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The Crystal Structure of Acrylic Acid

by

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O.K.
R. L. [Signature]

For my parents

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Introduction

The crystal structure of acrylic acid, CH_2CHCOOH , was determined by means of x-ray diffraction in order that the structure might be available for comparison with that of propionic acid, $\text{CH}_3\text{CH}_2\text{COOH}$ (1). The structure of acrylic acid was thought to be quite similar to that of propionic acid since the carbon-oxygen skeleton is much the same, and the hydrogen-bonding system should be nearly identical. The fact that the end carbon-carbon bond in acrylic acid is double would suggest that the molecule is planar. A comparison of the structures of propionic acid and acrylic acid would thus allow one to study the effect of molecular planarity or non-planarity on crystal packing in the situation where the strong hydrogen-bonding forces are hoped to be identical.

Preparation of the Crystals

A few milliliters of "Eastman grade" acrylic acid were placed in a weighing bottle. The bottle was placed in a beaker containing glass beads, and cooled to -10°C . After the acrylic acid had partially solidified, the excess liquid acid was poured off; and the bottle was again cooled to -10°C in the glass beads to insure complete solidification. By means of this technique, a large number of single crystals were left extending from the frozen mass in the bottom of the bottle. Although many of the crystals were too large, a few were of proper size; all were well-formed, rectangular needles. The crystals were broken from the solid mass in the bottom of the bottle and transferred to a metal plate which rested on a block of dry ice. An appropriate crystal was selected and pushed into a 0.03 cm diameter capillary tube. The capillary tube containing the crystal was glued to a brass pin. This assembly was placed in a groove in a small piece of dry ice, carried to the camera, and mounted on the goniometer head in a stream of cold nitrogen. The apparatus used to supply the stream of nitrogen was described by Scheuerman (2). The temperature of the crystal was kept between 0°C and -35°C for alignment, but was lowered to -113°C to record the diffraction data. No phase change was observed between the melting point and -113°C .

Unit Cell and Space Group

From oscillation and Weissenberg photographs the crystal was found to be body-centered orthorhombic. The reflections found to be systematically absent were of the type

$$hkl \text{ if } h + k + l = 2n + 1,$$

$$Ok\ell \text{ if } k = 2n + 1,$$

$$h0\ell \text{ if } h = 2n + 1,$$

$$hk0 \text{ if } h + k = 2n + 1.$$

The crystal thus belongs to one of two space groups, $Ibam$ or $Iba2$.

The cell constants a and b were determined from a zero-layer Weissenberg photograph which was calibrated with a superimposed sodium chloride powder diffraction pattern. c was determined from a rotation photograph which was calibrated by superimposing a sodium chloride rotation diffraction pattern. The following values were obtained:

$$a = 9.966 \pm 0.007$$

$$b = 11.744 \pm 0.013$$

$$c = 6.306 \pm 0.016 \text{ \AA}.$$

These constants with eight molecules per unit cell gave a density of solid acrylic acid of 1.296 gms/cc. There has been no experimental density determination made on solid acrylic acid, but the density of the liquid at 12°C has been reported to be 1.0600 gms/cc (3).

Data

Zero-, first-, second-, and third-layer Weissenberg photographs were made with four films in the camera. The intensities of the reflections on the zero-, first-, and second-layers were measured visually by comparison with a standard calibrated intensity strip in the usual manner. The intensities were corrected with the proper Lorentz, polarization, and Tunnell factors. No correction for absorption was deemed necessary since μ_r was calculated to be 0.148.

Planarity

The fact that the intensity of a reflection for given h and k depended on whether l was odd or even but was otherwise independent of l was observed from the zero-, first-, second-, and third-layer Weissenberg photographs. This dependence must also be shown by the calculated structure factors.

In general, the structure factor, F_{hkl} , is given by the following equation:

$$F_{hkl} = \sum_{j=1}^J f_j e^{2\pi i (hx_j + ky_j + lz_j)} \quad (1)$$

where the summation is taken over the J atoms in the unit cell, f_j is the atomic scattering factor of the j th atom, and x_j , y_j , and z_j are the coordinates of the j th atom in a coordinate system with the three unit cell edges - a , b , and c - as coordinate axes and the magnitudes of the coordinates are equal to fractions of the unit cell dimensions.

The coordinates of equivalent positions for space group $Iba2$ are $(0,0,0)$ and $(1/2,1/2,1/2)$ plus (x,y,z) , (\bar{x},\bar{y},z) , $(x,\bar{y},1/2+z)$, and $(\bar{x},y,1/2+z)$. Upon substitution of these coordinates into Equation 1, the following is obtained:

$$F_{hkl} = 2 \sum_j f_j \left[1 + e^{2\pi i \left(\frac{h+k+l}{2} \right)} \right] e^{2\pi i lz_j} \left\{ \cos 2\pi (hx_j + ky_j) + e^{2\pi i \frac{1}{2}} \cos 2\pi (hx_j - ky_j) \right\}$$

According to the systematic absences $h + k + l = 2n$ so

$$e^{2\pi i \left(\frac{h+k+l}{2} \right)} = 1.$$

Therefore

$$F_{hkl} = 4 \sum_j f_j e^{2\pi i l z_j} \left[\cos 2\pi (hx_j + ky_j) + e^{2\pi i l/2} \cos 2\pi (hx_j - ky_j) \right]$$

The coordinates of equivalent positions for space group Ibam are (0,0,0) and (1/2,1/2,1/2) plus (x,y,0), ($\bar{x},\bar{y},0$), ($\bar{x},y,1/2$), and (x, $\bar{y},1/2$). When these are substituted into Equation 1, the following is obtained:

$$F_{hkl} = 4 \sum_j f_j \cos 2\pi (hx_j + ky_j) + e^{2\pi i l/2} \cos 2\pi (hx_j - ky_j).$$

It may be seen that the structure factor for space group Ibam depends only on whether l is even or odd, but that of space group Iba2 does not. However, if $z = 0$ the structure factor for Iba2 is identical with that of space group Ibam and depends only on whether l is even or odd. If acrylic acid has the planar structure that was indicated by this observation, space group Iba2 reduces to Ibam.

