THE CRYSTAL STRUCTURES OF
SORBIC AND CROTONIC ACIDS

THESIS

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CHAPTER I

X-RAY ANALYSIS OF CRYSTAL STRUCTURES

1. Diffraction of X-Rays by Crystals

1.1 X-Ray Scattering from a Single Atom

The atomic scattering factor f represents the proportion of the X-ray beam which is scattered without increase in wave length by the electrons of a particular atom. For small scattering angles, this factor approaches z, the atomic number, but the value falls off rapidly with increasing angle because of interference from phase differences in the waves scattered from each individual electron, and also an increase in the proportion of incoherent scattering.

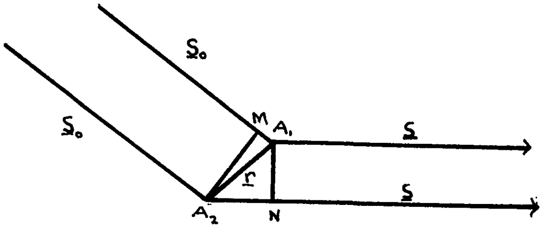
The value of f for an atom is equal to the sum of the f_e's for each electron; where f_e is given by

$$f_e = \int |\psi_k|^2 \; e^{i\,k\,\underline{s}\cdot\underline{r}_k} \, dv_k \qquad (1)$$

where $|\psi_k|^2$ is the probability that the electron is in a given region v and $\int_0^\infty |\psi|^2 \, dv = 1$. The amplitude of f depends on the phase difference caused by displacement of the scattering electrons from the atomic centre, given by $e^{i\,k\,\underline{s}\cdot\underline{r}}$ where $\underline{r}$ is a vector representing the position of the electron with respect to the atomic centre, $\underline{s}$ is a vector normal to the plane of reflection and $k = 2\pi/\lambda$. Scattering curves have been calculated for various atoms and ions, first by Hartree (1928) and later by Pauling & Sherman (1932), McWeeny (1952), and others.

1.2 X-Ray Scattering from an Array of Atoms

In a crystal, the atoms are arrayed in a regular three dimensional array.



When a monochromatic beam of X-rays strikes this array or lattice, the beam will be scattered separately by each atom. These scattered waves will interfere so as to cancel each other out except when the difference in path length between different waves is an integral multiple of the wave length. In the diagram, where $\underline{s}_0$ and $\underline{s}$ are vectors of magnitude $^1/\lambda$ representing the incident and reflected beam from two lattice points A_1 and A_2, the path difference is $A_1N - A_2M$ where $A_1N - A_2M = \lambda(\underline{r}.\underline{s} - \underline{r}.\underline{s}_0)$. Reinforcement would occur when $(\underline{r}.\underline{s} - \underline{r}.\underline{s}_0) = $ integer. For a three dimensional lattice where the distance between points, $\underline{r}$, could be expressed as (ua + vb + wc), a b and c being unit translations along the axes, then $(ua + vb + wc)(\underline{s} - \underline{s}_0)$ must be integral as must each component of the equation.

Thus
$$a(\underline{s} - \underline{s}_0) = h$$
$$b(\underline{s} - \underline{s}_0) = k \qquad (2)$$
$$c(\underline{s} - \underline{s}_0) = \ell$$

where h k and ℓ are integers. These are Laue's equations for X-ray reflection. Bragg (1933) showed that these integers are identical with the Miller indices, which are direction ratios of normals to the crystal planes.

The vector $\underline{s} - \underline{s}_o$ represents the normal to a plane which would reflect $\underline{s}_o$ into $\underline{s}$. This is referred to as the plane of reflection. If the angle of incidence to the plane is θ, the angle between $\underline{s}$ and $\underline{s}_o$ is $2\,\theta$ and

$$\left| \underline{s} - \underline{s}_o \right| = \frac{2 \sin \theta}{\lambda} \tag{3}$$

The spacing between planes of index h kℓ is given as d, the projection of $^a/h$ $^b/k$ or $^c/\ell$ on $\left| \underline{s} - \underline{s}_o \right|$ such that

$$\frac{\frac{a}{h} \cdot (\underline{s} - \underline{s}_o)}{\underline{s} - \underline{s}_o} = d \tag{4}$$

From this, and equations (2) and (3), it may be shown that for reflection to occur

$$\lambda = 2d \sin \theta \tag{5}$$

This is Bragg's equation, which forms the basis for the study of the structure of crystals by X-ray methods.

