein, G.E. The Crystal Structure of Nepheline. Thesis M.I.T. (1947)

### The Space Group

The space group  $P_{2,2,2}$  was determined by M.J. Buerger using the Weissenberg photographs. Characteristic absences noted indicating this space group are:

hoo        where h odd  
oko        where k odd  
ool        where l odd

Reflection	Condition for non-extinction	Interpretation of Extinction	Symbol of symmetry element
hoo	$h = 2n$	$[00\bar{1}]$ screw axis, component $c/2$	2,
oko	$k = 2n$	$[0\bar{1}0]$ screw axis, component $b/2$	2,
ool	$l = 2n$	$[00\bar{1}]$ screw axis, component $c/2$	2,

Only general positions occur in this space group. The equi-points with the conventional origin<sup>6</sup> of this space group are:

$$xyz; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z.$$

(5) M.J.Buerger. X-Ray Crystallography, John Wiley and Sons Inc. (1942) 83.

(6) Internationale Tabellen zur bestimmung Kristallstrukturen. I (Gebruder Borntraeger), Berlin (1935).

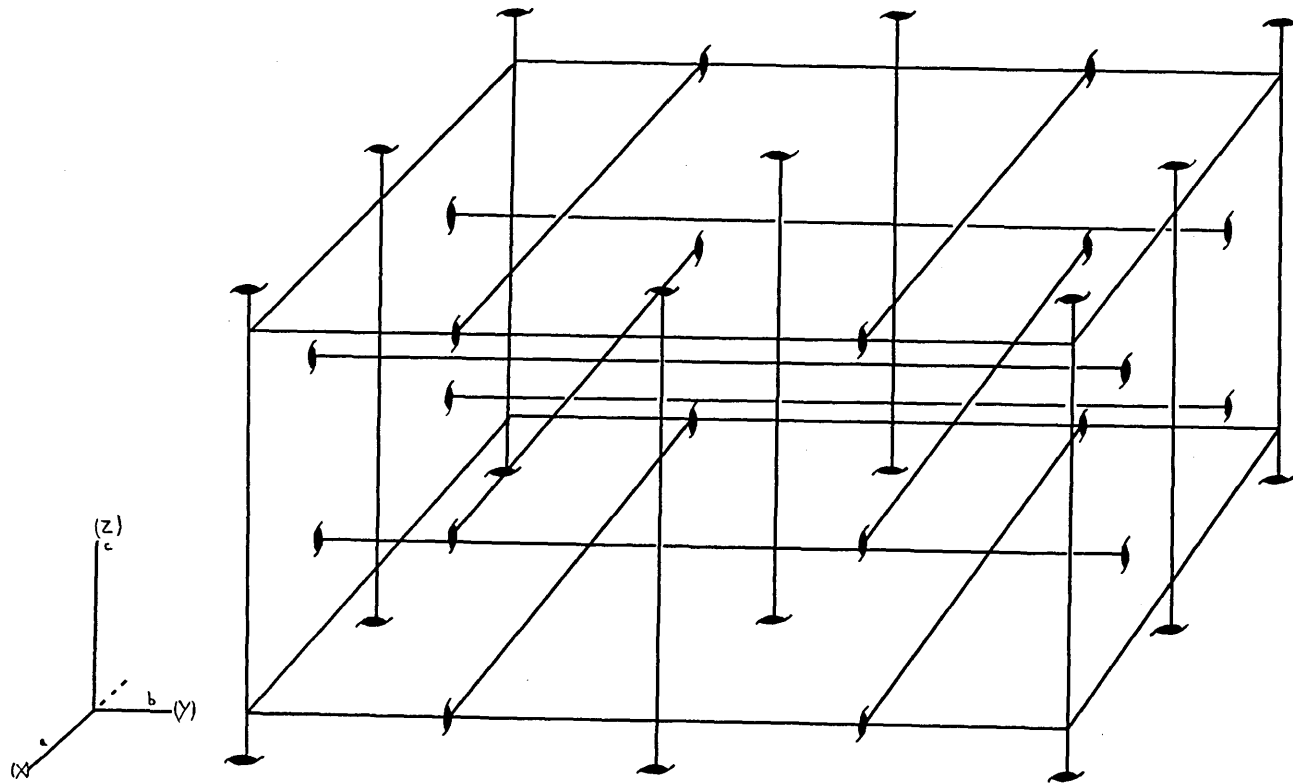
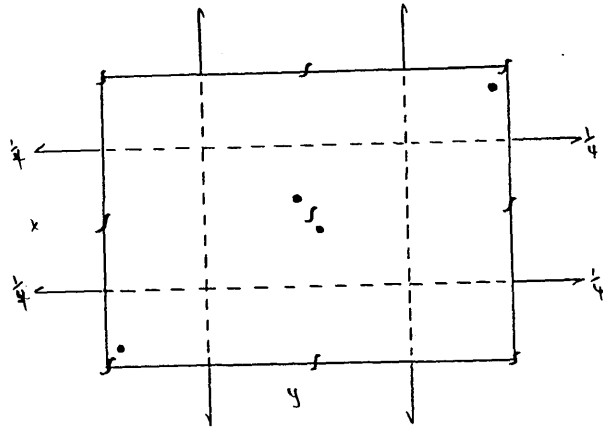
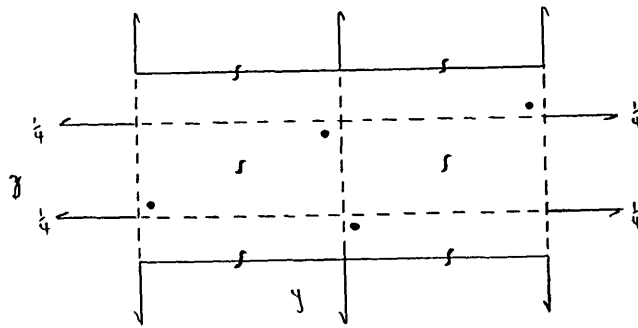


Figure 2. Perspective view of space group  $P2_12_12_1$ . The symmetry elements consist only of horizontal and vertical 2-fold screw axes.

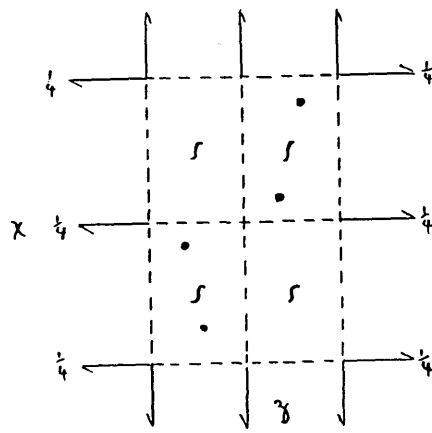




$$x, y; \frac{1}{2}x, \frac{1}{2}y; \frac{1}{2}x, \frac{1}{2}y; \frac{1}{2}x, \frac{1}{2}y; \bar{x}, \bar{y}.$$



$$y, z; \frac{1}{2}y, \frac{1}{2}z; \frac{1}{2}y, \frac{1}{2}z; \bar{y}, \bar{z}.$$



$$x, z; \frac{1}{2}x, \frac{1}{2}z; \bar{x}, \bar{z}; \frac{1}{2}x, \bar{z}.$$

Equi-points.  $x, y, z; \frac{1}{2}x, \frac{1}{2}y, \bar{z}; \frac{1}{2}x, \frac{1}{2}y, \frac{1}{2}z; \bar{x}, \bar{y}, \frac{1}{2}z.$

Figure 3

However, for this work the origin was taken on a two fold screw axis because for the prism zone reflections the B terms of the structure factor vanish. In general simplification of the structure results if the origin of the coordinates to which the positions of the atoms are referred is taken as a symmetry center of the space group. With this origin the equi-points are

$$x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z; \bar{x}, \bar{y}, \frac{1}{2}+z.$$

The space group symmetry elements are shown in Figure 2. Figure 3 indicates the derivation of the equi-points of the general position as used in this work.

#### Determination of Parameters

First Patterson Projection (xy0).

Initially  $F^2$  values from a De Jong photograph taken by M.J. Buerger were used to obtain a Patterson projection (xy0). The  $F^2$  values were obtained directly as the intensities which are usually obtained experimentally were corrected for by means of a mechanical cam. The Patterson and Tunell<sup>7</sup> method was used for all the Patterson projections for this crystal. The  $|F|^2$  values for the various hko reflections used in this summation are given in Table I.

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(7) E. L. Patterson and G. Tunell. A Method For The Summation of The Fourier Series Used in The X-ray Analysis of Crystal Structure. Amer. Mineral. 27 (1942) 655-679.

Table I.

De Jong  $|F|^2$  and F values.

Reflection	Observed $F^2$	$10 F^2 =$ $F^2$ used in series	F signs based on Br.
020	.2	2	14
040	1.2	12	34
060	.2	2	14
080	4.0	40	-64
0100	1.1	11	-34
0120	8.4	84	-92
0140	5.4	54	-74
	0.0	0	0
110	7.6	76	87
120	0.0	0	0
130	.5	5	22
140	1.2	12	-35
150	5.1	51	71
160	6.6	66	-81
170	0.0	0	0
180	8.5	85	-92
190	1.2	12	-35
1100	10.6	106	-103
1110	2.0	20	-32
1120	7.8	78	-88
1130	.5	5	-22
1140	0.0	0	0
1150	4.1	41	-64
200	.4	4	-20
210	1.2	12	-35
220	5.7	57	-75
230	5.7	57	-75
240	1.1	11	-33
250	1.8	18	-42
260	1.8	18	-42
270	15.8	158	-126
280	2.9	29	54
290	7.5	75	-87
2100	8.5	85	92
2110	1.6	16	-28
2120	.1	1	10
2130	3.9	39	-62
2140	5.3	53	73
2150	1.1	11	33
310	11.7	117	-108
320	.4	4	20
330	5.3	53	-73
340	1.3	13	36
350	3.2	32	-57

Table I (cont.-)

De Jong  $|F|^2$  and F values.

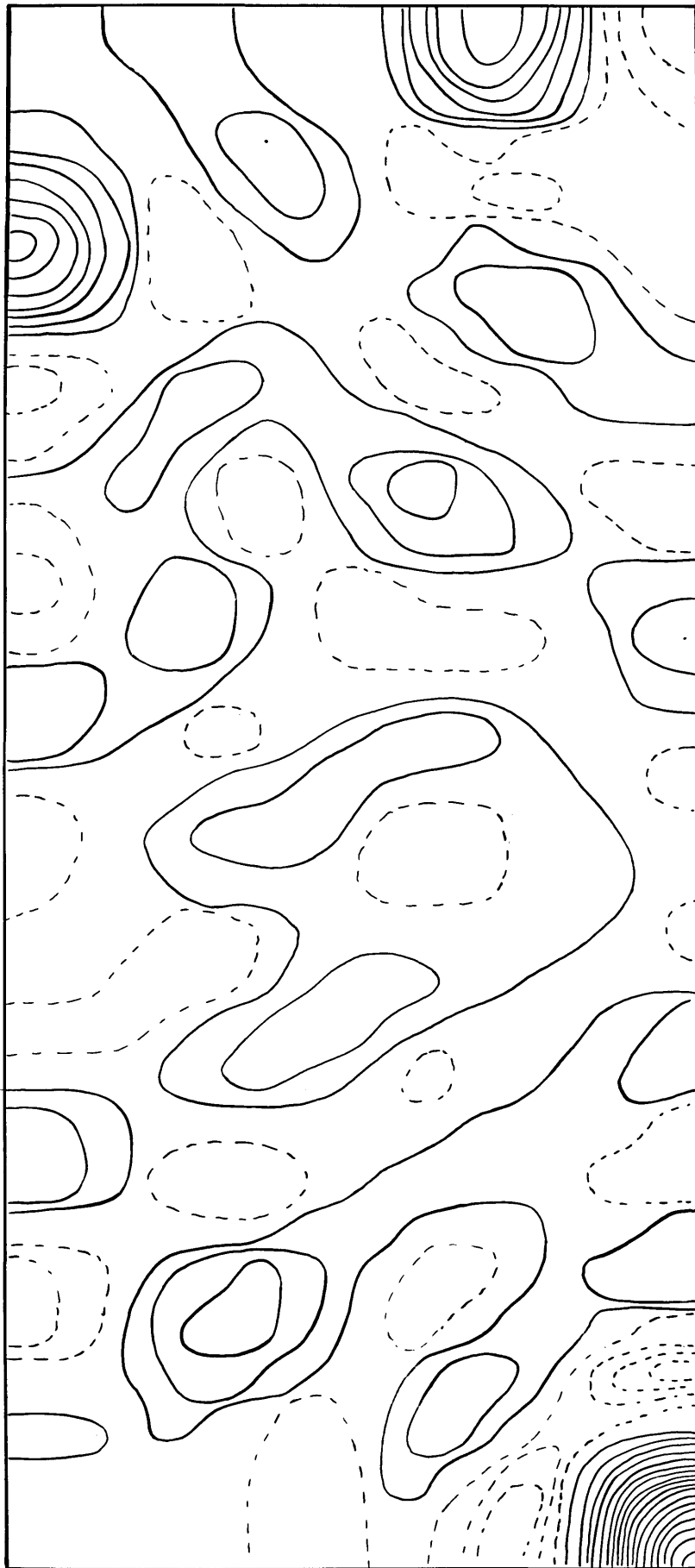
Reflection	Observed $F^2$	$10F^2$ <small><math>F^2</math> used in series</small>	F <small>signs based on Br</small>
360	.8	8	28
370	.9	9	-30
380	.4	4	20
390	.3	3	17
3I00	4.2	42	65
3I10	7.1	71	84
3I20	.3	3	17
3I30	28.0	280	167
400	.2	2	-14
410	3.9	39	62
420	.5	5	-22
430	.3	3	17
440	.4	4	-20
450	8.0	80	89
460	.9	9	-30
470	13.0	130	144
480	.4	4	20
490	9.7	97	98
4I00	0	0	0
4I10	13.6	136	117
4I20	.8	8	28
510	5.7	57	75
520	.7	7	28 18
530	11.8	118	84 107
540	2.9	29	109 54
550	.4	4	54 20
560	9.9	99	99
570	0	0	0
580	5.0	50	71
590	1.1	11	-33
5I00	2.2	22	47
5I10	4.9	49	-70
600	5.4	54	74
610	.4	4	-20
620	6.0	60	77
630	0	0	0
640	4.5	45	67
650	0	0	0
660	.8	8	28
670	5.1	51	-71

The prism zones of this space group project as the plane group  $C_{2v}$  which is shown in figure 3. Pertinent data for the interpretation of the Patterson projection of this plane group follows.<sup>8</sup>

Group	No. Equi-pts	Coordinates of equi-points	Fourier Series Data	*F <sup>z</sup> Series Data		
				Group	Wt.	Rep. Pts.
C <sub>2v</sub>	2	(a) 0 0; $\frac{1}{2}$ $\frac{1}{2}$ (b) $\frac{1}{2}$ 0; 0 $\frac{1}{2}$	$(hk) = (-1)^{h+k}(\bar{h}\bar{k})$ $=(\bar{h}\bar{k}) = (-1)^{h+k}(hk)$  h0 = 0, h odd 0k = 0, k odd	C <sub>2v</sub>	$2Z_r^z$	$2x_r + \frac{1}{2}, \frac{1}{2};$ $\frac{1}{2}, 2y_r + \frac{1}{2}.$
	4	(c) $x, y; \frac{1}{2}-x, y + \frac{1}{2};$ $\bar{x}, \bar{y}; \frac{1}{2}+x, \frac{1}{2}-y.$			$Z_r^z$	$2x_r, 2y_r.$
					$2Z_r Z_s$	$x_r - x_s, y_r - y_s;$ $x_r - x_s + \frac{1}{2},$ $y_r + y_s + \frac{1}{2};$ $x_r + x_s, y_r + y_s;$ $x_r + x_s + \frac{1}{2},$ $y_r - y_s + \frac{1}{2}.$

The Patterson projection depends on  $F^z$  and not on  $F$ . Thus it is independent of the phase constants. The distance from the origin to a peak corresponds to an interatomic distance in the crystals. The Patterson projection (xyo) of one fourth of the cell (the motif) of diglycine hydrobromide obtained is given in Figure 4. In view of the high atomic weight of bromine in the molecule undoubtedly the intense peaks 1127, 1260 and 543 represent the Br-Br interatomic distances. These points occur at the points  $2x \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 2y \frac{1}{2};$  and  $2x, 2y,$  respectively. With information from the above table the x and y parameters of the heavy bromine atom were determined as shown in the following table.