In order to give a more quantitative proof of the planarity than the observation from the films, \hat{F}_0 was plotted against \hat{F}_2 where \hat{F}_l is given by $\frac{F_{hkl}}{f_{hkl}}$ and f_{hkl} is the unitary scattering factor.

The unitary scattering factor is defined as the atomic scattering factor normalized to unity for zero angle of scattering instead of the atomic number and has the same value for all atoms. The average of this quantity for the atoms in the unit cell is used, or in this case

$$\hat{f}_{hkl} = \frac{1}{2} \left(\frac{f_o}{s} + \frac{f_c}{l} \right).$$

The values of f_o and f_c were obtained from McWeeny (4). The plot should result in a straight line through the origin; for when l is

even,

$$F_{hkl} = 8 \sum_j f_j \cos 2\pi h x_j \cos 2\pi k y_j ;$$

and if \hat{f}_{hkl} is substituted for f_j ,

$$F_{hkl} = 8 \hat{f}_{hkl} \left\{ \sum_0^1 8 \cos 2\pi h x_0 \cos 2\pi k y_0 + \sum_c 6 \cos 2\pi h x_c \cos 2\pi k y_c \right\};$$

or

$$F_{hk2} = 8 \hat{f}_{hk2} \left\{ \sum_0^1 8 \cos 2\pi h x_0 \cos 2\pi k y_0 + \sum_c 6 \cos 2\pi h x_c \cos 2\pi k y_c \right\};$$

$$F_{hko} = 8 \hat{f}_{hko} \left\{ \sum_0^1 8 \cos 2\pi h x_0 \cos 2\pi k y_0 + \sum_c 6 \cos 2\pi h x_c \cos 2\pi k y_c \right\};$$

so

$$\frac{F_{hk2}}{F_{hko}} = \sqrt{K} \frac{\hat{f}_{hk2}}{\hat{f}_{hko}} .$$

The constant, K, may be regarded as the correlation factor between the relative intensities of the zero- and second-layer films. A straight line of slope 1.33 and intercept at the origin was obtained when \hat{F}_0 was plotted versus \hat{F}_2 . The graph is shown in Figure 1.