2 Structure Factors

The structure factor of a reflection obtained by impingement of X-rays on a given set of planes of a crystal is a measure of the number of electrons in the reflecting plane. This quantity would reach its maximum value if all the atoms were exactly on the plane, however interference due to phase differences from scattering by atoms located away from the planes causes diminution in the observed amplitudes. The values of the structure factors observed for all the reflecting planes thus depends on the arrangement of the atoms in the lattice.

The structure factor $F(hk\ell)$ for a reflecting plane in a structure containing j atoms is related to the atomic scattering factor f_j by the equation

$$F(hk\ell) = \sum_j f_j \exp \left[2\pi i\left(h \frac{xj}{a} + k \frac{yj}{b} + \ell \frac{zj}{c}\right)\right] \qquad (6)$$

where ${}^{xj}/a$, ${}^{yj}/b$ and ${}^{zj}/c$ are the coordinates of the atom with respect to the axes a, b and c of the unit cell. This expression is complex, showing that phase change has occurred during reflection. This change in phase angle cannot readily be determined, and cannot be measured experimentally.

The structure factor may be expressed in terms of sine and cosine functions $F = A + iB$ where

$$A = \sum_j f_j \cos 2\pi \left(h\frac{x}{a} + k\frac{y}{b} + \ell\frac{z}{c}\right) \qquad (7)$$

and $$B = \sum_j f_j \sin 2\pi \left(h\frac{x}{a} + k\frac{y}{b} + \ell\frac{z}{c}\right) \qquad (8)$$

This expression may be simplified for a particular case by the use of space group symmetry for a centrosymmetric structure $B = 0$. Other symmetry relations may also be applied. These give rise to systematic absences characteristic of particular space groups. Expressions for all the space groups have been published (Lonsdale; 1936)(Henry and Lonsdale; 1952).

Although the phases of structure factors are not determined directly, the amplitudes $|F_o|$ may be derived from the observed integrated intensities, I, of coherent X-ray scattering from the crystal planes. In a perfect single crystal in which all the planes are correctly orientated, $|F_o|$ is proportional to the intensity of the reflected beam. In practice, however, most crystals are of the mosaic type, that is, they contain small regions of perfection slightly out of alignment with one another. Reflections from planes in mosaic crystals are such that $|F_o| \propto \sqrt{I}$.

As a single crystal is rotated in the X-ray beam, the reflection is not instantaneous as the crystal turns through the Bragg angle for a plane, but due to variation in the orientation of the crystal planes, may occur over several seconds of arc. The integrated reflection from a plane, that is, the total energy reflected as the crystal turns through the Bragg angle, is given as $E\omega/I_o$, where E is the energy reflected by a crystal rotating with an angular velocity of ω in a beam of intensity I_o. For a small crystal,

$$\frac{E\omega}{I_o} = \int_{\theta-\epsilon}^{\theta+\epsilon} R(\theta)d\theta \tag{9}$$

where $R(\theta)$ is the ratio of the power of the diffracted beam to the incident intensity, θ is the Bragg angle and $\pm\ \epsilon$ the limits of the angle of reflection.

The integrated intensity is related to the structure factor by the expression

$$\frac{E\omega}{I_o} = \frac{N^2\lambda^3}{\sin 2\theta} |F_o|^2 \left(\frac{e^2}{mc^2}\right)^2 \left(\frac{1+\cos^2 2\theta}{2}\right) dv \tag{10}$$

where N is the number of atoms per unit volume, λ is the wave length of the X-radiation, e and m are the charge and mass of one electron, and c is the velocity of electromagnetic radiation. Included in the expression is a polarization factor $(1+\cos^2 2\theta)/2$ which corrects for the fact that the incident beam is not polarized with the electric vector perpendicular to the plane of incidence, and the Lorentz factor $^1/\sin 2\theta$ which corrects for the speed at which the given lattice point passes through the reflecting sphere. These correction terms are normally combined.