(8) A. L. Patterson. Tabulated Data For The Seventeen Plane Groups. Zeits. Krist. vol. 90 (1935) 517-542.



30	86	68	49	137	454	454	15	352	291	36	200	114	23	212	296	50	310	310	55	276	112	0	285	506	13	398	1260	767	135	50	10
29	186	73	47	108	427	445	22	327	267	45	204	127	70	201	264	56	288	299	40	251	94	23	247	471	20	833	1173	726	107	57	14
28	190	87	22	110	358	355	33	257	207	58	213	150	85	177	248	67	233	271	1	174	31	84	163	383	49	655	734	632	36	69	16
27	183	110	9	67	247	270	58	147	127	70	214	189	111	135	190	89	140	223	67	63	48	158	19	255	86	394	595	295	49	110	11
26	62	101	5	9	104	153	84	19	35	76	209	201	151	93	116	102	42	135	141	60	117	210	105	111	114	121	230	51	121	73	6
25	127	86	5	67	58	25	111	-111	46	53	186	280	197	40	26	104	60	124	223	174	146	211	198	31	123	121	34	125	139	40	31
24	78	63	8	147	224	104	129	225	99	3	135	318	247	5	67	87	135	77	285	246	125	151	235	141	107	286	302	221	108	7	64
23	43	57	15	218	370	225	138	307	126	66	67	331	281	37	161	55	191	37	321	283	57	36	208	213	72	363	394	210	17	68	91
22	63	76	11	251	472	315	137	359	131	149	23	305	287	92	267	14	203	10	331	275	39	107	139	253	25	363	356	127	81	96	59
21	75	102	39	262	541	396	100	373	121	214	100	267	285	108	320	52	222	50	273	205	158	246	51	247	24	296	275	30	209	124	35
20	142	169	102	222	543	432	63	360	112	263	114	182	238	137	369	116	201	93	190	114	246	333	12	224	53	220	151	158	274	85	58
19	226	252	183	135	479	427	19	318	108	246	257	75	77	164	384	159	166	138	3	11	287	344	44	182	45	157	43	249	281	2	188
18	306	323	257	34	368	350	24	261	116	235	297	45	65	165	360	191	116	173	49	85	273	279	32	129	8	124	20	268	225	113	312
17	321	336	273	71	222	298	60	198	134	167	307	162	32	147	305	213	45	185	164	156	197	133	24	72	54	124	36	219	143	208	397
16	295	300	220	139	70	185	81	123	152	72	276	249	109	102	210	216	38	174	257	205	84	43	96	7	127	140	10	213	6	264	405
15	218	202	173	152	66	57	79	60	159	30	225	307	162	29	91	202	123	143	322	223	53	232	163	56	193	151	30	0	100	244	306
14	127	81	26	99	175	80	64	19	151	127	144	332	189	52	35	184	211	86	357	224	186	395	197	129	236	126	57	125	184	139	91
13	173	24	120	12	218	189	23	95	118	180	70	369	182	116	126	167	276	40	356	197	280	480	190	211	227	77	74	220	208	30	183
12	96	54	247	102	219	249	15	110	81	222	114	258	160	163	188	149	314	1	344	178	338	500	137	230	183	21	55	290	207	236	500
11	226	8	307	217	165	300	52	138	29	238	91	194	154	148	188	143	312	2	336	140	563	476	71	252	102	130	37	355	193	444	812
10	318	149	280	275	169	306	74	161	39	199	130	126	131	121	162	128	283	11	311	114	338	383	29	259	10	264	9	391	184	549	930
9	635	345	163	281	30	255	86	157	86	161	166	62	127	146	92	122	218	118	295	186	290	267	114	229	118	355	16	431	185	651	1127
8	795	525	16	203	16	183	76	143	122	96	155	22	142	58	6	124	150	82	264	78	227	158	166	179	208	391	10	469	224	609	1075
7	742	559	174	88	63	71	46	112	151	39	177	13	120	116	66	75	36	144	236	63	144	45	189	110	372	391	33	464	234	511	724
6	464	437	306	86	56	37	2	64	122	22	96	39	108	159	102	37	46	163	88	45	62	50	192	40	286	317	88	446	254	337	658
5	69	116	372	282	19	139	54	27	104	67	27	50	72	157	104	0	102	125	112	26	21	135	126	25	262	201	147	394	248	130	327
4	804	370	352	476	50	225	109	20	65	142	42	57	9	106	66	14	130	84	3	3	100	206	143	74	199	62	196	300	224	82	20
3	1631	943	268	641	126	292	154	64	37	196	112	59	61	28	14	125	140	4	105	37	163	260	115	106	122	76	232	207	168	259	329
2	2179	1477	150	765	198	338	193	92	8	233	16	69	133	62	75	169	127	78	207	61	220	307	95	126	49	196	350	101	110	391	573
1	2912	1860	56	843	332	218	110	14	263	207	71	188	131	135	200	111	137	272	77	251	331	32	128	6	274	257	29	66	474	728	
0	3078	1995	25	870	268	371	226	119	12	271	219	73	205	155	157	210	165	163	301	85	263	341	76	131	24	303	264	6	51	501	782
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30

y

Figure 4

1" = 1 Å

Peak	$2x+\frac{1}{2}$	$2y+\frac{1}{2}$	$2x$	$2y$	$x$	$y$
543			$\frac{20.5}{60}$	$\frac{4.35}{60}$	.171	.036
1127	$\frac{51.35}{60}$				.178	
1260		$\frac{34.1}{60}$				.0342

Preliminary Electron Density  $\rho(x,y,z)$

In view of the high atomic scattering power ( $f$ ) of bromine compared with that of the other atoms oxygen, nitrogen and carbon in the molecule it was assumed that the heavy bromine determined the phases. Since in projection the crystal is centrosymmetrical the phases will be either 0 or  $\pi$  i.e. + or -.

For the space group  $P_{2,2,2}, D_2^4$ , choosing the origin at a symmetry center the components of the structure factor for an atom in the general position are as follows:

$$A = 4 \left\{ \cos 2\pi(hx+ky+lz) + \cos 2\pi\left(h\left[\frac{1}{2}+x\right]+k\left[\frac{1}{2}-y\right]-lz\right) + \cos 2\pi\left(h\left[\frac{1}{2}-x\right]+k\left[\frac{1}{2}+y\right]+l\left[\frac{1}{2}-z\right]\right) + \cos 2\pi(-hx-ky+l\left[\frac{1}{2}+z\right]) \right\} .$$

$$B = 4 \left\{ \sin 2\pi(hx+ky+lz) + \sin 2\pi\left(h\left[\frac{1}{2}+x\right]+k\left[\frac{1}{2}-y\right]-lz\right) + \sin 2\pi\left(h\left[\frac{1}{2}-x\right]+k\left[\frac{1}{2}+y\right]+l\left[\frac{1}{2}-z\right]\right) + \sin 2\pi(-hx-ky+l\left[\frac{1}{2}+z\right]) \right\} .$$

For the various reflections these may be reduced to:

Ref.	A	A	B
	$h+k = 2n$	$h+k = 2n+1$	
$hko$	$4\cos 2\pi hx \cos 2\pi ky$	$-4\sin 2\pi hx \sin 2\pi ky$	0
$\bar{h}ko$	$4\cos 2\pi kx \cos 2\pi ky$	$4\sin 2\pi kx \sin 2\pi ky$	0
	$k+l = 2n$	$k+l = 2n+1$	
$okl$	$4\cos 2\pi ky \cos 2\pi lz$	$-4\sin 2\pi ky \sin 2\pi lz$	0
$o\bar{k}l$	$4\cos 2\pi ky \cos 2\pi lz$	$4\sin 2\pi ky \sin 2\pi lz$	0
	$h+l = 2n$	$h+l = 2n+1$	
$hol$	$4\cos 2\pi hx \cos 2\pi lz$	$-4\sin 2\pi hx \sin 2\pi lz$	0
$h\bar{o}l$	$4\cos 2\pi hx \cos 2\pi lz$	$4\sin 2\pi hx \sin 2\pi lz$	0



## Structure Factor Calculations

Equi-points:  $x, y; \frac{1}{2}x, \frac{1}{2}y; \frac{1}{2}x, \frac{1}{2}y; \bar{x}, \bar{y}$ .

hko

$$A = A_1 + A_2 + A_3 + A_4 \quad A_1 = \cos 2\pi(hx + ky + lz)$$

$$A = \cos 2\pi(hx + ky) + \cos 2\pi[h(\frac{1}{2}x) + k(\frac{1}{2}y)] + \cos 2\pi[h(\frac{1}{2}x) + k(\frac{1}{2}y)] + \cos 2\pi(-hx - ky).$$

$$\cos B = \cos A \quad \cos A + \cos B = 2 \cos \frac{1}{2}(A+B) \cos \frac{1}{2}(A-B)$$

$$A = 2 \cos 2\pi(hx + ky) + 2 \cos 2\pi \frac{1}{2}(\frac{1}{2}x + \frac{1}{2}x - \frac{1}{2}y - \frac{1}{2}y + \frac{1}{2}x - \frac{1}{2}x + \frac{1}{2}y + \frac{1}{2}y) \cos 2\pi \frac{1}{2}[\frac{1}{2}x + \frac{1}{2}x + \frac{1}{2}y - \frac{1}{2}y - \frac{1}{2}x + \frac{1}{2}x - \frac{1}{2}y - \frac{1}{2}y].$$

$$A = 2 \cos 2\pi(hx + ky) + 2 \cos 2\pi(\frac{1}{2}x + \frac{1}{2}y) \cos 2\pi(hx - ky).$$

if  $h+k = 2n \quad \cos \pi(h+k) = +1$

$$A = 2 \cos 2\pi(hx + ky) + \cos 2\pi(hx - ky)$$

$$A = 4 \cos 2\pi \frac{1}{2}(hx + ky + hx - ky) \cos 2\pi \frac{1}{2}(hx + ky - hx + ky)$$

$$A = 4 \cos 2\pi hx \cos 2\pi ky.$$

if  $h+k = 2n+1 \quad \cos \pi(h+k) = -1$

$$A = 2 \cos 2\pi(hx + ky) - 2 \cos 2\pi(hx - ky)$$

$$\cos A - \cos B = -2 \sin \frac{1}{2}(A+B) \sin \frac{1}{2}(A-B)$$

$$A = -4 \sin 2\pi \frac{1}{2}(hx + ky + hx - ky) \sin 2\pi \frac{1}{2}(hx + ky - hx + ky)$$

$$A = -4 \sin 2\pi hx \sin 2\pi ky$$

$$B = B_1 + B_2 + B_3 + B_4$$

$$B_1 = \sin 2\pi(hx + ky + lz)$$

$$B = \sin 2\pi(hx + ky) + \sin 2\pi[h(\frac{1}{2}x) + k(\frac{1}{2}y)] + \sin 2\pi[h(\frac{1}{2}x) + k(\frac{1}{2}y)] + \sin 2\pi(-hx - ky).$$

$$\sin A = -\sin A \quad \therefore \sin 2\pi(-hx - ky) = -\sin 2\pi(hx + ky)$$

$$\sin x + \sin y = 2 \sin \frac{1}{2}(x+y) \cos \frac{1}{2}(x-y)$$

$$B = 2 \sin 2\pi \frac{1}{2}[h(\frac{1}{2}x) + k(\frac{1}{2}y) + h(\frac{1}{2}x) + k(\frac{1}{2}y)] \cos 2\pi \frac{1}{2}[h(\frac{1}{2}x) + k(\frac{1}{2}y) - h(\frac{1}{2}x) - k(\frac{1}{2}y)].$$