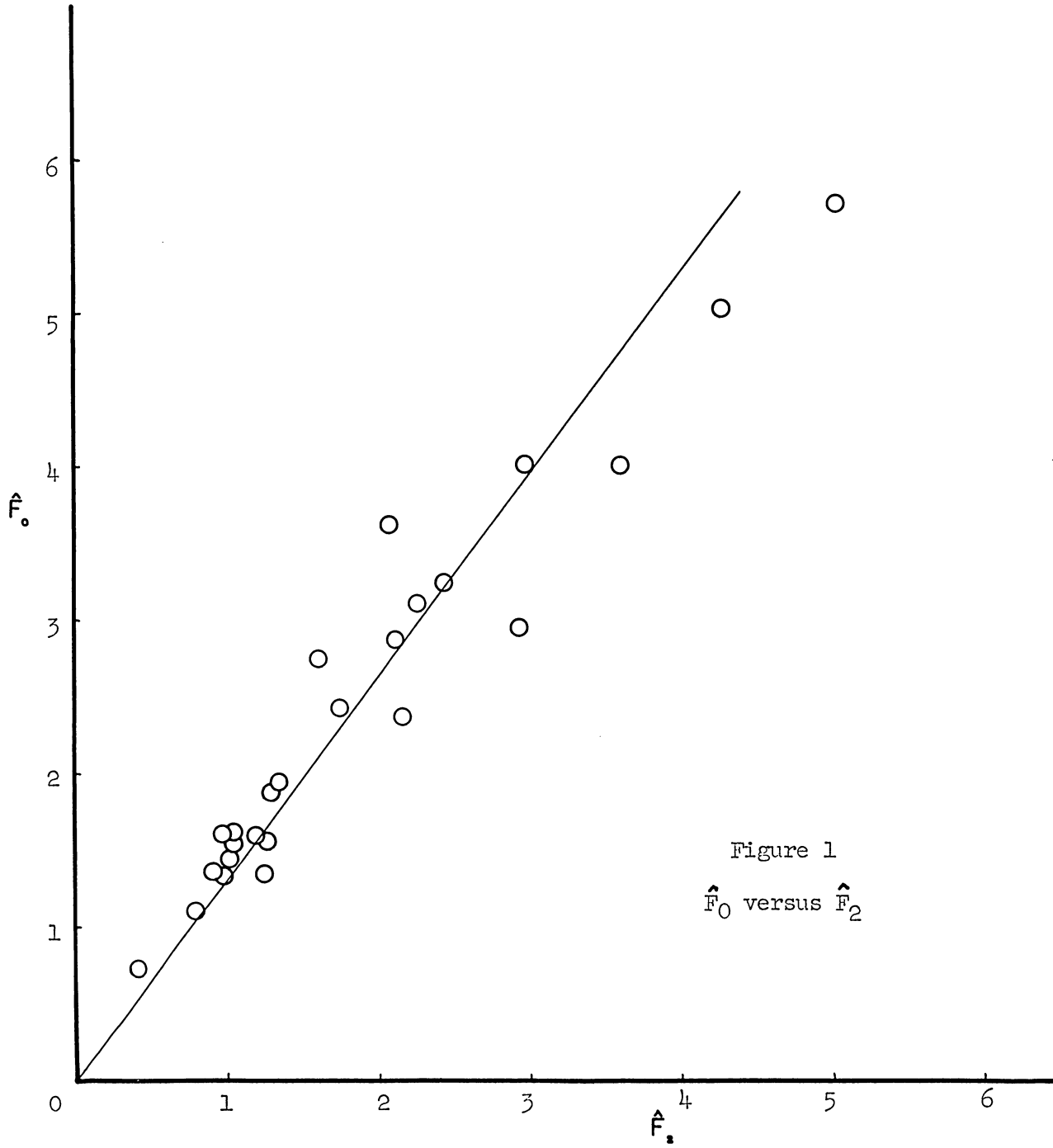


Figure 1
 \hat{F}_0 versus \hat{F}_2

Patterson Function

Assuming that the molecules lie in the xy plane at $z = 0$ and $z = 1/2$, the appropriate Patterson projection to calculate is $P(u,v)$. This projection would include not only the interatomic vectors between atoms in the same plane, but also the projections of those vectors between the atoms in the $z = 0$ plane and those in the $z = 1/2$ plane. These vectors would complicate the solution of the Patterson map, but they would not be present in the Patterson map of the primitive cell. The relation between the structure factors of the body-centered cell and those of the primitive cell were investigated in order that the primitive cell Patterson map might be synthesized from the body-centered data.

In the case of the body-centered cell

$$F_{hko} = 8 \sum_j f_j \cos 2\pi hx_j \cos 2\pi ky_j$$

$h+k=2n$

and

$$F_{hki} = -8 \sum_j f_j \sin 2\pi hx_j \sin 2\pi ky_j$$

$h+k=2n+1$

In the case of the primitive cell

$$F_{hko} = 8 \sum_j f_j \cos 2\pi hx_j \cos 2\pi ky_j$$

$h+k=2n$

and

$$F_{hki} = -8 \sum_j f_j \sin 2\pi hx_j \sin 2\pi ky_j$$

$h+k=2n+1$

Thus to calculate the Patterson function of the primitive cell the F_{hkl}^2 's for the zero-layer could be used as they were for the reflections where $h + k = 2n$, and the F_{hkl}^2 's for the first-layer could be converted to zero-layer type reflections where $h + k = 2n + 1$ by multiplying by the factor, $\left(\frac{f_{hk0}}{f_{hkl}}\right)^2$. The correlation factor between the intensities of the zero- and first-layers was considered to be unity since both were exposed for an equal length of time. The calculation of the Patterson function of the primitive cell gives the same result as the calculation of the Harker section of the Patterson function of the body-centered crystal through the plane $z = 0$.

A planar model of the molecule was made to scale using expected bond distances and Van der Waal's radii and was moved around over the contour map of the Patterson function. An orientation of the molecule in the cell was found which would explain the peaks in the Patterson map and would cause minimum overlap of the molecules when they were placed in the unit cell in the positions demanded by the symmetry conditions of the space group.

The Patterson function for the body-centered crystal was calculated and plotted also. It was compared with the Patterson map that was given by the primitive cell. This comparison aided the solution in that the molecules in the plane $z = 0$ must take a position in the unit cell so that the interatomic vectors between its atoms and the atoms of the molecules in the plane $z = 1/2$ would be those missing from the Patterson map of the primitive cell.

The Patterson maps of the primitive and of the body-centered crystals are shown in Figures 2 and 3 respectively.