3. Temperature Factor

3.1 Isotropic Thermal Vibrations

The structure factors so far considered have been geometrical; that is, account has been taken of diminution of intensities due to phase differences in scattering from point atoms, but motions of the atoms themselves have not been described. At any temperature higher than 0°K, atoms in a crystal are not at rest, the amount of vibration increasing with temperature. Thus an atom which from crystal symmetry would be in position to scatter in phase with another would in fact be slightly displaced, at random, from the lattice point.

If the vibration is isotropic and the lattice points uncoupled, the diminution of diffracted intensity due to phase change caused by this displacement may be given by

$$\Delta = e^{-B \sin^2\theta/\lambda^2} \tag{11}$$

where

$$B_o = 8\pi^2 \bar{u}^2 . \tag{12}$$

Here $\bar{u}^2$ is the mean square amplitude of the vibration and $B_{\bullet}$ is the Debye temperature factor (Debye; 1914).

For all non-cubic crystals, the vibration is not isotropic. The amplitude must then be expressed with respect to the axes of the ellipsoid of vibration.

3.2 Anisotropic Thermal Vibrations

If an atom vibrates anisotropically, the mean square amplitude of vibration is given by

$$\bar{u}^2 = \sum_{i=1}^{3} \sum_{i=1}^{3} U_{ij}\, \ell_i\, \ell_j \tag{13}$$

where U_{ij} is a symmetric tensor and $\underline{\ell}$ is a unit vector characterizing the direction of vibration (Cruickshank; 1956a). The temperature exponent thus becomes

$$T(s) = \exp \quad -2\pi^2 (\sum_i \sum_j U_{ij}\, s_i\, s_j)]\ \underline{s}^2 \tag{14}$$

where $\underline{s}$ is a reciprocal vector equal to $^{2 \sin\theta}/_{\lambda}$. This may be written in the form

$$T(hk\ell) = \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell) \tag{15}$$

where, for example

$$\beta_{11} = 2\pi^2 a^{*2}\, U_{11}$$

and

$$\beta_{12} = 4\pi^2 a^* b^* U_{12} \tag{16}$$

where a^* and b^* are reciprocal axes.

The atoms in a molecule do not vibrate independently. The thermal effects may in some cases be described in terms of rigid body motions of the molecule as a unit. If this is the case the motions may be resolved into vibrational and rotational components, T and ω, given with respect to the centre of mass (Cruickshank; 1956b). These are represented by two 3 x 3 matrices

$$\bar{t}^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} T_{ij} \ell_i \ell_j \qquad (17)$$

where $\bar{t}^2$ is the mean square amplitude of vibration

$$\text{and } \bar{\omega}^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} \omega_{ij} \, a_1 \, a_2 \qquad (18)$$

where $\bar{\omega}^2$ is the mean square amplitude of libration about an axis $\underline{a}$. The values of the molecular motions T_{ij} and ω_{ij} are related to the atomic vibrations U_{ij} by the relationships:

$$\begin{aligned}
U_{11} &= T_{11} + z^2\omega_{22} + y^2\omega_{33} - 2yz\,\omega_{23} \\
U_{22} &= T_{22} + z^2\omega_{11} + x^2\omega_{33} - 2xz\,\omega_{13} \\
U_{33} &= T_{33} + y^2\omega_{11} + x^2\omega_{22} - 2xy\,\omega_{12} \\
U_{12} &= T_{12} - xy\omega_{33} - z^2\omega_{12} + xz\omega_{23} + yz\,\omega_{13} \\
U_{23} &= T_{23} - yz\omega_{11} + xz\omega_{12} - x^2\omega_{23} + xy\,\omega_{13} \\
U_{31} &= T_{13} - xz\omega_{22} + yz\omega_{12} + xy\omega_{23} - y_2\,\omega_{13}
\end{aligned} \qquad (19)$$

where x y and z are coordinates with respect to molecular axes.

4. Representation of a Crystal by a Fourier Series

Any finite, continuous, periodic function may be expressed in terms of a Fourier series. It was suggested by Bragg (1915) that the variation of electron density, , in three dimensions throughout a regular crystal may be considered as such a function.