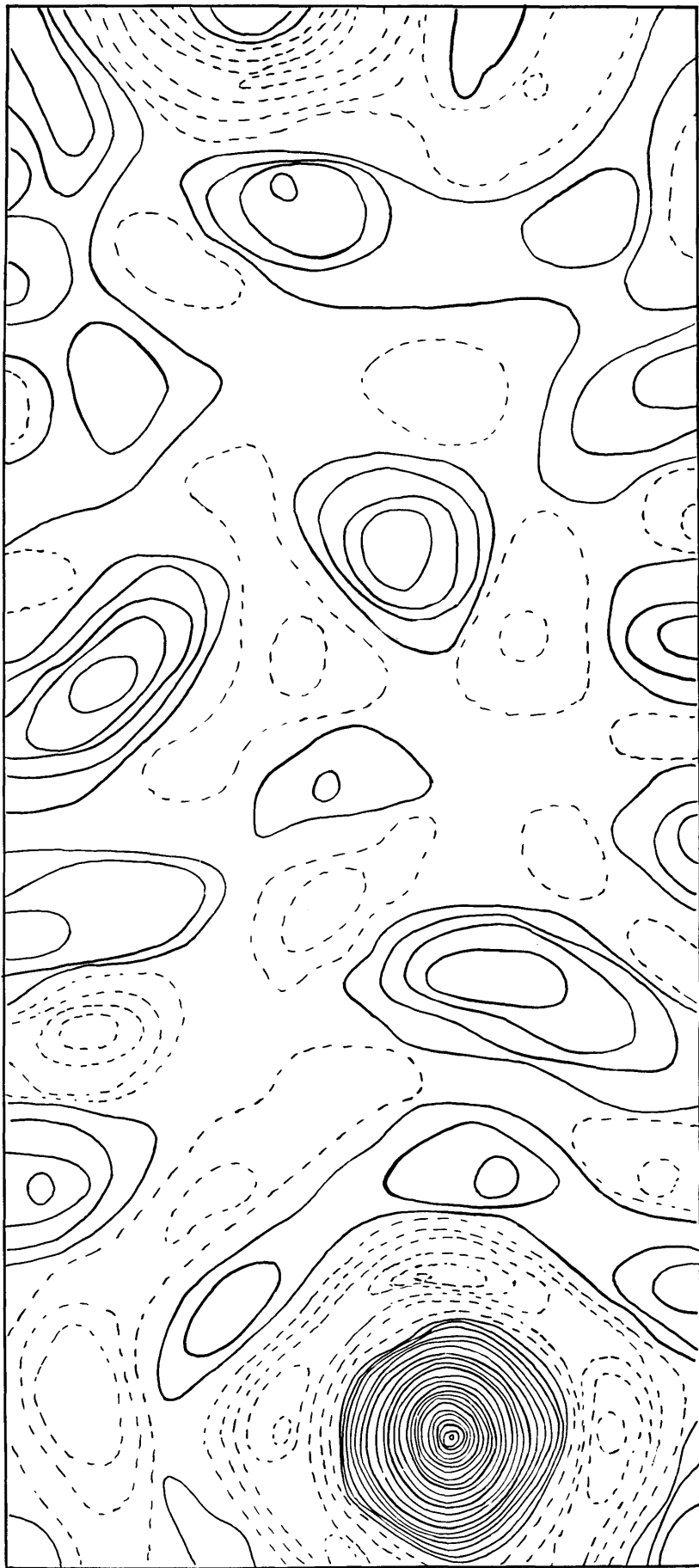
$$B = 2 \sin 2\pi \frac{1}{2}[h+k] \cos 2\pi \frac{1}{2}[2hx - 2ky].$$

if  $h+k = 2n \quad \sin \pi(h+k) = 0$

$$B = 0$$

if  $h+k = 2n+1 \quad \sin \pi(h+k) = 0$

$$B = 0$$



26	26	31	130	177	176	279	116	291	153	189	264	93	256	81	122	36	290	199	94	145	34	65	111	157	44	209	134	7	18	187	262
25	6	163	244	309	270	134	120	305	144	249	357	36	240	130	104	53	356	216	12	178	27	55	440	79	68	186	144	98	188	255	232
24	64	192	329	372	319	173	83	280	129	251	431	108	217	127	90	50	360	393	59	154	73	45	33	24	47	137	97	126	255	290	94
23	136	252	365	380	312	192	31	226	116	274	455	166	183	149	68	25	360	441	161	90	77	38	88	102	111	62	16	236	194	84	
22	184	259	528	373	251	190	45	132	86	233	426	187	164	166	57	26	269	448	252	9	62	23	112	148	103	16	25	29	146	46	236
21	197	264	234	39	148	165	127	18	50	170	350	172	148	175	146	83	192	407	318	84	38	6	110	160	75	92	150	24	48	106	313
20	137	122	141	75	27	108	188	98	4	97	249	177	118	169	46	135	78	327	322	141	21	27	74	140	36	150	143	57	45	226	293
19	46	63	68	6	74	40	214	194	57	50	152	98	101	146	36	164	20	220	289	156	19	60	27	90	14	173	160	42	104	207	186
18	32	7	90	13	111	34	187	251	109	15	61	55	70	122	74	163	109	78	178	99	57	111	25	39	49	158	85	31	110	335	34
17	66	40	178	89	117	114	117	259	155	21	16	52	5	48	15	127	131	28	57	24	94	125	49	1	75	174	3	115	108	360	96
16	33	171	331	238	46	120	34	220	191	43	10	74	81	24	7	67	128	128	81	72	120	131	67	26	82	112	108	210	89	410	165
15	63	281	468	394	107	141	46	158	195	79	120	90	153	99	3	3	99	199	189	138	104	113	55	34	80	25	191	275	100	419	131
14	198	386	554	489	85	85	97	81	187	118	41	100	201	188	6	61	60	232	251	154	100	64	45	41	67	11	249	309	80	458	18
13	315	384	454	455	287	38	84	12	149	129	40	75	206	211	30	84	36	237	240	91	16	13	21	50	72	25	249	288	84	478	128
12	408	262	165	247	301	353	43	36	114	152	58	55	183	215	39	107	7	187	187	7	116	72	18	60	49	59	249	265	93	488	302
11	400	32	314	105	278	305	46	75	65	150	47	11	115	200	64	90	14	146	103	124	324	85	57	65	57	57	265	265	92	408	400
10	305	442	92	555	183	247	147	94	16	176	12	95	21	143	81	57	13	103	17	235	328	156	56	122	59	49	157	131	79	344	408
9	129	902	836	1006	83	573	260	102	35	107	24	153	84	119	112	8	14	83	46	317	392	171	93	164	76	31	81	52	62	208	315
8	18	1260	2020	1381	4	1271	299	125	65	112	33	252	169	64	109	3	6	70	55	298	355	122	135	187	67	41	47	13	70	108	198
7	131	475	2289	1576	107	533	298	164	97	97	56	306	231	25	93	6	11	87	15	236	280	73	155	184	152	47	21	70	100	41	63
6	165	1496	2289	1548	112	564	248	196	105	91	78	338	257	14	94	9	16	106	61	110	168	21	149	166	40	84	14	108	125	22	35
5	96	1242	1928	1305	47	520	161	223	99	85	102	353	249	26	99	5	75	100	145	27	46	17	119	125	23	72	25	119	162	32	66
4	54	843	1390	905	59	428	6	219	69	71	141	355	226	46	99	3	23	162	244	139	55	39	71	71	1	94	69	87	182	89	32
3	186	279	761	448	160	366	16	190	29	40	190	340	157	88	110	12	26	158	231	198	108	30	3	22	0	86	102	42	186	255	109
2	293	188	171	27	289	190	72	122	40	19	219	307	98	127	112	19	44	145	190	183	113	3	66	28	76	137	21	153	192	133	
1	313	348	286	290	266	79	93	26	102	8	254	246	22	147	102	32	68	115	120	122	90	20	114	72	1	57	156	90	84	186	187
0	236	458	930	447	237	16	87	76	154	41	248	201	44	136	65	46	95	78	16	39	72	29	152	120	9	34	149	135	16	136	184
	84	742	528	744	240	110	67	160	190	66	245	118	89	91	4	44	120	35	93	42	65	10	170	160	29	8	108	126	25	66	136
	94	310	1029	336	33	165	37	210	199	65	187	154	124	13	92	26	134	9	181	86	99	45	169	206	55	57	35	68	27	12	62
	232	5	206	168	76	224	32	209	168	67	117	74	130	82	192	5	132	64	238	92	187	115	160	255	92	60	66	44	26	9	6
	282	187	18	9	174	209	44	157	111	65	34	145	94	199	290	36	122	61	256	43	261	189	153	241	116	99	126	177	134	31	26

1" = 1 Å

Figure 5. Electron Density  $\rho(x,y)$

A sample calculation of the determination of the phases is given below.

Reflection	Parameters		Structure Factor /m		Phase
	x	y	$\cos 2\pi hx$	$\cos 2\pi ky$	
220	.178	.034	-.618	.910	--
130	.178	.034	.437	.802	+

With the phase constants determined in the above manner and using the  $F'$  values of Table I as obtained from the De Jong photograph an electron density map  $\rho(x,y,z)$  was made. The electron density map  $\rho(x,y,z)$  of  $\frac{1}{8}$  of the cell, the motif, is given in Figure 5. With 4 molecules per cell the position of 4 carbons, 1 bromine, 2 nitrogens and 4 oxygens (i.e. 11 positions) should appear in the electron density map of  $\frac{1}{4}$  of the cell. In the electron density map obtained the bromine appeared where it was put in the structure. However, many more than 10 other peaks are seen to occur indicating quite some error.

#### Second Approximation-

Due to the error just indicated it was necessary to obtain more x-ray data. This was done by means of the Weissenberg method for the hko and hol reflections using  $\text{CuK}\alpha$  radiation and the precession method for okl reflections using  $\text{MoK}\alpha$  radiation. The intensities were determined by the Dawson method and corrections to obtain  $|F|^2$  are given below. Since intensities are obtained experimentally and  $F'$ 's or their squares are used as coefficients of a Fourier series for electron density maps and Patterson projections it is necessary to compute  $F'$ 's. As  $\frac{1}{L\rho}$  is a function of  $\sin \theta$

( $\frac{1}{L_p} = \sin 2\theta \frac{2}{1 + \cos^2 \theta}$ ),  $\sin \theta$  must be calculated for all reflections. This

was done by means of the formula

$$\sin \theta = \frac{1}{2} \sqrt{a^*{}^2 h^2 + b^*{}^2 k^2 + c^*{}^2 l^2}$$

$$a^* = \frac{\lambda}{a} = \frac{1.539}{8.21} = .18745$$

$$b^* = \frac{\lambda}{b} = \frac{1.539}{18.42} = .08355$$

$$c^* = \frac{\lambda}{c} = \frac{1.539}{5.40} = .2850$$

$I \sim L_p F^2$

Reflection hkl	$\sin \theta$ $c$	$\frac{1}{L_p}$ <sup>(9)</sup>	I Average	$F^2 =$ $I(\frac{1}{L_p})$	$4F^2 =$ F <sup>2</sup> fused in series	$20F^2 =$ Fused in Series <small>signs based on Br</small>
020	.0835	.1688	14.95	2.52	10	32
040	.1671	.3482	15.6	5.43	22	47
060	.2506	.5500	.55	.30	1	11
080	.3342	.7861	5.83	4.58	18	-43
0100	.4177	1.0661	.33	.35	1	-12
0120	.5013	1.3910	5.63	7.83	31	-56
0140	.5848	1.7252	.93	1.60	6	-25
0160	.6684	1.9664	.85	1.67	7	-26
0180	.7519	1.9495	.10	.19	1	-19
0200	.8355	1.5873	.28	.44	2	-13
0220	.9190	.9823	.10	.098	0	6
110	.1026	.2085	4.21	.88	4	19
130	.1565	.3246	5.75	1.87	7	27
140	.1915	.4046	9.43	3.82	15	-39
150	.2290	.4950	29.59	14.65	59	77
160	.2675	.5945	25.73	15.30	61	-78
170	.3071	.7050	.21	.15	1	-8
180	.3470	.8258	14.35	11.85	47	-69
190	.3875	.9593	.90	.86	3	-19
1100	.4280	1.1041	6.58	7.26	29	-54
1110	.4690	1.2612	.49	.62	2	-16
1120	.5100	1.4265	1.71	2.44	10	-31
1130	.5500	1.5893	.05	.08	0	-6
1150	.6325	1.8843	.38	.72	3	-17
1160	.6799	1.9832	.11	.22	1	9
1170	.7163	1.9979	.13	.26	1	-10
1180	.7576	1.9356	.51	.99	4	20
1190	.7987	1.7865	.08	.14	1	-7
1200	.8407	1.5552	.81	1.26	5	22
1220	.9238	0.9432	.32	.30	1	11

(9) M.J. Buerger and G.E. Klein. Correction of X-ray Diffraction Intensities for Lorentz and Polarization Factors. J. App. Phys. Vol. 16 No. 7 July 1945 408-418.

Reflection hko	$\sin^2 \alpha$	$\frac{1}{L_p}$	I Average	$F^2 =$ $I(\frac{1}{L_p})$	$4F^2$	$20 F$
200	.1874	.3950	1.33	.53	2	-15
210	.1920	.4057	6.19	2.51	10	-32
220	.2050	.4365	44.12	19.26	77	-88
230	.2255	.4864	26.13	12.71	51	-71
240	.2510	.5510	2.20	1.21	5	-22
250	.2805	.6299	2.67	1.68	7	-26
260	.3130	.7220	1.62	1.17	5	-22
270	.3474	.8268	20.91	17.29	69	-83
280	.3838	.9443	1.60	1.51	6	25
290	.420	1.0746	3.37	3.62	14	-38
2100	.4579	1.2178	2.94	3.58	14	38
2110	.4964	1.3711	.24	.33	1	-11
2130	.5745	1.6862	.41	.69	3	-17
2140	.614	1.8282	.47	.86	3	19
2150	.6540	1.9387	.11	.21	1	9
2160	.6942	1.9962	.14	.28	1	11
2180	.7799	1.8653	.29	.54	2	15
2190	.8155	1.7025	.22	.37	1	12
2210	.8981	1.1559	.44	.51	2	14
2230	.9789	.4348	.92	.40	2	13
310	.2840	.6394	37.86	24.21	97	-98
320	.2933	.6654	.36	.24	1	10
330	.3078	.7071	10.00	7.07	28	-53
340	.3270	.7639	1.21	.92	4	19
350	.3503	.8362	2.65	2.22	9	-30
360	.3766	.9220	.29	.27	1	10
370	.4057	1.0230	.30	.31	1	-11
3100	.5037	1.4007	.76	1.06	4	21
3110	.5386	1.5433	1.10	1.70	7	26
3130	.6115	1.8199	3.00	5.46	22	47
3150	.6868	1.9906	.43	.86	3	19
3170	.7638	1.9189	.73	1.40	6	24
400	.3749	.9163	.25	.23	1	-10
410	.3772	.9241	5.23	4.83	19	44
420	.3840	.9470	.36	.34	1	-12
430	.3953	.9864	.16	.16	1	8
440	.4105	1.0402	.05	.26	1	-10
450	.4292	1.1085	4.40	4.88	19	44
460	.4509	1.1906	.14	.17	1	-8
470	.4755	1.2870	4.66	6.00	24	49
480	.5015	1.3918	.06	.08	0	6
490	.5305	1.5103	1.85	2.79	11	33
4110	.5930	1.7556	1.59	2.79	11	33
4120	.6260	1.8657	.18	.34	1	12
4170	.8030	1.7662	.36	.64	3	-16
4180	.8402	1.5583	.10	.16	1	8
4190	.8778	1.3011	.48	.64	3	-16
4210	.9540	.6840	.58	.40	2	-13