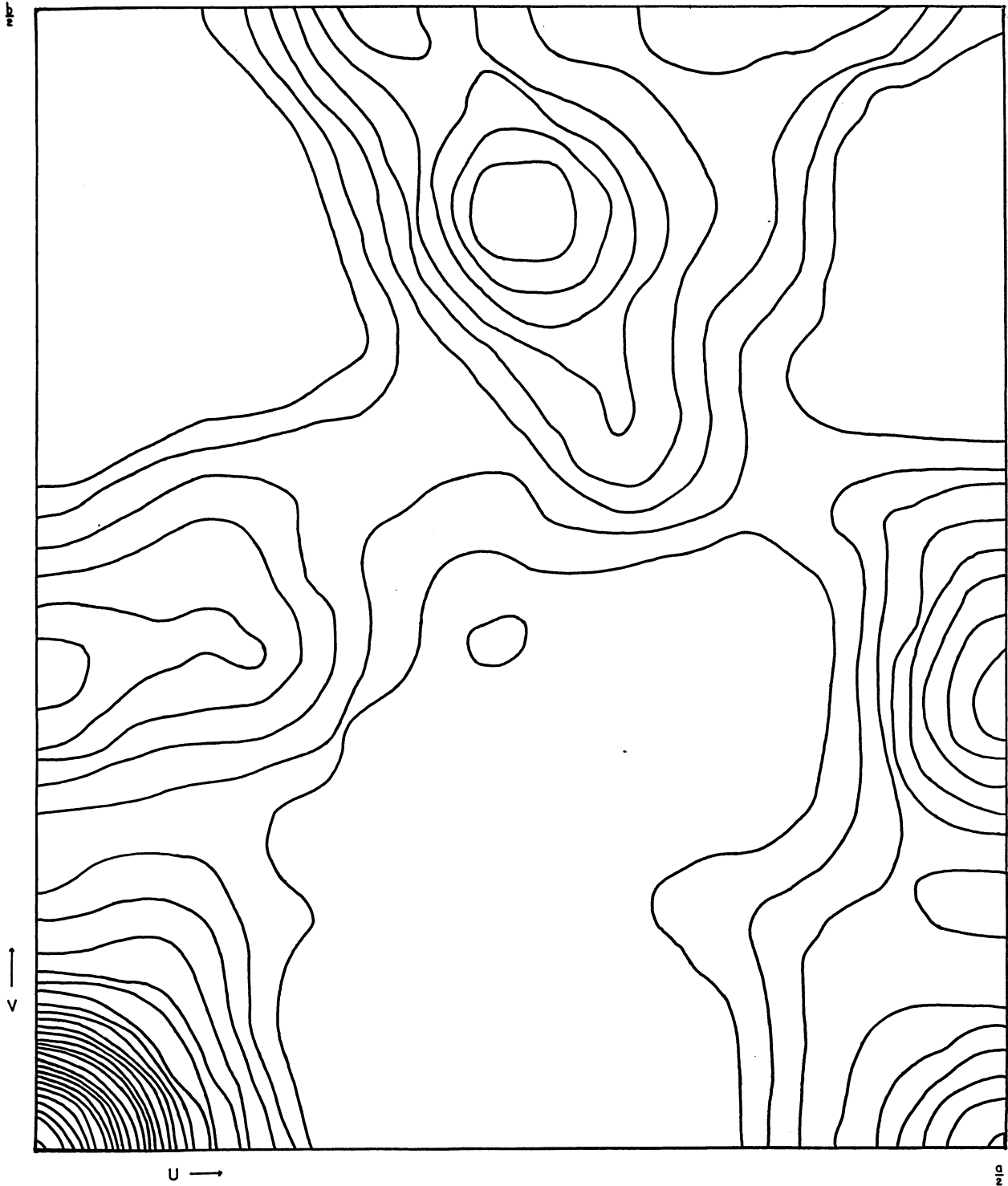


Figure 2
 $P(u,v)$ of the Primitive Cell

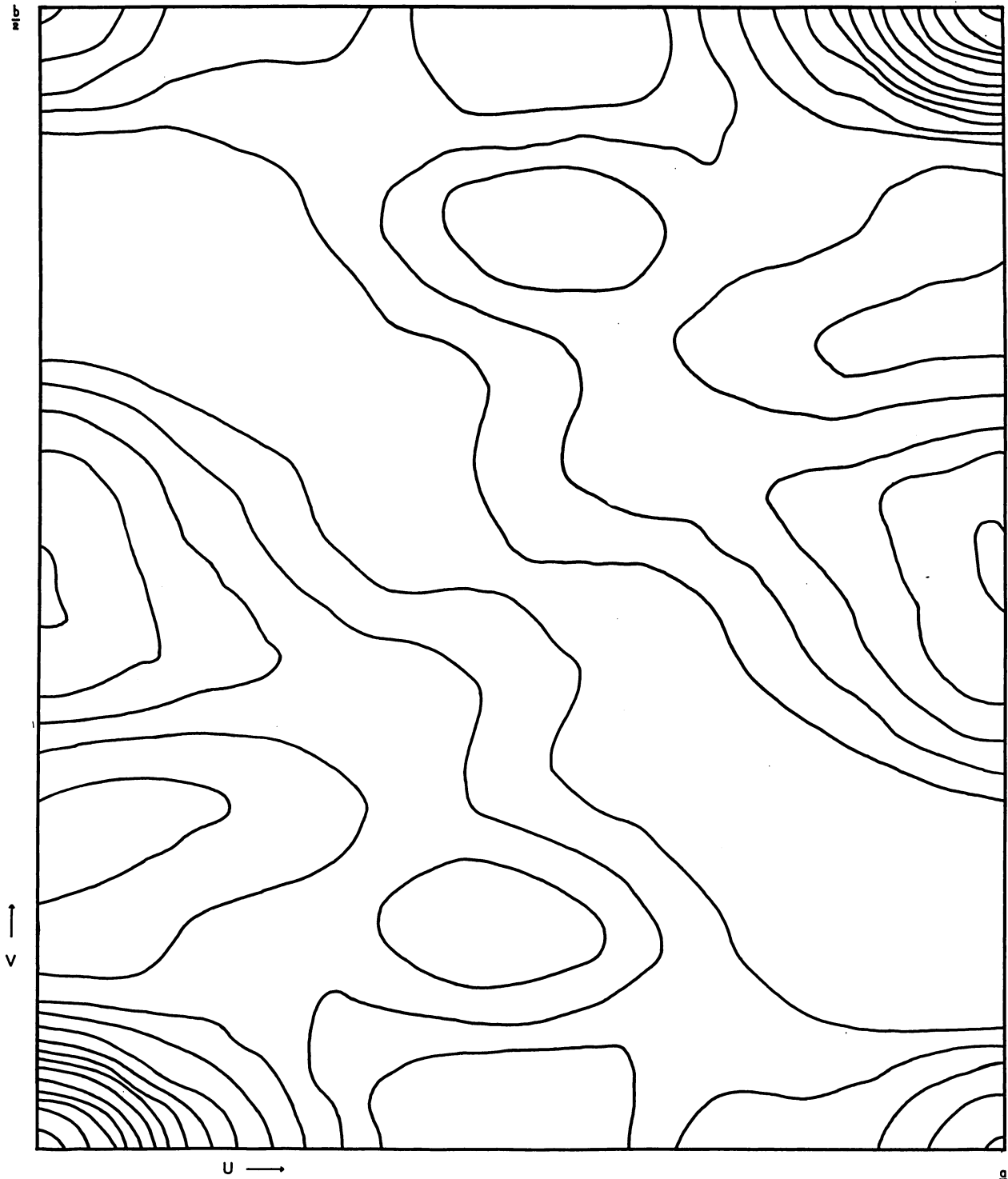


Figure 3
 $P(u,v)$ of the Body-centered Cell

Trial Structure

Trial x and y parameters were assigned to the atoms; they are presented in Table 1. The structure factors that would be given by such a structure were calculated for the zero- and first-layers. The signs of the calculated structure factors were assigned to the observed structure factors where the agreement in the magnitude of the two numbers would justify it. The first-layer structure factors were converted to zero-layer type by multiplying by $\frac{f_{hk0}^A}{f_{hkl}^A}$ as before. The electron density projection, $\rho(x,y)$, was calculated for the primitive cell and for the body-centered cell. The resolution of the atoms in the electron density projection of the primitive cell indicated that the trial parameters were essentially correct. The electron density projection for the body-centered and primitive cells are given in Figures 4 and 5 respectively.