The relationship may be expressed by:

$$\rho(x,y,z) = \sum_{h'}\sum_{k'}^{\infty}\sum_{\ell'=-\infty} C(h',k',\ell') \exp 2\pi i(h'x + k'y + \ell'z) \qquad (20)$$

The Fourier coefficients C may be related to the structure factors by the equation:

$$F(h,k,\ell) = C(\bar{h}'\bar{k}'\bar{\ell}')V \qquad (21)$$

where V is the unit cell volume. The electron density may thus be described by

$$\rho(x,y,z) = \frac{1}{V}\sum_{h}\sum_{k}^{\infty}\sum_{\ell=-\infty} F(h,k,\ell) \exp -2\pi i(h\frac{x}{a} + k\frac{y}{b} + \ell\frac{z}{c}) \qquad (22)$$

For computational purposes, this summation is resolved into its real and imaginary parts, to give

$$\rho(x,y,z) = \frac{1}{V}\Big[F(000) + 2\sum_{h}\sum_{k}\sum_{\ell}\big(A_o \cos 2\ (hx + ky + \ell z)$$

$$+ B_o \sin 2\ (hx + ky + \ell z)\big)\Big] \quad , \qquad (23)$$

where the F(000) term is equal to the total number of electrons in the cell.

It is only recently that the use of electronic computers has made practicable the evaluation of triple Fourier series. W.L. Bragg (1929), however, showed that some structures could be determined by analysis of projections of electron density down each of the axes in turn. For the 010 projection, for instance, the expression simplifies to

$$\rho(x,z) = \frac{1}{A}\sum_{h}\sum_{\ell} F(h0\ell) \exp -2\pi i(hx + \ell z) \qquad (24)$$

which may be readily summed.

This method is particularly applicable to the solution of molecules, whose atoms may be completely resolved in projections, but it is subject to inaccuracies if atoms overlap.

5. Methods of Structure Determination

5.1 The Phase Problem

The main concern in the solution of a crystal structure, from X-ray data is in the determination of the phase angles of the reflected waves where

$$\begin{aligned} A_o(hk\ell) &= |F_o(hk\ell)| \cos\alpha(hk\ell) \\ \text{and}\quad B_o(hk\ell) &= |F_o(hk\ell)| \sin\alpha(hk\ell) \end{aligned} \qquad (25)$$

Normally according to Friedels law (1913), it may be assumed that

$F(hk\ell) = F(\bar{h}\,\bar{k}\,\bar{\ell})$; when the electron density will be real at every point and may be expressed as

$$\rho\,(x\ y\ z) = \frac{1}{V}\left[F(000) + 2\sum_{h}\sum_{k}\sum_{\ell}|F(hk\ell)|\ \cos\left(2\pi(hx+ky+\ell z) - \alpha(hk\ell)\right)\right] \tag{26}$$

The values of α cannot be determined experimentally.

If the structure is centrosymmetric about the origin, then $\sin\alpha = 0$; thus α must be either zero or π, and $\cos\alpha = \pm 1$.

Some methods used for phase determination include use of sign relationships (Karle and Hauptmann, 1950), isomorphous replacement technique, Cork, (1927), Hargreaves, (1957), and by indirect means such as analysis of Fourier transforms or Patterson functions.

5.2 Fourier Transforms

The transform G of a set of points related to the origin by a set of vectors $\underline{r}_n$ is a continuous function whose value is given by:

$$G(s) = \sum_{n=1}^{N} f_n \exp 2\pi i\, \underline{r}_n . \underline{s} \tag{27}$$

where $\underline{s}$ is a vector in reciprocal space, and f_n is the weighting factor of each point. If the point set is centrosymmetric, the equation may be reduced to:

$$(G(s) = 2\sum_{n=1}^{\frac{n}{2}} f_n \ \cos 2\pi(hx + ky + \ell z) \tag{28}$$

where x, y and z are related to arbitrary axes and h, k and ℓ may have any value. If the set has no centre of symmetry, the transform is complex, and the real and imaginary parts must be computed separately.