Reflection h k l	$\sin \theta$	$\chi^{(h)}$ LP	I Average	$F^2$	$4F^2$	$20F$
510	.4795	I.2672	4.07	5.12	20	45
520	.4760	I.2890	.14	.18	I	8
530	.4852	I.3258	4.87	6.46	26	51
540	.4975	I.3755	.71	.98	4	20
550	.5130	I.4386	0	0	0	0
560	.5315	I.5144	I.88	2.85	11	34
580	.5755	I.6900	.64	I.08	4	21
590	.6008	I.7809	.19	.34	I	-12
5100	.6277	I.8707	.28	.52	2	14
5110	.6560	I.9429	.49	.95	4	-19
5130	.7173	I.9975	.24	.48	2	-14
5150	.7852	I.8449	.10	.18	I	-8
5190	.9217	.9604	.39	.37	I	-12
5200	.9579	.6481	.75	.49	2	-14
600	.5624	I.6391	I.22	2.00	8	28
610	.5639	I.6449	.08	.13	I	-7
620	.5685	I.6590	I.20	I.99	8	28
630	.5867	I.7323	.64	I.11	4	21
660	.6156	I.8332	.10	.18	I	8
670	.6338	I.8880	.55	I.04	4	-20
690	.6765	I.9786	.19	.38	2	-12
6100	.7006	I.9990	.18	.36	I	-12
6120	.7536	I.9457	.48	.93	4	-19
6130	.7818	I.8582	.05	.09	0	-6
6140	.8114	I.7241	.74	I.28	5	-23
6160	.8735	I.3323	.45	.60	2	-15
6170	.9058	I.0882	.18	.20	I	9
6180	.9390	.8163	.45	.37	I	-12
6190	.9728	.5016	.13	.07	0	5
720	.6614	I.9539	.66	I.29	5	-23
740	.6770	I.9794	.64	I.27	5	-23
760 <sub>v</sub>	.7023	I.9996	.79	I.58	5	-25
780	.7364	I.9788	.40	.79	3	-18
7100	.7778	I.8730	.53	.99	4	-20
7120	.8257	I.6457	.21	.35	I	-12
7140	.8789	I.2930	.01	.01	0	2
800	.7498	I.9544	.45	.88	4	-19
820	.7544	I.9439	.26	.51	2	-14
840	.7682	I.9053	.16	.30	I	-11
850	.7780	I.8723	.20	.37	I	-12
860	.7906	I.8226	.10	.18	I	-8
870	.8061	I.7511	.30	.53	2	-15
890	.8388	I.5669	.01	.02	0	-3
8100	.8582	I.5070	.16	.24	I	10
8120	.8794	I.2894	.02	.03	0	-3
8120	.9019	I.1187	.23	.26	I	10
8140	.9509	.7121	.92	.66	3	16

Reflection hkd	$\sin \theta$ cu	$\frac{1}{hP}$	I Average	$F^2$	$4F^2$	$20F$
910	.8445	1.5307	.50	.76	3	-18
930	.8528	1.4764	.13	.19	1	-9
940	.8599	1.4283	.15	.21	1	9
950	.8690	1.3646	.06	.08	0	-6
960	.8800	1.2850	.12	.15	1	8
980	.9073	1.0764	.23	.25	1	10
990	.9235	.9456	.10	.09	0	6
9110	.9606	.6227	.20	.12	1	7
I000	----	<del>1.5307</del>	0	0	0	0
I010	.9382	.8228	.05	.04	0	4
I030	.9451	.7630	.24	.18	1	8
I050	.9602	.6266	.65	.41	2	13
I070	.9818	.4008	.65	.26	1	10

## hol Reflections

Reflection hol	$\sin \theta$ cu	$\frac{1}{hP}$ ( $\frac{1}{hP}$ )	I Average	$F^2$	$4F^2$	$20F$
002	.2850	.6423	28.97	18.61	74.44	86
004	.5700	1.6686	.97	1.62	6.48	-25
006	.8550	1.4618	.83	1.21	4.84	-22
I01	.1706	.3564	13.15	4.69	18.76	43
201	.2355	.5113	40.67	20.79	83.16	-91
301	.3152	.7288	2.52	1.84	7.36	27
401	.4011	1.0067	.31	.31	1.24	-11
501	.4899	1.3448	1.71	2.30	9.20	-30
701	.6714	1.9712	.90	1.77	7.08	-27
901	.8551	1.4611	.20	.29	1.16	-11
I02	.3000	.6845	4.29	2.94	11.76	-34
202	.3411	.8074	1.58	1.28	5.12	23
302	.4004	1.0042	2.93	2.94	11.76	-34
502	.5485	1.5833	1.54	2.44	9.76	-31
602	.6305	1.8787	.10	.19	.36	-9
802	.8022	1.7700	.13	.23	.92	-10
902	.8904	1.2071	.33	.40	1.60	13
203	.4668	1.2587	6.11	7.65	30.60	-55
403	.5686	1.6634	1.76	2.93	11.72	-34
503	.6343	1.8894	.10	.19	.76	-9
803	.8631	1.4062	.025	.035	.14	4



Reflection hol	$\sin^2$	$\frac{1}{h^2}$	I Average	$F^2$	$4F^2$	$20F$
104	.5776	1.6980	.14	.24	.96	-10
204	.6004	1.7820	.18	.32	1.28	-11
304	.6549	1.9404	1.36	2.64	10.56	-32
404	.6822	1.9859	.09	.18	.72	8
504	.7379	1.9764	.33	.65	2.60	-16
604	.8007	1.7773	0	0	0	0
804	.9680	.5510	00	0	0	0
105	.7186	1.9970	.43	.86	3.44	-19
205	.7367	1.9783	.05	.10	.40	-6
405	.8051	1.7560	.05	.09	.36	-6
505	.8523	1.4797	.04	.06	.24	5
605	.9078	1.0726	.03	.03	.12	-3
705	.9685	.5459	.71	.39	1.56	12
200	.1875	.3952	.53	.21	.84	9
400	.3749	.9163	.15	.14	.56	-7
600	.5624	1.6391	1.05	1.72	6.88	-26
800	.7498	1.9544	.53	1.04	4.16	-20
106	.8601	1.4269	0	0	0	0
206	.8753	1.3193	.28	.37	1.48	-12
306	.9005	1.1296	0	0	0	0

## okl Reflections

Reflection o kl	$\sin^2$ $m_0$	$\frac{1}{h^2}$ P	$\frac{1}{k^2}$ graphically	I Average	$F^2$	$15F^2$	$16F$
020	.0385	1.0030			1.32	2	-18
040	.0770	1.0119	.74	3.36	2.52	4	24
060	.1154	1.0270	1.10	.67	.76	1	-14
080	.1540	1.0485	1.40	1.88	2.76	4	-26
0100	.1924	1.0767	1.72	.88	1.63	2	20
0120	.2309	1.1122	1.97	4.58	10.04	15	-50
0140	.2694	1.1555	2.18	2.07	5.21	8	36
0160	.3079	1.2072	2.31	1.30	3.63	5	-28
0180	.3464	1.2677	2.38	.50	1.51	2	20
0200	.3849	1.3376	2.32	.81	2.51	4	-26
031	.0875	1.0154	.85	12.28	10.55	16	-52
041	.1124	1.0256	.95	17.43	16.98	25	64
051	.1165	1.0275	1.08	2.43	2.70	4	26
061	.1328	1.0360	1.24	27.79	35.70	54	-96
071	.1498	1.0459	1.37	4.32	6.78	10	-47
081	.1674	1.0584	1.51	.97	1.55	2	20

Reflection $hkl$	$\sin \theta$ $m\lambda$	I/p	$I/L^{(10)}$ I/L	I	$F^2$	$1.5 F^2$	(C.F)
091	.1852	1.0710	1.65	.55	.97	1	16
0101	.2033	1.0861	1.78	2.43	4.70	7	-35
0130	.2587	1.1427	2.11	.06	.15	.22	6
0180	.3524	1.2780	2.37	.72	2.18	3	24
0191	.3714	1.3125	2.35	.67	2.07	3	23
0201	.3904	1.3483	2.28	.76	2.34	4	-24
0211	.4093	1.3868	2.19	.40	1.22	2	-16
0221	.4284	1.4278	2.06	.70	2.06	3	23
002	.1313	1.0350	1.22	7.18	9.07	14	-48
012	.1327	1.0359	1.22	7.17	9.06	14	-48
022	.1368	1.0381	1.23	2.30	2.94	4	27
032	.1435	1.0420	1.31	12.42	16.95	25	64
092	.2173	1.0989	1.88	2.15	4.42	7	32
0112	.2488	1.1314	2.06	.70	1.63	2	-20
0120	.2656	1.1509	2.16	.80	1.99	3	23
0132	.2824	1.1721	2.22	.48	1.25	2	18
0142	.2997	1.1955	2.29	.61	1.67	3	-21
0152	.3170	1.2207	2.34	1.20	3.43	5	-30
0162	.3346	1.2482	2.37	.22	.63	1	13
0172	.3524	1.2780	2.38	.13	.40	1	10
0192	.3884	1.3444	2.29	.25	.77	1	-14
013	.1979	1.0813	1.73	.62	1.16	2	-17
033	.2052	1.0877	1.79	2.68	5.22	8	37
053	.2192	1.1007	1.89	3.33	6.93	10	-42
073	.2384	1.1201	2.02	3.20	7.24	11	43
093	.2621	1.1468	2.13	2.23	5.45	8	-37
0113	.2891	1.1809	2.25	.13	.35	1	9
0193	.4153	1.3995	2.17	.47	1.43	2	-19
0213	.4494	1.4751	1.83	.53	1.43	2	19
004	.2626	1.1474	2.13	1.43	3.50	5	-30
014	.2631	1.1479	2.13	1.85	4.52	7	34
034	.2688	1.1548	2.17	1.69	4.24	6	-33
064	.2868	1.1778	2.24	.18	.48	1	11
084	.3042	1.2018	2.30	.20	.55	1	12
094	.3144	1.2167	2.33	.03	.09	0	-5
0114	.3372	1.2524	2.36	.19	.56	1	12
0124	.3497	1.2734	2.38	.03	.09	0	5
0134	.3626	1.2959	2.35	.48	1.46	2	-19
0154	.3902	1.3479	2.30	.03	.09	0	5
0174	.4192	1.4079	2.12	.10	.30	0	-9
045	.3370	1.2520	2.37	.57	1.69	3	-21
065	.3478	1.2701	2.38	.45	1.36	2	19
075	.3547	1.2820	2.37	.40	1.22	2	-16
085	.3623	1.2954	2.36	.33	1.01	2	-16
095	.3710	1.3113	2.35	.10	.31	0	9
0105	.3804	1.3290	2.33	.38	1.18	2	17

Reflection OK <sub>2</sub>	$\sin \alpha$ ms	i/p	$I/L$ (10)	I Average	$F^2$	$13 F^2$	$16 F$
006	.3939	1.3554	2.26	.95	2.91	4	28
026	.3958	1.3590	2.24	.20	.61	1	-12
046 <sub>2</sub>	.4013	1.3703	2.22	.13	.40	1	10
0106	.4384	1.4504	1.90	.08	.22	0	8
0126	.5466	1.4927	1.62	.20	.48	1	-11
0146	.4772	1.5406	1.08	.80	.59	1	12

### Patterson Synthesis-

Patterson projections were obtained using the new above  $|F|^2$ . The three projections  $\rho(xy0)$ ,  $\rho(0yz)$ , and  $\rho(x0z)$  for  $\frac{1}{4}$  of the cell are given in Figures 6, 7 and 8. The Br-Br vectors <sup>of</sup> the  $\rho(xy0)$  projection are the same as obtained in the initial Patterson using De Jong values although the rest of the plot is different. The complete Pattersons for all three projections are given in Figure 9. The origins of the three projections are seen displaced as in each case the origin is on the symmetry element, the two fold screw axis, and the relation to one another may be seen from the space group representation of Figure 2.

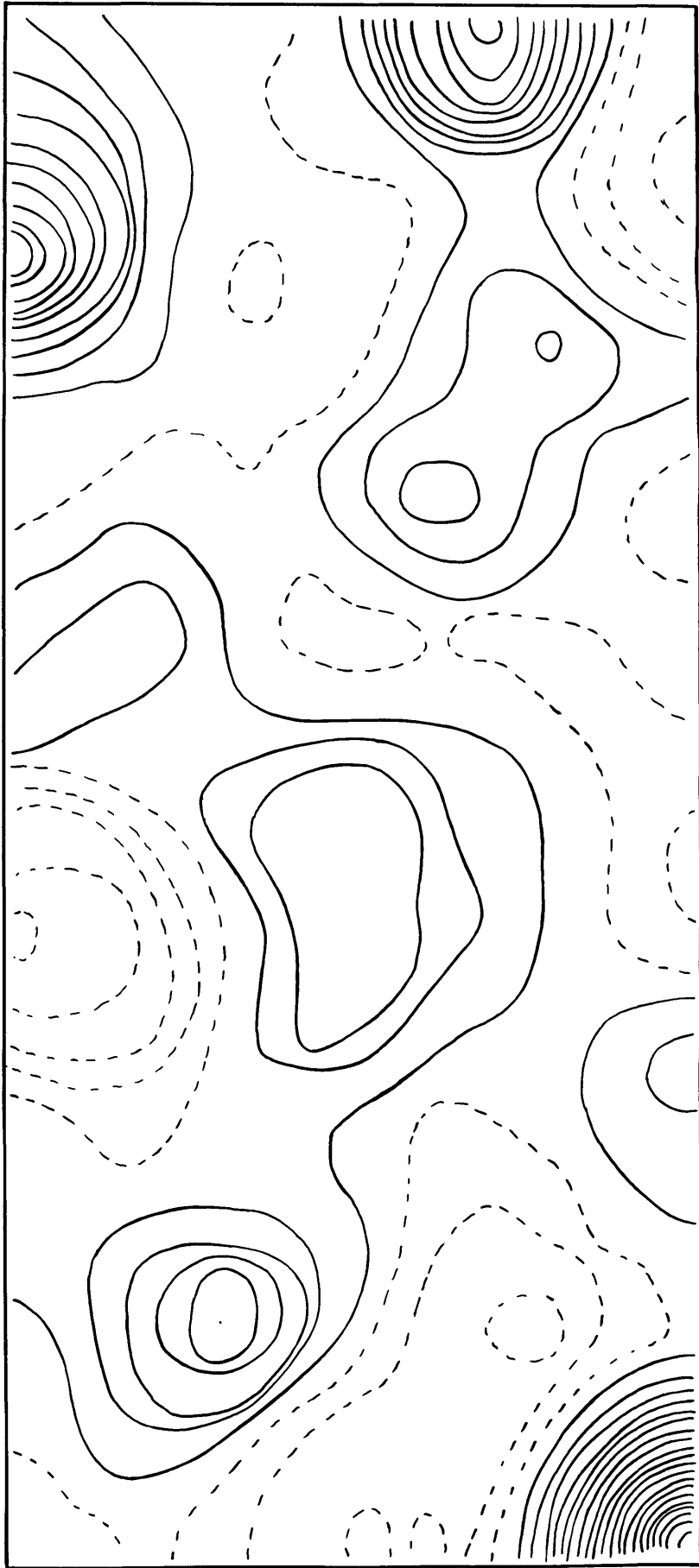
§

### Second Electron Density-

Using the new  $F$  values for hko reflections, a second electron density  $\rho(xy0)$  was prepared. This second electron density resulted in the correct number of atomic position peaks. The first electron density  $\rho(xy0)$  seems to be much in error due to an insufficient number of terms having been used in the series. In the second electron density  $\rho(xy0)$  137 terms were used, whereas in the first one only 75 terms were used. See Figure 10 a