In order to refine the structure, the difference synthesis or $(\rho_o - \rho_c)$ synthesis was calculated and is shown in Figure 6. The x and y parameters and the temperature factors were changed upon inspection of this map. The new parameters and temperature factors are given in Table 2. This refinement brought the reliability index down to 0.144 from 0.182 for the 41 observed reflections on the zero-layer. The reliability index for the first-layer changed from 0.235 to 0.260 for the 36 observed reflections. The same scale factor was used for the zero- and first-layers. The calculated and observed structure factors are given in Table 3.

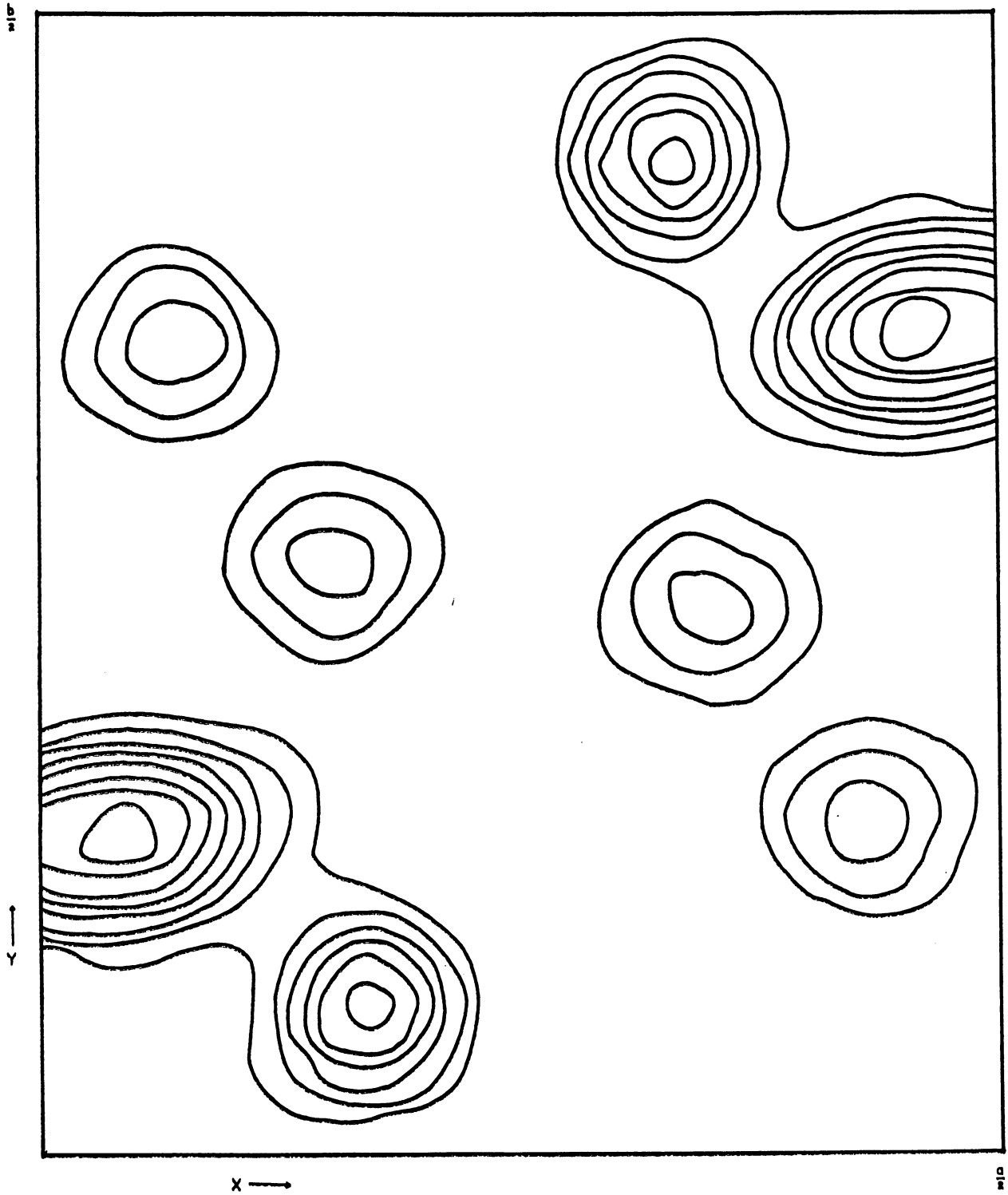


Figure 4
 $p(x,y)$ of the Body-centered Cell

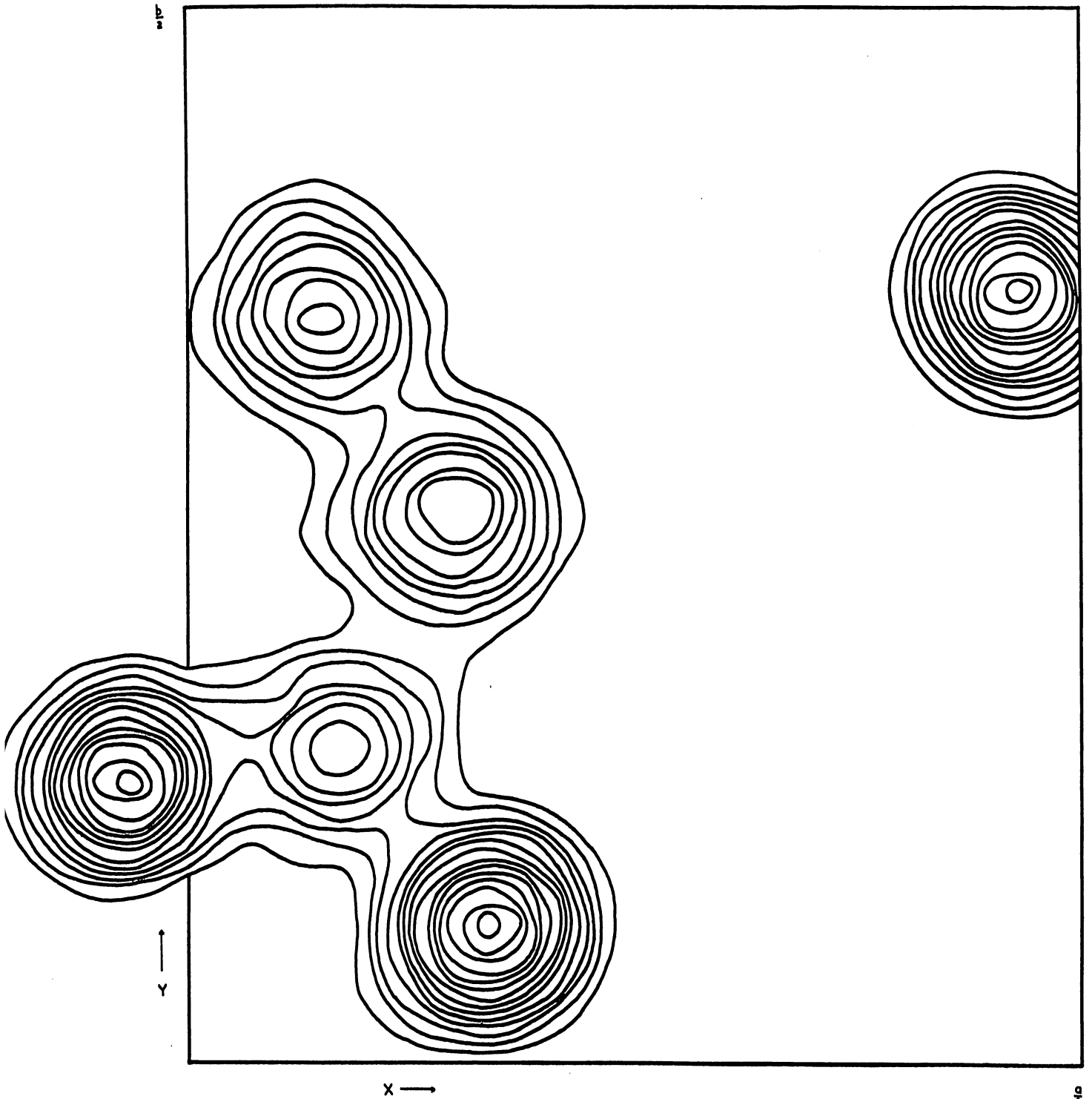


Figure 5
 $\phi(x,y)$ of the Primitive Cell

- Positive contour
- Zero contour
- - - Negative contour

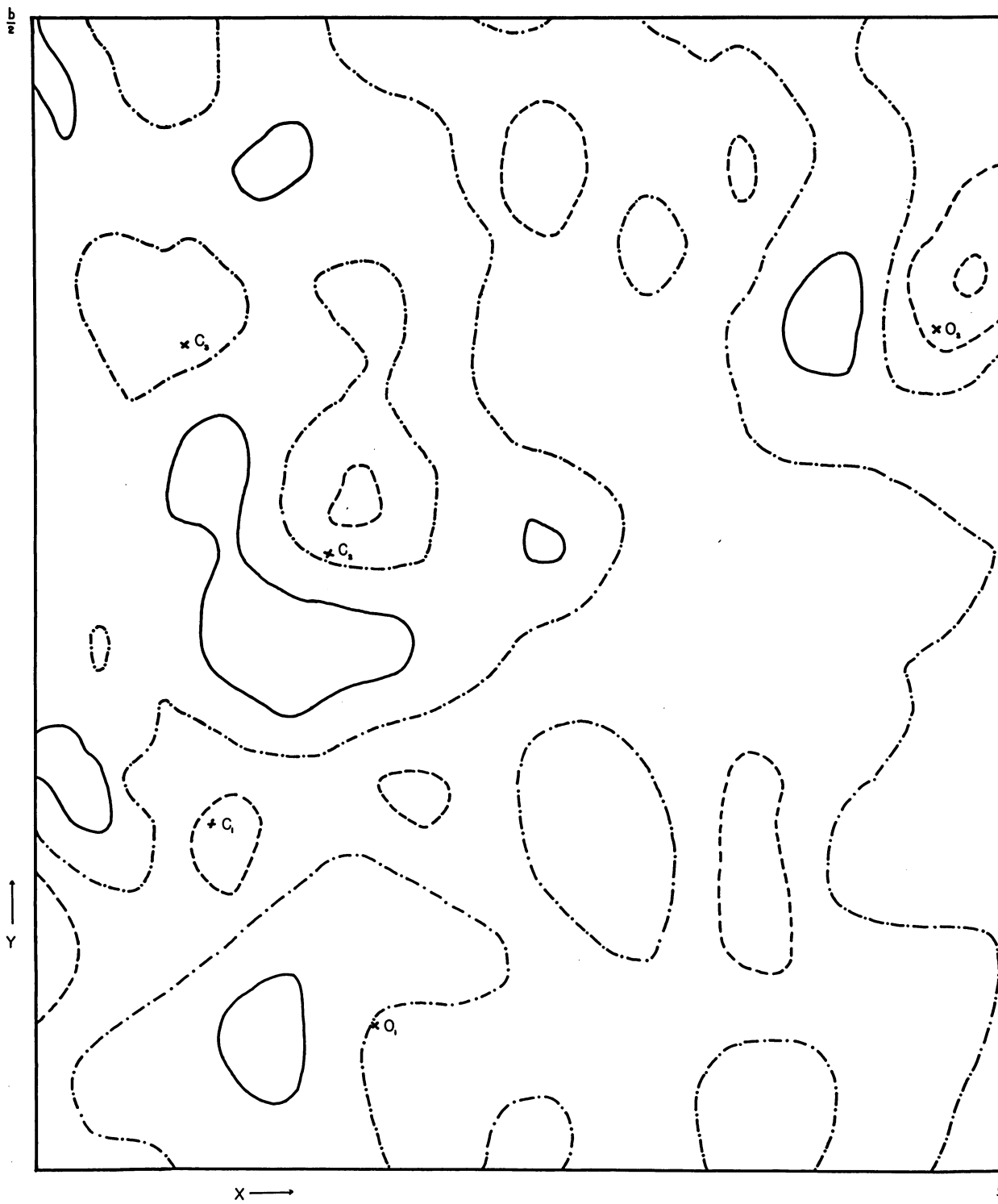


Figure 6
Difference Synthesis

TABLE 1

Initial Parameters

<u>Atom</u>	<u>Trial</u>		<u>$\rho(x,y)$</u>	
	<u>x</u>	<u>y</u>	<u>x</u>	<u>y</u>
O ₁	1.73	0.72	1.68	0.76
O ₂	-0.32	1.55	-0.36	1.60
C ₁	0.95	1.74	0.85	1.75
C ₂	1.53	3.17	1.49	3.05
C ₃	0.74	4.22	0.76	4.16

TABLE 2

Final Parameters

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>
O ₁	1.73	0.72	0	2.5
O ₂	-0.340	1.58	0	2.1
C ₁	0.918	1.74	0	2.2
C ₂	1.48	3.11	0	2.4