The transform of a repeating lattice of finite size is another lattice in reciprocal space. When a large number of points is considered, then the transform will have finite values only at points corresponding to reciprocal spacings of the original lattice. If the repeating pattern is a unit cell, then the transform of a large number of cells, i.e. a crystal of finite size, would have finite values, corresponding to the structure factors, only at the reciprocal lattice points.

The use of Fourier transforms for the elucidation of crystal structures is largely confined to the study of molecules which may be resolved in projection. These have transforms of constant section which may be readily evaluated. The molecule is represented by a vector set of point atoms whose origin is chosen, if possible, at a centre of symmetry. The transform of this vector set in two dimensions is a continuous function on to which the weighted reciprocal lattice may be fitted.

5.3 The Patterson Function

Patterson (1934) suggested a new method for the determination of atomic positions. If $\rho(x,y,z)$ and $\rho(x+u,y+v,z+w)$ are two regions of electron density ρ at points x, y, z and x+u, y+v, z+w, then:

$$P\ (u,v,w) \ = \ \frac{1}{V}\int_0^a\int_0^b\int_0^c \rho(xyz)\,\rho(x+u,\ y+v,\ z+w)\ dxdydz \qquad (29)$$

The values of P are large only when ρ has maxima at both points. A peak in $P(uvw)$ at u_1, v_1, w_1 corresponds to two maxima in $\rho(x,y,z)$ whose distance apart is given by a vector with components u_1, v_1 and w_1. Peaks in the map therefore represent interatomic vectors for every pair of atoms in the crystal.

Since for every vector, there will be a corresponding one of opposite sign, the function is necessarily centrosymmetric. The electron density may be expressed in terms of $F(hk\ell)$, and $P(uvw)$ being a periodic function may be represented by a Fourier series, therefore the integral may be reduced to:

$$P\ (u,v,w) \ = \ \frac{1}{V}\sum_h \sum_k \sum_\ell |F_o|^2(h,k,\ell)\ \cos 2\ (h\frac{u}{a} + k\frac{v}{b} + \ell\frac{w}{c}) \qquad (30)$$

If the summation is on an absolute scale, then the height of a peak P_{ij} for a vector between two atoms of atomic number z_1 and z_2 is given by

$$P_{ij} \simeq P_o \times \frac{z_1 z_2}{\sum z^2} \qquad (31)$$

where P_o is the height of the origin peak.

This method was first applied to projections. If atoms were point sources it would be possible to resolve all the vectors in two dimensions, however, the maxima obtained are diffuse, and the considerable overlap serves to make complete interpretation difficult. Imperfect resolution may in some cases be obviated by the introduction of appropriate sharpening functions. Application of the method to three dimensions, made possible by the use of computers, has aided the solution of Patterson maps of complex substances whose interatomic vectors could not be resolved in projection.

6. Methods of Structure Refinement

6.1 Difference Syntheses

For a centrosymmetric structure, the electron density determined from summation of a Fourier series using as coefficients the signed F_o's, is subject to error from series termination as well as from random errors of measurement. The true atomic positions may thus not correspond to the peak maxima. More accuracy may be obtained by choosing coordinates such that $\varphi = \sum_n w(F_o - F_c)^2$ is minimized. For any atom i, φ is minimized when

$$\frac{\partial \varphi}{\partial x_i} = \frac{\partial \varphi}{\partial y_i} = \frac{\partial \varphi}{\partial z_i} = 0 \qquad (32)$$

If in the Fourier summation the coefficients F_o are replaced by $(F_o - F_c)$ the resulting map is $D = \rho_o - \rho_c$ (Cochran, 1951). The function φ is minimized with respect to the atomic coordinates when the slope of D at the atomic centre is zero. If $\frac{\partial D}{\partial x} \neq 0$, the atom must be moved up the slope by a distance Δx_n, where

$$\Delta x_n = -\left(\frac{\partial D}{\partial x}\right)_n \Big/ \left(\frac{\partial^2 \rho_c}{\partial x^2}\right)_n \qquad (33)$$

Errors in the temperature factor B will alter the value of D at the atomic centre. If B is too high, at the atomic centre $\rho_c < \rho_o$, thus in the difference map the atom would lie on a peak. The value for the temperature factor may be improved by applying the formula

$$\Delta_j = \frac{A(\partial^2 D/\partial r^2)_j}{2\pi^2 \sum_n f_j s^4} \qquad (34)$$

where A is the area of projection f_j is the atomic scattering factor of the j^{th} atom and $s = 2 \sin\theta/\lambda$.