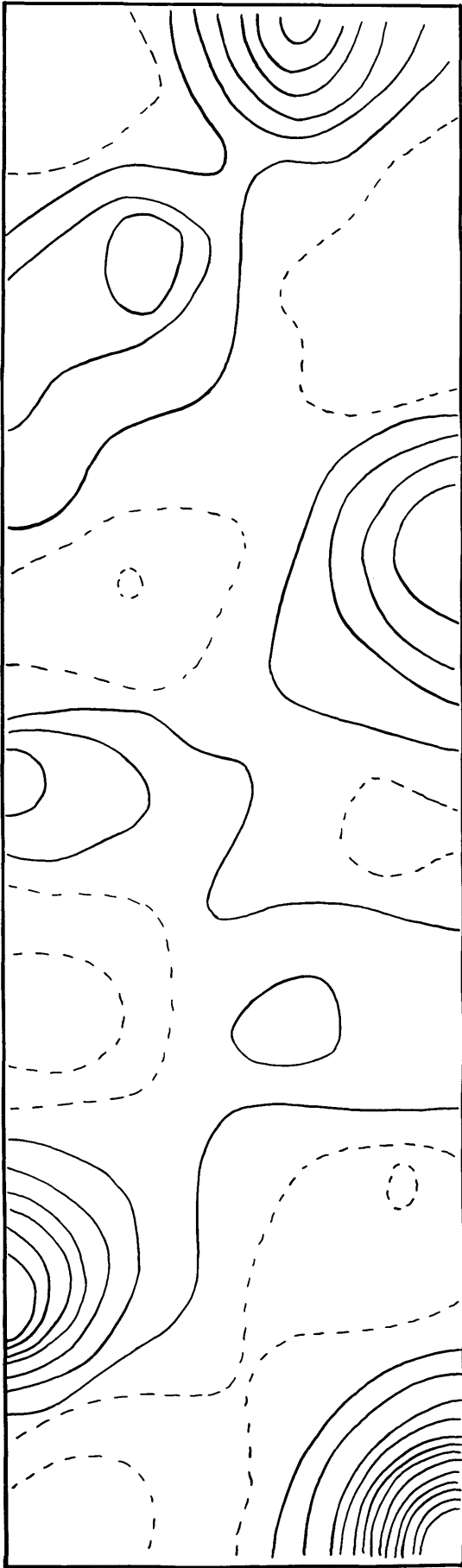
### Preliminary Comparison of Intensities-

A preliminary check of intensities for hko reflections was made using the atomic positions as indicated in the second electron density  $\rho(xy0)$  and assuming an average value of the atomic scattering factor ( $f$ ) for the nitrogen, oxygen and carbon as it was impossible to determine which of these positions represented which atoms. A sample calculation of intensity follows.



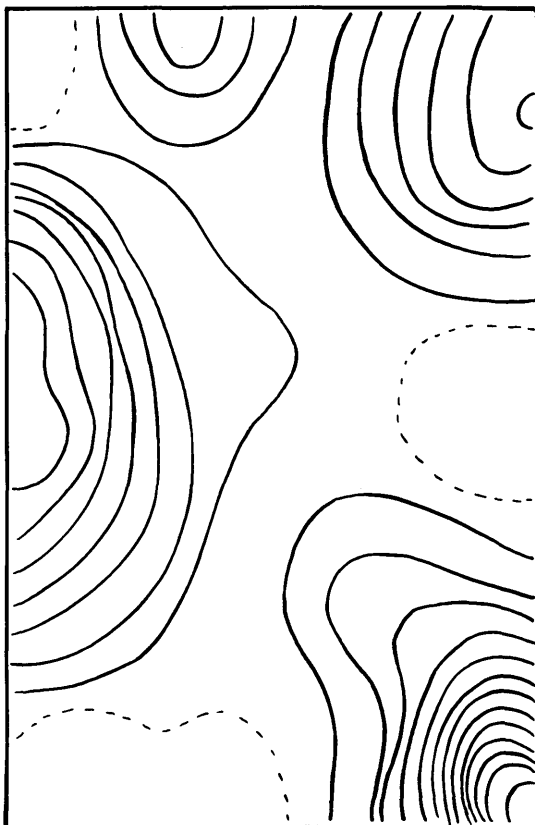
30	715	60	37	19	10	84	15	30	22	36	105	163	204	191	131	36	55	77	38	1	29	76	94	54	77	380	408	289	139	56	22
29	74	60	34	14	3	11	19	32	18	41	108	160	197	183	124	34	52	73	39	6	26	73	92	54	63	275	377	268	132	56	22
28	60	45	13	4	12	24	27	30	12	51	115	166	194	179	123	31	49	69	44	20	17	69	90	56	45	224	310	224	111	43	10
27	56	28	18	33	31	61	33	20	4	57	115	156	185	167	110	23	40	59	57	32	3	59	78	54	15	125	213	161	86	30	6
26	42	7	43	58	168	74	49	18	14	62	113	149	173	150	93	16	35	54	59	47	7	44	64	52	7	76	126	100	53	9	22
25	57	1	55	91	108	106	54	6	21	54	103	138	150	118	65	7	23	42	66	56	15	37	59	50	24	14	46	4	9	27	41
24	38	3	60	115	158	142	62	6	11	37	82	121	124	95	37	6	25	45	69	51	16	25	49	54	44	28	9	3	18	49	66
23	44	11	47	126	199	173	68	4	8	20	53	90	96	55	2	26	22	35	56	46	11	20	48	64	64	59	49	34	19	57	68
22	64	34	29	128	220	194	81	11	5	1	27	57	59	17	35	45	23	31	47	27	5	23	43	65	79	82	70	56	63	76	18
21	80	57	7	123	232	203	83	19	11	15	11	15	21	22	76	68	27	16	22	5	25	35	49	77	95	97	89	69	67	75	20
20	89	70	11	104	262	184	77	16	12	28	44	29	15	50	77	85	27	4	1	11	34	48	58	86	97	102	98	74	59	62	61
19	111	91	40	65	168	153	63	17	8	30	65	65	50	88	131	99	25	18	30	35	47	46	54	79	99	103	102	81	54	57	63
18	134	116	68	30	126	122	50	2	3	41	87	93	81	102	141	105	25	30	49	45	45	39	43	74	92	92	94	73	52	46	52
17	141	124	81	3	72	77	36	3	1	44	101	119	109	120	142	110	30	32	61	55	39	26	29	63	82	81	92	69	35	32	35
16	147	135	104	37	26	43	22	7	11	41	100	128	126	126	138	112	38	28	66	48	18	1	9	51	76	77	86	67	34	25	29
15	152	140	108	59	15	7	4	21	21	37	93	132	133	127	132	116	48	25	61	40	1	33	21	35	70	73	81	65	34	8	4
14	157	141	113	75	52	28	19	40	35	23	79	119	129	110	114	116	58	18	55	31	25	65	43	20	59	64	76	59	27	13	45
13	147	138	115	88	75	62	39	48	47	6	64	102	121	103	104	110	56	25	61	16	52	90	63	4	29	46	63	52	27	46	91
12	158	147	124	105	100	90	67	64	58	8	31	75	106	92	88	99	52	26	52	5	65	102	78	20	7	22	42	41	3	99	168
11	143	139	127	118	117	109	82	74	61	22	24	62	88	78	71	80	41	36	46	10	86	114	81	42	22	7	11	20	29	171	267
10	121	120	130	137	140	126	103	82	64	34	1	42	65	51	45	63	31	33	51	8	83	106	76	50	47	30	6	1	58	232	351
9	94	112	126	146	153	134	108	75	53	31	7	27	57	38	29	40	17	44	51	5	59	91	73	55	64	58	21	10	72	264	390
8	44	65	108	143	153	133	108	74	47	30	17	11	33	26	13	21	1	46	53	5	51	68	59	62	82	67	31	10	72	259	362
7	14	11	68	133	159	135	96	67	41	22	13	9	17	13	7	10	13	51	57	21	25	46	49	71	92	63	19	1	54	321	330
6	100	58	32	109	151	125	86	50	22	10	4	3	4	6	8	6	28	60	56	23	10	28	36	72	76	59	9	15	26	150	228
5	222	154	18	83	129	107	62	35	14	7	8	11	20	21	15	13	35	63	56	31	10	3	12	65	92	41	17	37	14	72	128
4	400	284	88	39	104	92	39	13	3	15	7	16	39	48	36	32	50	64	57	32	25	25	1	53	73	22	40	63	48	2	24
3	666	438	158	3	84	77	24	1	12	25	16	24	62	73	60	55	64	55	34	32	38	39	20	37	58	1	68	101	94	66	52
2	816	594	230	26	65	61	16	1	12	41	30	25	76	91	82	73	72	45	22	37	56	53	28	15	28	25	85	120	130	108	94
1	974	710	278	44	51	48	4	7	22	51	36	22	78	99	97	88	77	43	14	40	68	63	44	3	16	36	103	148	150	132	126
0	1026	752	297	52	42	47	0	8	30	61	44	23	85	109	105	92	73	37	13	45	75	71	48	2	14	35	102	150	159	146	138
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30

Figure 6. Patterson Projection (x<sub>10</sub>)









30	21	27	29	35	38	15	8	24	57	60	81	100	116	132	137	135	127	128	130	130	127	120	99	68	28	9	38	55	69	73	70	
29	26	30	34	37	29	14	6	23	40	58	75	98	115	130	135	133	129	126	126	125	123	116	104	76	46	29	8	37	55	66	70	70
28	25	27	30	33	26	15	4	23	37	56	74	92	108	124	126	135	124	117	118	116	114	104	93	58	20	12	36	50	58	61	61	
27	24	25	27	31	25	16	2	15	36	49	67	83	99	109	115	113	111	107	105	103	97	87	68	48	10	18	38	46	54	55	54	
26	23	24	26	32	24	14	3	14	30	47	64	78	97	100	100	96	93	87	84	78	67	52	34	2	22	37	46	54	48	47	44	
25	22	23	24	34	23	9	2	22	36	48	60	70	79	82	82	78	73	68	60	52	40	24	7	10	25	34	36	34	30	28	28	
24	21	22	23	35	27	10	1	15	26	37	46	59	67	65	64	61	55	48	42	33	24	11	3	16	27	30	24	19	14	10	10	
23	20	21	22	38	28	15	3	7	16	24	32	38	43	46	47	44	39	32	27	16	4	5	15	23	25	24	17	6	2	8	8	
22	19	20	21	40	30	20	11	3	6	11	19	25	29	33	34	28	25	17	9	1	4	13	21	26	30	24	14	2	14	19	19	
21	18	19	20	42	32	25	19	13	5	2	5	10	14	17	18	17	12	6	1	5	15	17	23	25	26	20	7	10	23	30	30	
20	17	18	19	44	36	30	28	20	17	11	7	11	15	17	18	14	3	4	3	1	7	13	17	22	24	24	17	9	18	34	36	36
19	16	17	18	46	38	35	37	30	33	31	24	22	26	28	28	23	9	7	1	9	12	17	21	27	33	35	31	24	7	19	23	30
18	15	16	17	48	40	40	41	43	43	44	36	33	39	42	42	35	11	11	1	11	14	19	24	29	35	38	31	24	7	19	23	30
17	14	15	16	50	42	45	46	47	46	45	43	40	46	50	50	40	13	13	1	13	17	22	27	33	38	41	25	18	3	18	22	22
16	13	14	15	52	44	48	48	48	48	48	43	41	47	51	51	40	15	15	1	15	20	25	31	37	42	45	37	34	24	14	3	0
15	12	13	14	54	46	50	50	50	50	50	45	43	49	53	53	41	17	17	1	17	22	28	34	40	45	48	40	36	38	32	23	17
14	11	12	13	56	48	52	52	52	52	52	47	45	51	55	55	43	19	19	1	19	24	30	36	42	47	50	42	44	38	31	27	20
13	10	11	12	58	50	54	54	54	54	54	49	47	53	57	57	45	21	21	1	21	26	32	38	44	49	52	44	46	40	33	29	22
12	9	10	11	60	52	56	56	56	56	56	51	49	55	59	59	47	23	23	1	23	28	34	40	46	51	54	46	48	42	35	31	24
11	8	9	10	62	54	58	58	58	58	58	53	51	57	61	61	49	25	25	1	25	30	36	42	48	53	56	48	50	44	37	33	26
10	7	8	9	64	56	60	60	60	60	60	55	53	59	63	63	51	27	27	1	27	32	38	44	50	55	58	50	52	46	39	35	28
9	6	7	8	66	58	62	62	62	62	62	57	55	61	65	65	53	29	29	1	29	34	40	46	52	57	60	52	54	48	41	37	30
8	5	6	7	68	60	64	64	64	64	64	59	57	63	67	67	55	31	31	1	31	36	42	48	54	59	62	54	56	50	43	39	32
7	4	5	6	70	62	66	66	66	66	66	61	59	65	69	69	57	33	33	1	33	38	44	50	56	61	64	56	58	52	45	41	34
6	3	4	5	72	64	68	68	68	68	68	63	61	67	71	71	59	35	35	1	35	40	46	52	58	63	66	58	60	54	47	43	36
5	2	3	4	74	66	70	70	70	70	70	65	63	69	73	73	61	37	37	1	37	42	48	54	60	65	68	60	62	56	49	45	38
4	1	2	3	76	68	72	72	72	72	72	67	65	71	75	75	63	39	39	1	39	44	50	56	62	67	70	62	64	58	51	47	40
3	0	1	2	78	70	74	74	74	74	74	69	67	73	77	77	65	41	41	1	41	46	52	58	64	69	72	64	66	60	53	49	42
2	0	0	1	80	72	76	76	76	76	76	71	69	75	79	79	67	43	43	1	43	48	54	60	66	71	74	66	68	62	55	51	44
1	0	0	0	82	74	78	78	78	78	78	73	71	77	81	81	69	45	45	1	45	50	56	62	68	73	76	68	70	64	57	53	46
0	0	0	0	84	76	80	80	80	80	80	75	73	79	83	83	71	47	47	1	47	52	58	64	70	75	78	70	72	66	59	55	48
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	