C ₃	0.757	4.17	0	2.3

TABLE 3

Observed and Calculated Structure Factors

<u>hk0</u>	<u> F_o </u>	<u>F_c</u>	<u>hk0</u>	<u> F_o </u>	<u>F_c</u>
020	4.05	-3.54	600	2.55	1.86
040	7.91	-8.74	620	1.80	1.63
060	0.43	0.16	640	2.95	3.17
080	2.59	2.65	660	3.49	-3.87
0.10.0	4.90	-5.40	680	1.52	-1.42
110	7.51	7.70	6.10.0	0.63	0.26
130	2.95	-3.18	710	0.72	0.82
150	3.25	-3.68	730	1.35	-0.02
170	1.94	2.34	750	0.76	-0.90
190	1.05	-1.11	770	0.60	0.85
1.11.0	0.61	-1.09	790	0.57	-0.81
200	6.60	5.95	7.11.0	0.45	0.16
220	3.03	-3.35	800	2.13	-2.46
240	9.00	-8.62	820	0.59	-1.24
260	5.49	4.84	840	2.06	1.52
280	3.38	4.07	860	0.91	-0.30
2.10.0	1.29	-1.06	880	0.49	0.53
310	3.35	-2.74	8.10.0	0.45	0.94
330	5.60	-5.61	910	1.54	-1.03
350	1.05	0.90	930	0.20	-1.06
370	3.22	3.22	950	0.59	0.72
390	2.15	3.25	970	0.54	0.92
3.11.0	0.83	-1.05	990	0.38	0.57
400	5.09	-4.37	10.0.0	1.79	-0.79
420	0.37	1.70			
440	2.69	-2.46			
460	1.86	1.25			
480	0.96	0.54			
4.10.0	1.13	1.34			
510	2.24	3.70			
530	0.45	0.04			
550	1.36	-1.44			
570	1.02	-0.69			
590	0.61	-0.44			
5.11.0	0.55	-0.84			

TABLE 3 (cont.)

Observed and Calculated Structure Factors

<u>hkl</u>	<u> F_o </u>	<u>F_c</u>	<u>hkl</u>	<u> F_o </u>	<u>F_c</u>
121	2.19	2.40	721	0.83	-1.77
141	6.58	5.79	741	2.10	3.02
161	2.47	2.32	761	2.24	3.10
181	0.44	0.03	781	0.70	-0.89
1.10.1	1.85	-3.57	7.10.1	1.10	-1.59