An atom vibrating anisotropically would appear in an F_o map to be extended in the direction of maximum vibration. A calculation of D based on the mean isotropic temperature factor would show positive values where the observed vibration is greater than calculated, and negative where the calculated value is greater. The resulting $\rho_o - \rho_c$ map would thus exhibit a saddle (Fig.V) whose centre coincides with the atomic centre.

6.2 Method of Least Squares

When a number of experimental values have been obtained for a function, it is possible to fit a suitable equation to these values by minimizing the squares of the discrepancies of the points observed from those calculated from the equation, if there are more observed values than there are variables in the equation. For the accurate determination of a crystal structure in three dimensions it is necessary to obtain values for 9n+1 unknowns where n is the number of atoms in the asymmetric unit. These comprise three positional and six temperature parameters, plus an overall scale factor. Since the number of independent reflections measured is generally much greater than the number of parameters sought, the method of least squares may be applied.

The function minimized is $D = \sum w \Delta^2_{hk\ell}$ where $\Delta_{hk\ell} = K F_o - F_c$ (for the centrosymmetric case), w representing a suitable weighting function and K the scaling factor. Considering the positional parameters, a change in the value of any coordinate x of an atom n by a quantity Δx_n would change the calculated structure factor by $\frac{\partial F_c}{\partial x_n} \Delta x_n$, the total change accruing from shifts of all coordinates of N atoms being

$$\Delta F_c = \sum_{n=1}^{N}\left(\frac{\partial F_c}{\partial x_n}\Delta x_n + \frac{\partial F_c}{\partial y_n}\Delta y_n + \frac{\partial F_c}{\partial z_n}\Delta z_n\right) \qquad (35)$$

Correct shifts would thus be those which cause the value of ΔF_c to approach $K F_o - F_c$.

A number of observational equations A may be formed, as in equation (35) for the values of each reflecting plane. To find the best value of ΔF_c, each observational equation A is multiplied in turn by the weighted coefficient of each unknown. The sum of the A equations, each multiplied by the coefficient of a given unknown yields the normal equation for that unknown. The normal equations are of the form

$$\sum_A w(F_o-F_c)\frac{\partial F_c}{\partial x_n} = \sum_A w\left[\left(\frac{\partial F_c}{\partial x_n}\right)^2 \Delta x_n + \frac{\partial F_c}{\partial x_n}\frac{\partial F_c}{\partial y_n}\Delta y_n + \right.$$

$$\left.\frac{\partial F_c}{\partial x_n}\frac{\partial F_c}{\partial z_n}\Delta z_n + \sum_B \frac{\partial F_c}{\partial x_n}\left(\frac{\partial F_c}{\partial x_B}\Delta x_B + \frac{\partial F_c}{\partial y_B}\Delta y_B + \frac{\partial F_c}{\partial z_B}\Delta z_B\right)\right] \qquad (36)$$

where $\sum_B$ represents the sum over all but the n^{th} atom.

These equations are frequently simplified by exclusion of cross terms which may be comparatively small. In three-dimensional analyses, where, in an ordered structure, there should be no overlap of atoms, terms of the form $\sum \frac{\partial F_c}{\partial x_n}\frac{\partial F_c}{\partial x_B}$ may be neglected.

Terms representing interaction between coordinates $\frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial z_n}$ are eliminated if the axes are orthogonal, and may be neglected if the angles are close to 90^o. The normal equations are thus simplified to

$$\sum_A w(K\,F_o - F_c) \frac{\partial F_c}{\partial x_n} = \sum_A w\left(\frac{\partial F_c}{\partial x_n}\right)^2 \Delta x_n \qquad (37)$$

Similar expressions may be obtained for other parameters.