z

x

Figure 8. Patterson Projection (x0z)

$$1'' = 1 \text{ \AA}$$

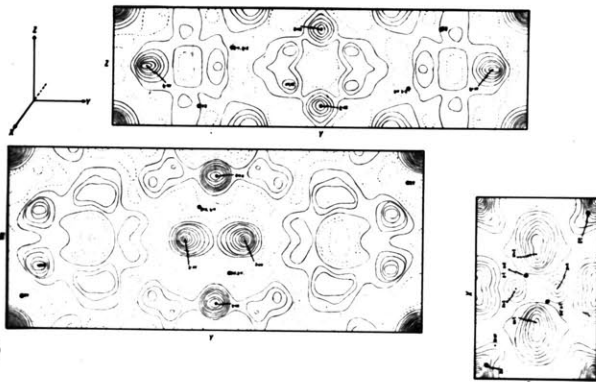


Figure 9. Patterson Projections

Reflection m atom	Parameters		$\sqrt{I_p}$ mf <sup>12</sup>	Structure Factor/m <sup>13</sup> cos2 $\pi$ hx	cos2 $\pi$ ky	$\sqrt{I}$	
	x	y				+	-
I50							
Br	.178	.036	41.51	.437	.426	7.75	
1	.093	.380	7.03	.834	.809	4.74	
2	.108	.430	7.03	.779	.588	3.22	
3	.417	.283	7.03	-.867	-.861	5.25	
4	.067	.180	7.03	.913	.809	5.19	
5	.150	.191	7.03	.588	.960	3.97	
6	.470	.113	7.03	-.982	-.918	6.34	
7	.470	.213	7.03	-.982	.918		6.34
8	.417	.283	7.03	-.867	-.861	5.25	
9	.200	.333	7.03	.309	-.509		1.11
10	.261	.430	7.03	-.107	.588		.44

$$\frac{\sqrt{I}}{4} = + 33.80$$

The atomic scattering factor,  $f$ , is determined for each atom for each reflection as a function of  $\sin \theta$ . The rough comparison of observed and calculated intensities is given in Table 2.

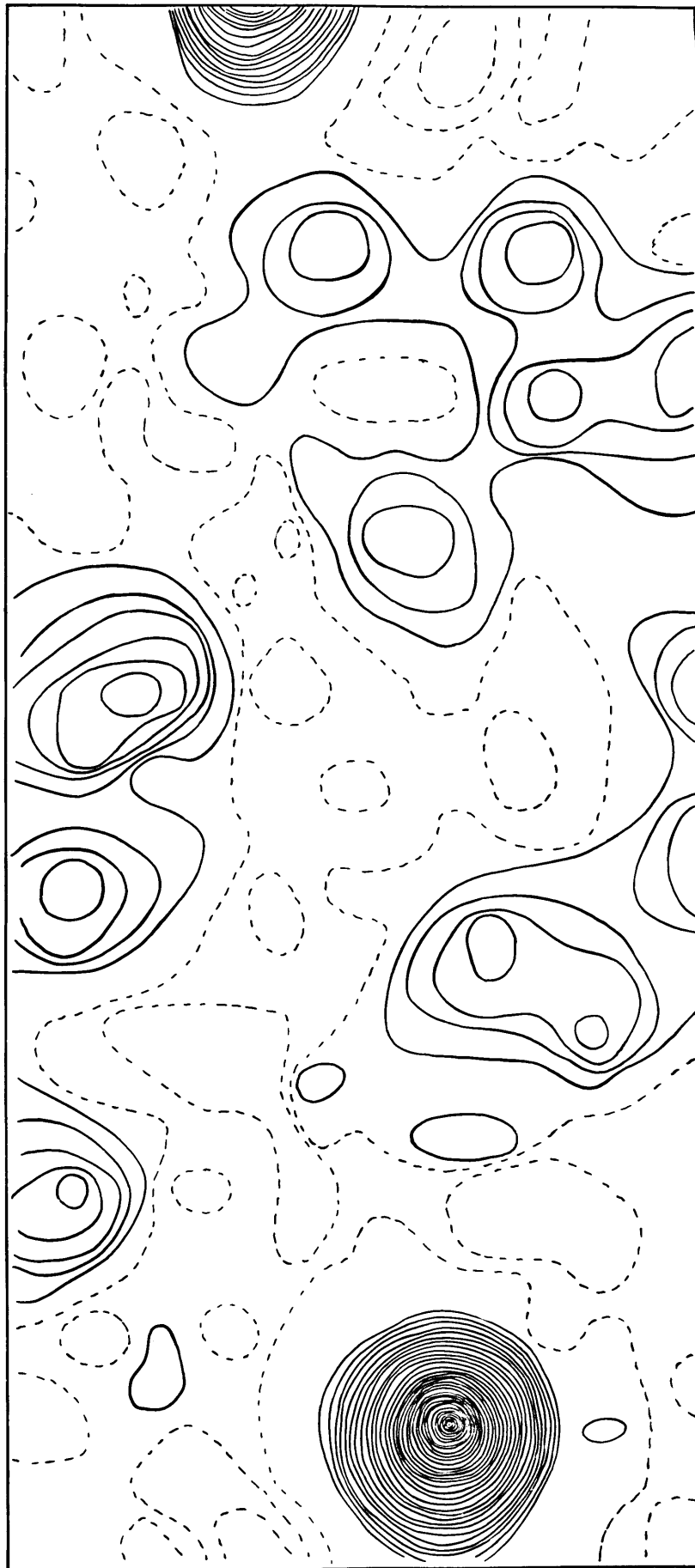
#### Electron Density maps $\rho(xoz)$ and $\rho(oyz)$ -

Electron density maps  $\rho(xoz)$  and  $\rho(oyz)$  using the same procedure as was used for  $\rho(xyz)$  were prepared and are given in Figure 10 and Figure 11. The three complete electron density maps all drawn to the same origin are given in Figure 12.

(11) M.J. Buerger and G.E. Klein. Correction of Diffraction Amplitudes for Lorentz and Polarization Factors. J. App. Phys. Vol. 17 No. 4 April 1946 285-306.

(12) Internationale Tabellen zur bestimmung Kristallstrukturen. I. (Gebruder Borntraeger, Berlin (1935).

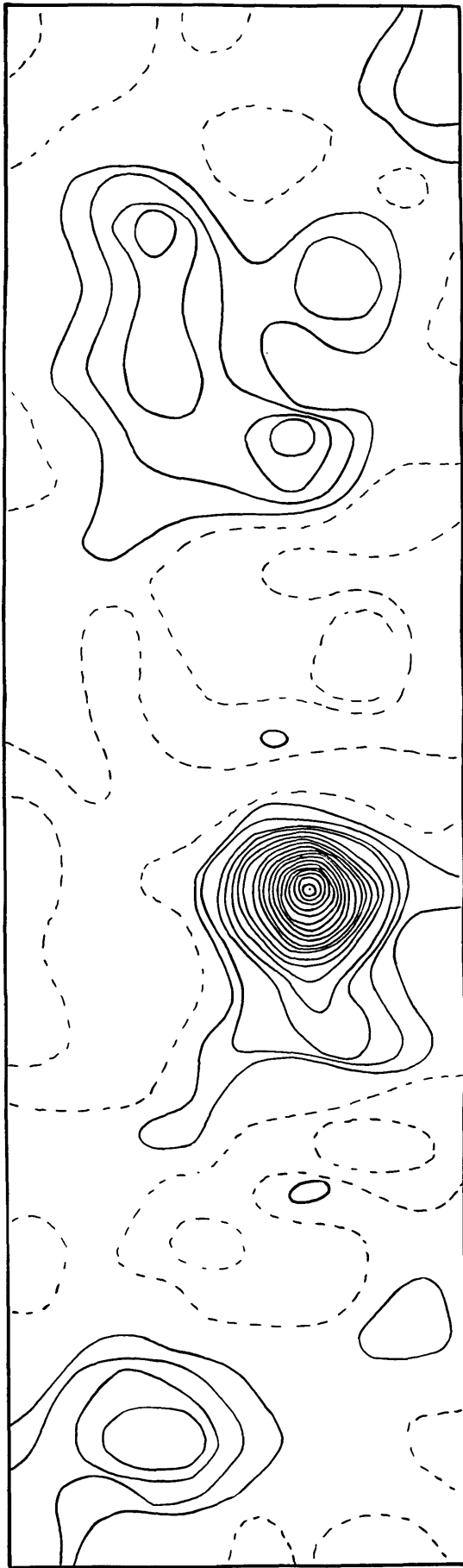
(13) M.J. Buerger. Numerical Structure Factor Tables. Geol. Soc. America Special Paper 33.



30	67	58	28	49	80	15	151	167	76	9	34	19	91	123	8	11	141	129	37	33	16	83	88	99	99	65	82	107	88	98	117
29	81	59	26	48	91	6	168	184	77	21	58	13	123	165	30	30	186	163	55	25	50	99	91	122	110	56	63	84	88	111	111
28	80	59	41	61	109	13	175	209	78	49	79	9	118	170	49	43	223	204	78	31	59	91	70	113	113	67	51	53	75	91	86
27	76	76	58	59	113	41	138	169	55	48	90	12	92	142	44	41	238	238	112	42	62	73	45	83	106	85	59	53	90	90	54
26	67	48	80	56	103	61	80	121	33	95	115	35	46	114	44	29	228	278	148	41	64	59	25	49	64	97	89	74	118	86	35
25	49	101	87	39	72	69	1	20	15	98	110	39	17	80	27	4	183	284	155	47	48	46	37	44	51	109	94	93	133	73	37
24	46	106	89	31	49	59	61	58	47	90	110	48	5	65	39	24	133	271	171	40	44	42	57	52	25	93	89	101	133	42	32
23	66	117	101	49	56	51	89	125	75	96	125	61	27	41	41	34	75	219	157	9	47	32	77	47	11	71	68	87	113	13	10
22	111	135	109	79	78	54	79	131	84	103	136	71	47	6	25	40	15	128	91	28	56	23	68	37	11	50	34	63	79	9	23
21	145	126	83	98	110	69	74	111	81	113	148	85	77	49	7	42	31	29	57	69	64	27	65	6	24	35	10	48	79	14	67
20	174	105	69	83	115	96	71	84	77	123	152	94	91	79	37	58	73	51	53	100	94	43	39	20	27	26	17	23	37	17	88
19	152	66	50	55	77	89	75	89	99	130	131	94	110	103	64	53	82	109	96	94	93	68	49	13	23	5	59	7	38	22	102
18	122	42	28	19	37	83	106	111	116	122	106	93	108	94	65	64	89	126	106	83	100	92	64	13	2	31	93	3	44	20	76
17	76	33	27	7	1	51	104	126	24	35	76	89	99	68	78	85	88	124	95	55	72	51	14	48	16	67	155	35	43	25	50
16	38	21	1	3	8	29	84	125	46	13	50	69	74	38	75	105	81	102	76	21	34	37	8	75	32	83	164	31	59	1	10
15	19	31	151	81	26	21	59	98	78	47	27	62	75	37	75	103	72	89	67	8	31	13	42	78	31	89	152	25	77	25	19
14	10	211	483	273	28	25	36	69	42	25	8	27	58	46	79	105	69	70	48	37	106	75	12	67	20	75	96	3	97	79	38
13	50	457	941	575	11	33	28	58	10	13	4	19	25	50	78	85	60	62	37	69	136	99	0	56	20	41	43	19	95	129	76
12	76	714	1342	873	75	47	60	75	2	6	22	75	34	32	63	62	53	44	4	89	160	96	14	59	14	25	7	41	94	168	122
11	102	866	1650	1047	121	49	85	87	5	10	25	126	98	5	44	53	58	47	4	94	143	69	25	51	23	13	15	33	66	166	152
10	88	841	1609	1011	113	52	103	106	15	19	4	140	143	35	43	76	79	45	5	62	90	29	11	22	17	22	9	25	57	145	174
9	67	652	1243	760	160	31	108	119	7	17	8	147	155	41	55	92	79	73	35	23	43	9	15	21	2	79	84	14	37	110	145
8	23	379	787	423	14	38	107	111	2	3	22	130	147	40	73	112	111	85	51	16	2	3	74	83	27	124	146	3	55	69	111
7	10	141	359	143	70	43	123	113	23	4	51	123	125	29	85	114	107	89	67	39	27	4	111	141	57	145	186	21	57	39	66
6	32	2	89	9	79	63	127	102	55	2	84	116	93	19	87	102	85	79	63	40	38	18	127	160	77	147	197	35	55	30	46
5	37	37	5	39	56	83	147	116	85	2	126	127	77	16	65	74	61	80	59	27	36	30	109	168	79	113	154	31	59	41	49
4	35	12	4	14	35	103	146	103	91	9	155	133	72	26	38	59	62	66	34	3	15	23	79	138	66	65	93	16	46	56	67
3	54	10	6	27	49	105	126	65	79	3	128	110	58	39	2	34	48	42	22	12	8	1	65	119	74	31	13	21	58	80	76
2	86	35	19	53	65	95	103	65	74	27	87	87	44	62	45	35	41	0	4	17	9	7	62	125	97	11	35	37	53	81	80
1	111	69	66	96	83	80	94	74	79	61	36	51	29	87	94	10	22	53	45	19	16	13	73	136	116	10	63	48	40	73	81
0	117	96	88	107	82	65	99	99	88	83	16	33	37	129	144	11	8	123	91	19	34	9	76	167	151	15	80	49	28	58	67
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30