211	12.68	-10.54	811	0.89	-1.58
231	2.51	1.85	831	1.00	-1.82
251	4.37	2.64	851	4.05	4.84
271	0.41	0.73	871	0.48	-0.84
291	0.73	1.56	891	1.03	-1.80
2.11.1	2.36	-2.59	921	1.15	-1.98
321	5.14	-4.10	941	0.49	0.12
341	0.32	0.16	961	0.47	0.29
361	1.70	1.36	981	0.40	-0.06
381	0.46	-0.19	9.10.1	0.83	-0.74
3.10.1	0.67	-1.17	10.1.1	1.58	-2.17
411	2.52	-2.11	10.3.1	0.87	-2.13
431	2.82	-2.61	10.5.1	0.44	-1.12
451	5.09	-4.98	10.7.1	0.37	-0.29
471	1.00	0.75	10.9.1	0.22	-1.14
491	0.50	0.56			
4.11.1	0.48	0.07			
521	5.65	-5.87			
541	2.37	-1.92			
561	1.38	2.08			
581	1.14	-2.13			
5.10.1	0.49	0.14			
611	3.57	-3.30			
631	0.42	0.12			
651	0.46	1.85			
671	1.03	1.41			
691	1.10	-1.77			

Discussion of the Structure

Acrylic acid was found to consist of hydrogen-bonded dimers located about a center of symmetry. The interatomic distances and angles were calculated and are given in Figure 7 and Table 4. These values for the bond lengths should be accurate to within 0.06 Å and are not unreasonable. The intermolecular distances were also calculated, and the smallest ones are shown in Figure 7. The smallest C-C distance of 4.49 Å is greater than that allowed by twice the Van der Waal's radius of a methyl group (4.0 Å) while the smallest C-O distance of 3.38 Å is just below that allowed by the sum of the Van der Waal's radii of oxygen and of a methyl group (3.4 Å).