Successful use of the method requires that ΔF_c be sufficiently small at the beginning of the refinement that the function (37) is linear (Hughes; 1941). In practice, the coordinates must lie within the tru Fourier peaks. Advantages of the method are that termination of series errors are eliminated and better resolving power may be obtained in projection than is possible from the use of Fourier methods. Original coordinates must, however, be better and, ideally all the signs of structure factors should be correct.

CHAPTER II

THE CRYSTAL STRUCTURES OF SORBIC AND CROTONIC ACIDS

Introduction

X-ray crystallography has, in the past three decades, developed into an increasingly powerful method for the investigation of organic compounds. Though the main emphasis at present is directed toward the solution of the molecular structure of large molecules, e.g. natural products, there are other problems confronting the chemist to which the X-ray method may be applied.

A certain amount of controversy exists over the question of bond delocalization in non-aromiatic compounds. Butadiene, $CH_2: CH\text{-}CH: CH_2$, the simplest alternant poly-unsaturated compound has been studied in the vapour phase by electron diffraction with a view to resolving the problem (Shomaker and Pauling 1939). The bond lengths deduced from these studies were 1.35 ± .02Å for the double bonds and 1.46 ± .03Å for the single bond. From these results and from theoretical studies these workers concluded that the observed shortening of the formal single bond from the normal length of 1.54Å, such as was found in the similar compound butene-2, $CH_3\cdot CH: CH\cdot CH_3$, (Brockway and Cross 1936) was indicative of conjugation. Other compounds which could admit of resonance forms were also observed to have shortened C-C bonds. Crotonaldelyde, $CH_3\cdot CH: CH\cdot CHO$, was found to have a bond length of 1.46 ± .03Å for the formal single bond adjacent to the carbonyl, while the methyl C-C bond length was 1.52Å (Mackle and Sutton 1951). These workers also found similar shortening in acrolein $CH_2: CH\cdot CHO$.

Recent theoretical calculations (Dewar and Schmeising 1959) have shown that an Sp^2 - sp^2 carbon-carbon bond length of 1.48Å may be a pure single bond. The presence of shorter C-C bonds could, however, indicate the possibility of resonance in the ground state.

All the above compounds were studied in the vapour phase by electron diffraction. It was therefore considered of interest to examine some similar compounds in the solid state by X-ray diffraction, which method allows a fuller study of the more complex molecules.

Trans-crotonic acid (Auwers and Wissenbach 1923) and trans, trans-sorbic acid (Doebner 1890, 1900) are the first two members of a series of unsaturated carboxylic acids of the general formula $CH_3\cdot(CH: CH)_N\cdot COOH$. These are the simplest compounds crystalline at room temperature containing systems in which conjugation could possibly occur. Cis-crotonic (isocrotonic) acid (M.P. 15°C) is known (Auwers 1923) as is cis, trans-sorbic (M.P. 35°C) (Eisner, Elvidge and Linstead 1953) but because of their instability and their low melting points, they are less suitable for X-ray investigation at room temperature.

Trans- forms of the higher homologues have also been prepared for N = 3 - 6, 8 (Kuhn 1937).

The investigations of sorbic and crotonic acids was thus undertaken with a view to comparing the observed bond lengths with results obtained from electron diffraction and theoretical studies.

[illegible]

The Fourier programme (Rollett 1961) is suitable for two and three-dimensional summations. These are computed at intervals of $^1/240$th of the cell edge or a desired multiple thereof. Three-dimensional summations are carried out in sections of constant z.

Structure factors were calculated using Facit and [illegible] hand calculators and later using DEUCE. The structure factor and least squares refinement programme (Rollett 1961) refines positional thermal and scale [illegible] parameters, which may be [illegible] values are nevertheless refined [illegible] values obtained from the [illegible]

1. Methods of Computation

Three methods were used for the summation of Fourier series. Hand calculations were carried out using Beever-Lipson strips (Beevers and Lipson 1934). Use was also made of RUFUS (Robertson 1954, 1961), an analogue computer which represents sine and cosine functions by systems of gears linked to revolution counters. All three-dimensional summations, and the two dimensional Fouriers for crotonic acid were carried out on the DEUCE computer.