Figure 10a Electron Density  $\rho(x,y)$

" = 1 Å



30	79	80	33	25	38	62	57	7	22	67	47	33	18	28	12	73	24	18	12	19	33	73	74	45	31	10	2	41	67	52	37
29	70	66	49	0	35	67	61	4	19	67	44	45	21	13	25	63	5	25	1	9	41	70	74	45	31	10	2	41	67	52	37
28	54	48	66	23	25	59	57	15	24	41	42	47	19	46	46	63	6	17	4	9	32	61	56	34	19	19	11	34	65	62	42
27	27	32	82	46	15	46	50	9	27	66	39	50	48	59	50	58	6	6	6	32	41	48	35	7	29	29	15	25	70	54	
26	5	22	104	79	3	35	47	24	35	71	57	60	88	69	97	48	17	32	41	41	12	17	26	17	13	7	6	80	73		
25	16	18	127	89	2	28	45	20	36	81	64	60	89	67	69	48	37	55	61	61	18	6	43	35	7	40	35	40	80	80	
24	26	24	150	105	8	16	46	35	25	85	78	60	95	52	46	48	60	80	69	27	35	15	15	62	34	76	59	20	72	75	
23	26	32	168	123	11	18	58	43	20	72	83	53	81	52	53	52	72	77	69	35	13	18	43	7	40	75	109	12	61	72	
22	19	52	180	124	10	24	67	48	3	67	89	55	62	56	45	55	74	74	66	37	1	19	112	103	95	142	82	8	44	59	
21	17	46	186	118	5	25	86	18	11	52	86	50	52	42	48	65	41	48	57	55	27	16	65	75	128	118	117	14	34	52	
20	9	73	155	111	3	31	96	108	15	11	34	73	53	49	56	51	37	39	47	48	41	12	73	73	128	117	155	17	21	43	
19	10	72	170	96	9	41	108	111	4	15	48	47	56	45	86	84	27	39	65	67	64	4	73	103	112	112	97	26	22	46	
18	22	75	164	150	24	58	108	71	1	20	48	20	63	45	77	88	46	46	65	72	71	4	73	103	112	112	97	96	102	25	52
17	35	72	95	50	25	65	104	67	17	4	5	56	15	53	63	96	21	97	75	67	71	12	73	83	83	11	63	50	57	52	
16	46	76	95	25	42	67	104	68	0	38	27	27	95	149	63	97	9	60	95	91	71	20	75	60	54	44	22	31	34	58	
15	57	74	67	10	43	80	100	58	4	52	4	19	140	293	39	95	6	149	293	92	92	6	95	60	30	22	5	71	46	57	52
14	58	74	41	41	43	86	94	44	16	69	75	15	267	471	127	91	1	149	471	89	73	73	117	28	12	18	57	75	48	46	46
13	57	55	20	18	44	95	87	28	78	26	79	62	411	665	227	80	3	149	665	66	51	66	135	41	17	7	9	72	45	45	46
12	52	27	27	25	44	98	87	15	88	22	88	93	535	336	365	74	3	149	336	73	73	3	84	106	12	12	18	75	48	46	46
11	46	20	2	34	35	97	80	2	89	30	95	134	639	955	358	64	10	149	955	61	61	10	84	135	3	7	36	70	38	22	22
10	43	21	4	35	25	97	80	2	89	30	95	134	639	955	358	64	10	149	955	61	61	10	84	135	3	7	36	70	38	22	22
9	52	20	16	36	19	85	72	0	103	38	112	152	628	936	366	67	24	110	936	67	40	110	66	123	6	6	47	52	24	12	26
8	59	22	22	38	14	71	63	6	115	43	117	135	540	822	307	71	29	124	822	71	112	112	87	18	11	89	54	10	47	19	19
7	74	27	26	39	3	53	52	19	134	43	117	135	540	822	307	71	29	124	822	71	112	112	87	18	11	89	54	10	47	19	19
6	78	36	31	37	12	36	58	33	134	43	117	135	540	822	307	71	29	124	822	71	112	112	87	18	11	89	54	10	47	19	19
5	80	34	31	37	12	13	41	47	136	57	94	42	145	263	25	92	38	140	263	92	139	100	26	27	18	78	36	23	28	2	16
4	67	40	48	45	17	8	25	58	36	58	41	16	51	136	27	96	23	140	136	96	100	115	37	28	3	28	5	43	12	43	5
3	54	40	52	45	17	9	35	43	115	115	115	6	9	46	60	14	15	115	46	78	115	44	28	15	22	2	27	56	0	66	29
2	47	44	60	43	17	9	35	43	115	115	115	6	9	46	60	14	15	115	46	78	115	44	28	15	22	2	27	56	0	66	29
1	47	44	69	43	5	1	33	52	90	108	72	12	21	31	9	62	7	115	31	47	115	44	28	15	22	2	27	56	0	66	29
0	72	52	67	41	2	16	31	45	74	73	23	19	12	18	24	73	12	115	24	115	44	28	15	22	2	27	56	0	66	29	
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30

Figure 10 Electron Density  $\rho$  (log3)

" = 1A





36	7	9	9	13	13	14	13	7	9	20	52	63	69	92	18	0	1	17	27	33	36	39	18	69	112	129	103	49	1	26	
35	4	5	7	11	13	10	3	4	14	25	42	57	67	59	92	16	4	15	23	27	39	47	46	24	11	46	65	47	7	21	22
34	9	7	2	7	10	1	10	25	31	49	60	67	67	54	38	11	10	18	23	29	38	55	61	55	30	1	14	5	14	27	5
33	20	12	2	6	3	26	49	68	74	75	66	65	42	28	5	10	18	25	30	43	60	72	73	54	27	10	6	18	18	17	
32	26	12	4	6	4	33	68	76	93	85	71	69	34	15	0	13	20	23	29	45	61	76	82	65	42	20	14	18	14	32	
31	30	13	3	6	10	44	56	102	103	89	64	57	17	1	11	23	25	27	33	47	67	82	88	74	48	28	21	19	8	39	
30	17	2	11	13	5	40	85	118	107	85	64	28	6	7	16	23	32	34	44	67	75	84	78	67	29	17	18	7	34		
29	0	10	24	14	2	41	82	165	104	76	61	12	9	20	26	32	41	48	58	64	78	91	76	95	64	45	28	26	15	15	
28	29	21	25	31	26	2	38	78	96	93	65	31	3	14	24	34	40	54	63	71	77	95	96	105	94	74	52	41	39	7	
27	53	40	36	33	24	1	34	64	83	85	53	22	1	16	29	38	57	66	77	84	97	97	105	107	87	68	55	52	30	33	
26	72	57	46	38	24	1	27	55	64	58	37	12	5	17	25	42	60	77	89	91	97	100	108	111	109	97	60	68	64	62	58
25	31	65	45	37	17	4	18	44	48	41	27	9	8	17	25	40	61	85	100	105	105	103	104	108	106	102	67	75	67	67	65
24	80	69	42	30	14	2	13	27	34	29	20	9	1	8	18	35	58	82	101	105	106	103	103	103	101	96	96	76	70	69	68
23	72	58	37	27	17	9	4	15	28	28	17	11	1	14	15	33	57	78	97	105	105	102	98	95	72	87	77	71	67	64	64
22	62	47	37	22	17	8	1	9	15	12	13	7	1	7	24	45	67	95	97	102	98	91	87	82	79	72	70	67	63	60	
21	60	52	46	36	31	21	21	15	1	13	16	13	6	4	18	34	52	71	86	95	96	91	81	72	67	66	69	68	66	60	
20	60	57	53	41	40	32	23	7	6	18	21	19	9	3	14	25	39	57	79	90	94	91	79	66	71	66	72	75	71	62	
19	61	62	57	47	41	35	30	21	12	6	19	25	21	14	7	15	28	45	67	86	94	81	70	65	69	79	87	84	73		
18	65	64	54	38	28	14	11	9	4	9	26	29	11	6	5	10	18	35	61	86	99	82	67	63	66	72	84	84	84	80	
17	65	55	33	2	19	20	22	18	10	15	27	38	32	23	9	2	7	13	25	57	77	97	102	94	78	71	81	93	89	85	81
16	52	32	12	58	90	71	79	53	32	28	31	42	37	27	12	2	5	19	44	73	94	100	93	85	79	86	97	94	86	72	
15	53	6	68	133	176	180	150	104	63	44	95	100	49	36	14	4	6	15	32	57	82	99	99	82	74	80	88	80	68	53	
14	7	49	133	219	274	278	228	152	94	57	57	57	53	92	20	6	0	2	9	25	47	67	78	78	72	70	68	67	57	45	29
13	15	70	190	292	303	352	351	198	119	68	59	57	52	47	22	6	1	7	15	34	54	65	68	67	65	63	58	48	34	16	8
12	36	119	266	349	413	405	333	325	130	73	53	54	56	44	27	10	3	6	4	27	43	52	57	53	47	39	24	12	7	20	
11	39	132	261	325	402	426	344	321	130	69	47	49	45	35	25	11	11	15	15	5	17	37	46	44	46	36	27	15	5	22	33
10	32	126	286	364	414	408	319	312	114	55	31	35	37	32	21	14	17	26	25	15	7	27	44	42	35	28	18	8	8	22	36
9	17	100	222	316	372	357	282	179	88	38	17	18	23	18	12	15	24	34	39	24	3	20	26	35	30	25	12	6	14	23	
8	5	65	140	207	246	237	220	123	53	11	0	3	5	6	6	17	34	44	47	31	6	17	31	33	26	17	12	9	0	3	9
7	25	79	135	203	246	181	70	48	11	15	11	7	3	2	18	40	55	55	43	16	7	24	26	25	20	17	15	11	7	4	
6	25	49	103	129	112	69	18	19	32	20	21	11	6	18	42	59	63	50	38	7	12	19	18	13	13	9	7	7			

2

$x$

$l'' = 1 \text{ \AA}$

Figure 11 Electron Density  $\rho(x_0)$

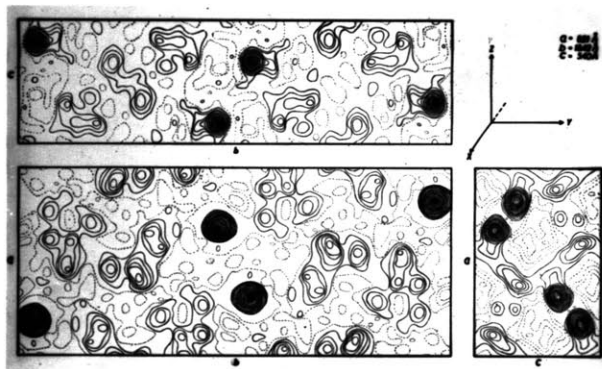


Figure 12 Electron Density Maps.

## Atomic Positions-

By comparing the three electron density maps and assuming the diglycine structure to be made up of glycine molecules of known structure<sup>14</sup> which of the peaks represented the oxygens, which the nitrogens and which the carbons were decided upon. The atomic positions so obtained are:

Atomic positions as determined from the electron density maps						Atomic positions referred to the same origin				
	x	y	y	z	x	z		x	y	z
Br	.178	.035	.215	.167	.072	.083	Br	.178	.035	.833
C	.089	.380	.370	.333	.161	.083	C	.089	.380	.833
C	.106	.430	.180	.120	.144	.370	C	.106	.430	.120
N	.268	.430	.180	.158	.482	.092	N	.268	.430	.158
O	.470	.112	.363	.183	.220	.433	O	.470	.112	.317
O	.196	.333	.417	.542	.054	.092	O	.196	.333	.842
C	.423	.283	.484	.017	.173	.233	C	.423	.283	.517
C	.065	.172	.422	.127	.315	.123	C	.065	.172	.373
N	.145	.193	.443	.342	.105	.408	N	.145	.193	.158
O	.475	.213	.037	.350	.225	.100	O	.475	.213	.650
O	.423	.283	.037	.350	.173	.400	O	.423	.283	.350

## Second Intensity Comparison-

Intensity calculations were made using the parameters as determined from the electron density maps. A comparison of the observed and calculated intensities using a specific atomic scattering factor,  $f$ , for each of the atoms for each reflection is given in Table 2.

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(14) G. Albrecht and E. Corey. J. A. C. S. 61, 5 (1939).

### Final Electron Density $\rho(x,y,z)$ -

Only <sup>five</sup> ~~four~~ sign changes were found from those determined by Br alone. The changes were for <sup>th</sup>  $h320$ ,  $0220$ ,  $610$  <sup>370</sup> and  $940$  reflections.

An electron density map  $\rho(x,y,z)$  made with these 4 sign changes showed a slight shift of parameters as indicated in Figure 13.

The new set of parameters from the final electron density  $\rho(x,y,z)$

are:

	x	y
Br	.178	.035
C	.095	.380
C	.104	.428
N	.278	.430
O	.462	.110
O	.200	.338
C	.450	.267
C	.072	.170
N	.149	.194
O	.472	.213
O	.418	.283

The agreement between observed and calculated intensities is somewhat improved with these new parameters as is shown for a few reflections in Table 2.