As was expected, the hydrogen-bonding system of acrylic acid was very similar to that of propionic acid. Aside from the fact that the arrangement of the acrylic acid molecules in the $z = 0$ plane is much the same as the arrangement of the propionic acid molecules in the [100] projection, there is no similarity in the crystal packing in the two acids.

TABLE 4

Bond Lengths and Angles

<u>Bond</u>	<u>Length</u> (Å)		<u>Angle</u>
C ₁ -O ₁	1.30	O ₁ -C ₁ -O ₂	121°19'
C ₁ -O ₂	1.27	O ₂ ••O ₁ -C ₁	110°22'
C ₁ -C ₂	1.48	O ₁ ••O ₂ -C ₁	128°18'
C ₂ -C ₃	1.29	O ₁ -C ₁ -C ₂	119°17'
O ₁ ••O ₂	2.69	O ₂ -C ₁ -C ₂	119°30'
		C ₁ -C ₂ -C ₃	123°15'

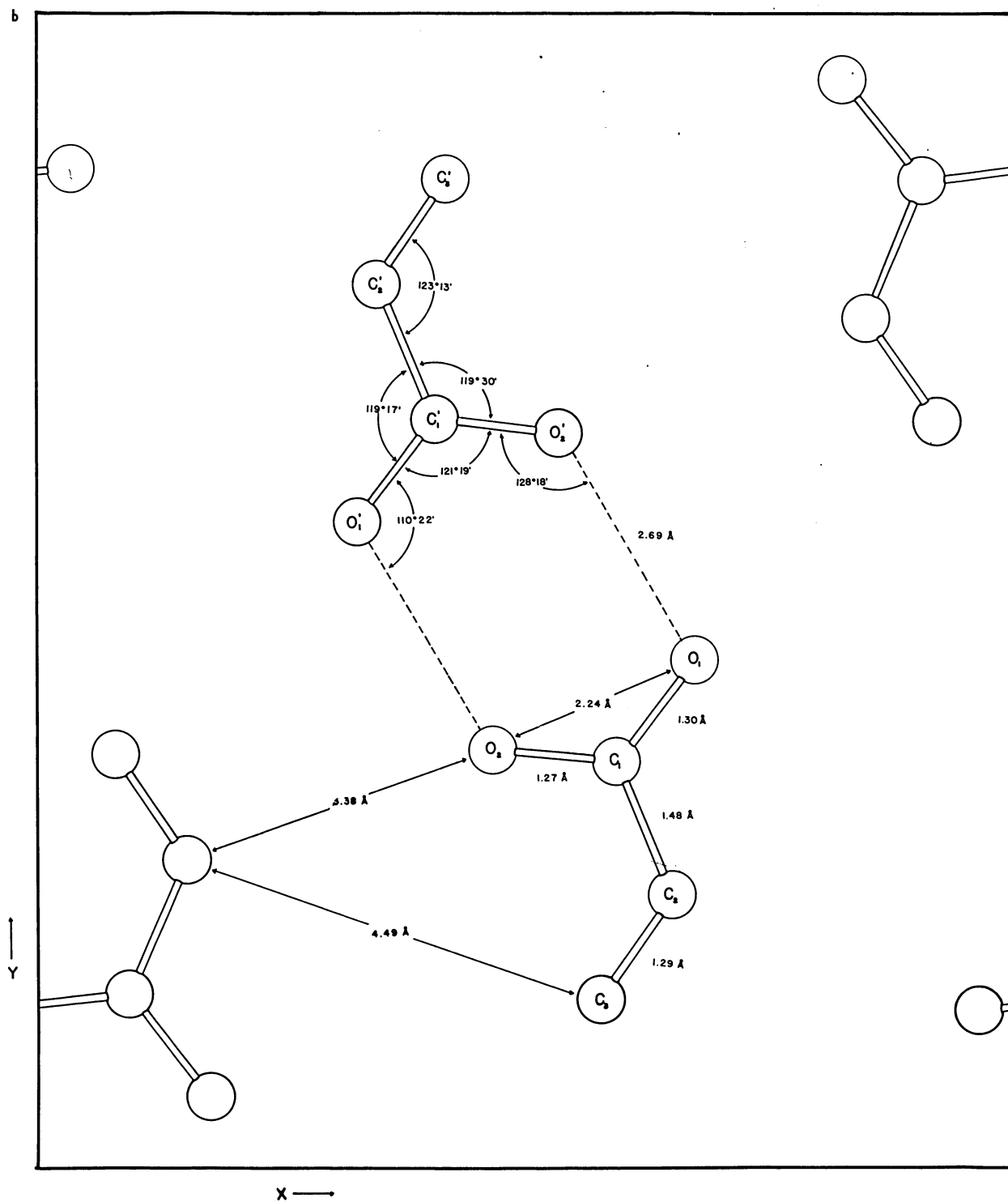


Figure 7
 $z = 0$ Plane Showing Bond Lengths and Angles

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