30	104	70	30	40	52	36	156	137	50	11	42	20	112	145	19	17	125	167	24	22	0	61	74	57	108	86	74	24	86	78	160
29	107	61	14	21	45	38	149	194	59	37	67	20	137	183	39	41	179	155	57	30	25	71	79	114	129	86	73	115	98	99	97
28	104	58	32	26	53	31	209	232	133	53	76	8	141	193	67	63	225	207	71	42	30	61	58	106	133	105	85	88	88	92	74
27	94	74	55	37	71	10	166	206	63	68	72	3	122	170	68	60	230	236	118	39	48	48	45	90	120	98	79	75	87	82	48
26	79	97	79	51	82	45	97	148	50	68	81	6	84	143	60	43	220	265	134	16	73	70	42	54	77	112	84	83	117	77	35
25	54	100	91	49	69	77	5	42	3	66	72	12	50	103	34	2	168	263	160	8	74	74	67	54	61	121	85	101	129	66	43
24	46	97	94	38	47	63	57	47	32	63	84	37	8	68	32	26	116	254	170	3	76	77	98	61	43	165	85	106	130	45	44
23	60	101	93	48	50	53	83	105	66	83	117	75	55	18	16	42	69	216	165	13	69	63	118	73	35	93	74	104	127	25	25
22	99	110	93	97	68	54	79	111	86	94	140	106	81	34	9	48	13	140	159	34	68	50	110	63	17	70	42	109	101	12	1
21	131	103	90	101	68	74	71	93	71	103	149	113	105	84	33	44	29	48	33	67	69	47	99	27	9	46	6	59	74	7	41
20	158	85	66	100	131	119	80	67	63	100	136	104	105	101	56	52	62	27	35	102	102	62	65	17	32	11	45	14	40	5	60
19	138	53	59	85	106	123	93	79	84	99	103	87	106	109	69	39	69	79	78	97	99	81	64	25	47	39	108	19	25	19	76
18	110	33	42	54	60	111	121	104	92	75	80	94	89	62	44	70	103	84	82	99	99	96	67	12	35	75	150	38	24	21	52
17	76	31	41	34	23	80	122	124	121	87	61	91	88	63	70	59	64	89	60	441	50	73	75	22	10	96	191	52	35	21	26
16	38	12	2	4	9	43	98	130	126	89	61	93	89	53	84	86	64	73	37	7	1	29	56	50	14	97	185	34	84	2	2
15	25	48	57	82	16	27	70	108	108	74	57	100	100	59	92	97	66	67	34	34	69	44	24	56	24	47	154	16	83	34	25
14	2	210	482	268	25	37	54	90	82	59	39	65	79	61	96	102	86	67	25	47	125	101	4	46	14	70	97	15	98	72	38
13	26	439	919	554	3	56	56	84	51	43	16	7	24	49	82	87	80	79	48	61	146	115	11	38	16	36	45	24	71	117	76
12	52	105	1358	820	66	67	87	102	39	32	9	68	50	19	64	70	88	85	40	58	157	104	7	38	7	23	2	34	76	143	110
11	66	847	1630	1037	124	57	101	113	28	31	19	125	122	15	37	55	89	81	26	67	143	75	16	33	21	5	14	35	53	141	138
10	60	829	1606	1020	141	37	98	109	11	38	4	138	165	57	32	70	98	67	9	52	106	52	3	7	26	7	7	42	48	125	158
9	41	647	1272	787	108	6	83	107	9	31	1	141	175	62	39	78	107	78	31	31	73	41	31	31	19	42	54	43	64	95	131
8	1	352	777	437	42	14	73	89	2	6	24	132	169	64	55	92	109	82	37	4	32	26	86	91	5	86	112	55	68	60	97
7	28	113	371	166	28	7	83	85	16	9	69	137	144	56	66	94	106	90	51	41	13	1	112	143	41	119	168	2	63	29	65
6	44	3	84	6	59	49	109	87	38	25	120	143	132	48	70	88	94	92	75	65	52	29	108	167	65	133	195	30	46	21	46
5	43	36	9	51	53	91	141	74	67	30	164	154	110	37	58	68	76	103	84	66	66	58	79	158	69	101	153	35	55	34	54
4	35	5	5	21	34	108	141	82	76	36	179	140	84	27	46	61	78	83	54	40	45	58	40	120	49	54	96	11	49	57	79
3	48	8	15	27	43	108	122	56	69	4	134	95	42	16	18	82	64	46	26	33	30	40	23	104	48	12	9	37	73	92	94
2	74	8	2	48	55	99	97	46	64	19	82	56	9	23	11	33	43	13	19	22	20	19	20	100	69	9	43	58	79	92	104
1	97	45	52	97	81	94	93	54	67	47	39	26	1	53	67	9	13	75	73	16	19	5	43	122	105	6	57	59	56	91	107
0	110	78	76	124	98	86	108	57	74	61	0	22	24	107	125	17	19	145	112	20	42	11	50	137	156	30	52	40	30	70	164
0	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30

y

1" = 1A°

Figure 13 Electron Density  $\rho(x,y)$

Table 2

## Comparison of Observed and Calculated Intensities Under Three Conditions

- Condition 1. Rough comparison using an average scattering factor  $f$ , for oxygen, nitrogen and carbon in intensity calculations.
- Condition 2. Intensity comparison using correct  $f$  for oxygen, nitrogen and carbon as well as for bromine.
- Condition 3. Intensity comparison using final  $x$  and  $y$  atomic positions and condition 2.

Reflection hko	Observed I	Observed $\sqrt{40I}$	Calc. $\sqrt{I}/4$ Condition 1	Calc. $\sqrt{I}/4$ Condition 2	Calc. $\sqrt{I}/4$ Condition 3
220	44.1	42	40	41	42
310	37.9	39	34.9	36	37
150	29.6	34	33.8	31	29
230	26.1	32		33	32
160	25.7	32	23.3	29	31
270	20.9	29	30	29	31
040	15.6	25	23.3	25	25
020	15.0	24	22	21	21
180	14.4	24	27.1	25	24
330	10.0	20	20.9	22	22
140	9.34	19	21.1	25	23
1100	6.6	16	16.6	19	17.5
210	6.2	16	14.7	12	12
080	5.8	15	20.1	17	13
130	5.75	15	9.6	17	18.7
0120	5.6	15	20.6	20	18
410	5.2	14	14.9	18	18
530	4.9	14	18.7	20	19
470	4.7	14	15.8	19	17
450	4.4	13	20.1	19.8	19
110	4.2	13	11	11	12
510	4.1	13	17	14	15
290	3.4	12	12.9	14.6	14.6
3130	3.0	11	16.3	17	17.8
2100	2.9	11	14.7	15	14.3

Reflection	Observed I	Observed $\sqrt{40I}$	Calc. $\sqrt{I}/4$ Condition 1	Calc. $\sqrt{I}/4$ Condition 2	Calc. $\sqrt{I}/4$ Condition 3
hko					
250	2.7	10	13.8	12	11
350	2.7	10	13.5	10.6	14
240	2.2	9	12.4	12.0	9.5
560	1.9	9	13.4	14.8	14.9
490	1.9	9	13.7	13	15.0
1120	1.7	8	13.4	13	15
260	1.6	8	7.6	10	12.4
280	1.6	8	9.6	10	10.6
4110	1.6	8	12.8	13	14
200	1.3	7	12.5	10	10.5
600	1.2	7	7.98	10	10
340	1.2	7	7.8	6	7
620	1.2	7	13.2	13	12
3110	1.1	7	13.5	13	11
0140	.93	6	11.8	11	11.6
8140	.92	6		17	17.7
2230	.92	6		19	
190	.96	6	8.2	8	
0160	.85	6	9.8	12.5	13
1200	.81	6	15.9	15	
760	.79	6		13	
3100	.76	6	11.3	11	
5200	.75	5	12.5	13	
6140	.74	5		14	
3170	.73	5	10.05	10	
540	.71	5	6.96	12	
720	.66	5		10	
1050	.65	5			
1070	.65	5			
740	.64	5		12	
580	.64	5	8.36	7	
640	.64	5	7.88	8	
4210	.58	5		14	
060	.55	5	3.6	6	
670	.55	5	8.7	9	
7100	.53	5		12	
1180	.51	5	9.7	10	
910	.50	4		11	
1110	.49	4	5.0	6	
5110	.49	4		7	
4190	.49	4		10	
6120	.48	4		9	
2140	.47	4		10	



Reflection	Observed I	Observed $\sqrt{40I}$	Calc. $\sqrt{I/4}$ Condition 1	Calc. $\sqrt{I/4}$ Condition 2	Calc. $\sqrt{I/4}$ Condition 3
hk0					
6180	.45			12	
800	.45			13	
6160	.45			11	
2210	.44			11	
3150	.43			9	
2130	.41			8	
780	.40			7	
5190	.39			12	
1150	.38			7	
320	.36			3	
4170	.36			12	
420	.36			3	
0100	.33			5	
1220	.32			8.5	
870	.30			8	
370	.30			6	
360	.29			7	
2180	.29			9	
5100	.28			4.5	
0200	.28			10	
820	.26			6	
400	.25			4.5	
440	.25			5	
5130	.24			9	
2110	.24			4.5	
980	.24			13.9	
8120	.23			10	
2190	.22			7.9	
7120	.21			5	
170	.21			5	
9110	.20			11	
850	.20			3	
690	.19			8	
590	.19			7	
6100	.18			6	
4120	.18			3	
6170	.18			6	
8100	.16			7	
840	.16			7	
430	.16			5	
940	.15			11	
460	.14			3.5	
520	.14			5	
2160	.14			5	
6190	.13			8.6	
930	.13			6	
1170	.13			6	
960	.12			5	
1160	.11			5	

Reflection	Observed I	Observed $\sqrt{40I}$	Calc. $\sqrt{I/4}$ Condition 1	Calc. $\sqrt{I/4}$ Condition 2	Calc. $\sqrt{I/4}$ Condition 3
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hko

2150	.11			6.5	
990	.10			6.8	
4180	.10			5	
5150	.10			5	
860	.10			6	
660	.10			6	
0180	.10			2	
0220	.10			4	
1190	.08			3.6	
610	.08			3	
480	.06			2	
950	.06			7	
6130	.05			6	
1130	.05			4	
1010	.05				
8110	.02			5	
890	.01			4	
7140	.01			2	
4100	0				
3120	0				
390	0				
380	0				
2120	0				
4140	0				
4200	0				
550	0				
570	0				
5120	0				
5140	0				
6110	0				
6150	0				
1000	0				

## Comparison of Observed and Calculated Intensities under Condition(2)

Reflection okc	Calc. $\sqrt{I}/4$ Calc	Calc. $I/10^3$	Observed I
061	41	27	28
041	34	18.5	17.4
032	33	17.4	12.4
031	31	15.4	12
002	27	11.6	7
012	28	12.5	7
071	19	5.7	4.7
0120	18	5.2	4.6
053	21	7.0	3.3
040	17	4.6	3.4
073	20	6.4	3.2
033	17	4.6	2.7
051	11	1.9	2.4
0101	15	3.6	2.4
022	12	2.3	2.3
093	14	3.1	2.2
092	13	2.7	2.1
0140	12	2.3	2.0
080	14	3.1	1.9
014	13	2.7	1.85
034	15	3.6	1.7
004	18.7	5.6	1.4
0160	11	1.9	1.3
0152	11	1.9	1.20
081	11	1.9	.97
006	20	6.4	.95
0122	10	1.6	.8
0146	12	2.3	.8
0200	8	1.0	.8
0020			
0181	10	1.6	.7
0221	10	1.6	.7
0112	12	2.3	.7
0201	8	1.0	.76
0191	5	.4	.7
060	4	.25	.67
013	5	.4	.6
0142	7	.8	.6
045	10	1.6	.65
091	7	.8	.55
0213	11	1.9	.5
0180	3	.14	.5
0132	7	.8	.5
0193	8	1.0	.5
0134	9	1.3	.5
065	15	3.6	.5
0211	4	.25	.4
075	9	1.3	.4
0105	9	1.3	.4
085	5	.4	.30
0192	7	.8	.25
0162	5	.4	.2
084	5	.4	.2

Reflection	Calc. $\sqrt{I}/4$	Calc. $I/I_0^3$	Observed I
OKC			
0114	7	.8	.2
0126	9	1.3	.2
064	3	.14	.2
0172	4	.25	.13
0113	2	.16	.13
046	6	.57	.13
0174	7	.8	.1
095	5	.4	.1
0131	3	.14	.06
094	5	.4	.03
0124	7	.8	.03
0154	9	1.3	.03
0106	4	.25	.08
024	4	.25	0

## Comparison of Observed and Calculated Intensities Under Condition (2)

Reflection h0c	Observed I	Observed $\sqrt{I}$	Observed $6\sqrt{I}$	Calc. $\sqrt{I}$
20I	40.67	6.38	38	36
002	28.97	5.38	32	31
10I	13.15	3.63	22	29
203	6.11	2.47	15	25
102	4.29	2.07	12	13.5
302	2.93	1.71	10	19.5
30I	2.52	1.59	9.5	8.3
403	1.76	1.33	8	13
50I	1.71	1.31	8	12.9
202	1.58	1.26	7.5	7.8
502	1.54	1.24	7.4	16
304	1.36	1.17	7.0	13
600	1.05	1.02	6.1	10
004	.97	.98	5.9	18.5
70I	.90	.95	5.7	13
006	.83	.91	5.5	23
705	.71	.84	5.0	21
200	.53	.73	4.4	10
800	.53	.73	4.4	13
105	.43	.66	3.9	7
902	.33	.57	3.4	9
504	.33	.57	3.4	9
40I	.31	.56	3.3	6
206	.28	.53	3.2	6
90I	.20	.44	2.7	9
204	.18	.43	2.5	3
400	.15	.39	2.3	4
104	.14	.37	2.3	4
802	.13	.36	2.2	5
602	.10	.32	1.9	7
503	.10	.32	1.9	.22
404	.09	.30	1.8	2
205	.05	.22	1.3	7
405	.05	.22	1.3	5
505	.04	.20	1.2	8
605	.03	.17	1.15	6
803	.025	.16	.95	8.5
60I	0			
402	0			
702	0			

## Structure

## Unit cell:

a	8.21 A
b	18.42 A
c	5.40 A

## Space group:

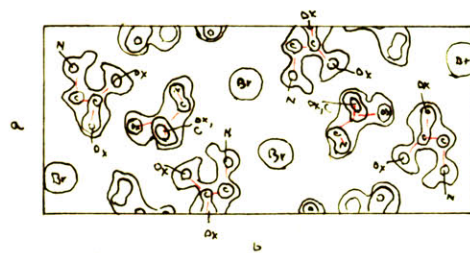
P 2<sub>1</sub> 2<sub>1</sub> 2<sub>1</sub>

## Atomic positions:

	x	y	z
Br	.178	.035	.833
C	.095	.380	.833
C	.104	.428	.120
N	.278	.430	.158
O	.462	.110	.317
O	.200	.338	.842
C	.450	.267	.517
C	.072	.170	.373
N	.149	.194	.158
O	.472	.213	.650
O	.418	.283	.350

## Discussion

The above structure can only be regarded as an approximate structure. The atomic positions are in some error due principally to the overlapping of the atoms in projection. The atoms could not be further resolved as only zero level photographs were taken so that only projections of the cell could be obtained. No account has been taken so far of the position of the hydrogen atoms in the structure or of their contribution to calculated intensities. A projection of the determined structure on  $xyo$  is given in Figure 13.<sup>14</sup> Here the shape of the glycine molecule may easily be seen.



N = Nitrogen  
 Ox = Oxygen  
 C = Carbon  
 Br = Bromine

Figure 14 Projection of Structure on (xy)

### Acknowledgment

The writer is indebted to Prof. M. J. Buerger for the suggestion of diglycine hydrobromide for crystal structure determination. Suggestions during the work and reading of the manuscript were most helpful.