The Fourier programme (Rollett 1961) is suitable for two and three-dimensional summations. These are computed at intervals of $^1/240$th of the cell edge or any desired multiple thereof. Three-dimensional summations are carried out in sections of constant z.

Structure factors were calculated using Facit and Olivetti hand calculators and later using DEUCE. The structure factor and least squares refinement programme (Rollett 1961) refines positional thermal and scale parameters. The thermal parameters, which may be inserted as isotropic values are nevertheless refined anisotropically for the values obtained from the expression

$$2^{-B\sin^2\theta} = 2^{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+\beta_{23}k\ell+\beta_{31}h\ell+\beta_{12}hk)}$$

The programme is divided into two sections. The first calculates structure factors for each reflection included in the data, punching decimally the index of the reflection, $|F_o| - |F_c|$, $|F_c|$, cos α and sin α, meanwhile accumulating totals for the least squares normal equations. Atoms included in the structure factor calculation may be omitted from the least squares refinement; e.g. hydrogens. The final totals, are punched in binary at the end of the structure factor calculation. These are used as input for a second programme which solves the normal equations. The full matrix is not computed, a block diagonal scheme being employed. Thus 3 x 3 matrices are calculated for each atomic position, 6 x 6 matrices for each vibration and a 2 x 2 matrix for the scale factor. The second term in this matrix is Q, an overall vibration parameter. This method has been shown to produce satisfactory convergence (usually) without undue use of machine time. The output consists of the new positional thermal and scale parameters and optionally (a) $\Sigma|F_o|$, $\Sigma|F_c|$, $\Sigma|F_o - F_c|$ and the quantity which is being refined, $\Sigma w\Delta^2$ where w is the weighting function applied to the reflection. If atoms are misplaced the values of β_{ii} may exceed the available computer storage, thus giving failures.

The full parameter shifts may be used, but provision is made for the output of new parameters shifted by only $\frac{1}{2}$ or $\frac{1}{4}$ of the predicted value. This slows the convergence but admits closer control, especially at an early stage of the refinement.

A second optional output (b) consists of the least squares totals for each atom, suitable for reconstruction of the normal equations and for calculation of standard deviations.

All other calculations were carried out either with hand calculating machines or using programmes written for the DEUCE computer.

A programme for reducing intensity data to structure amplitudes, correcting for Lorentz, polarization and Tunell factors was written by J.G. Sime. Dr Sime also prepared mean plane and mean plane Fourier, bond length, bond angle and thermal analyses programmes.

A mean plane programme which minimizes the weighted squares of the distance from the plane was prepared by D.G. Watson.

2. Previous Work on Sorbic Acid

A preliminary study of the sorbic acid structure was carried out by Lonsdale, Robertson and Woodward (1941). Cell dimensions were obtained and intensity data collected for the principal zones. From the absences, and lack of hemi hedry, the space group was assumed to be C2/c, with eight molecules in the cell, linked through their carboxyl groups as hydrogen-bonded dimers. From the stronger Bragg reflections, diffuse reflections and studies of magnetic anisotropy it was concluded that the molecules were inclined at an angle of 25° to 35° to the unique b crystal axis, with the chain length extended at an angle of 10° to 15° to the a axis. A set of structure factors was calculated for a trial structure based on these conclusions, using standard single and double bond lengths and angles for the molecular model. The discrepancy was 35%, indicating that the structure as postulated was substantially correct. No further refinement of the $h0\ell$ zone was carried out, nor were the other zones investigated.

Laue photographs of sorbic acid showed the presence of both broad diffuse patches, characteristic of layer structures, and fine streaks characteristic of long chain molecules. Additional studies of the diffuse reflections were reported by Lonsdale and Smith (1941-2). Comparison of Laue photographs taken at room temperature and liquid air temperature showed that almost all the diffuse reflections disappear on cooling the crystals. This indicated that the non-Laue spots were caused by thermal vibrations of the molecule rather than packing disorder.

3. Crystal data

Sorbic acid, $C_6H_8O_2$, M.W. 112.12, was purified by steam distillation and recrystallization from water and from acetone to a melting point of 134°C (134.5°C Heilbron and Bunbury 1953). For X-ray study, crystals were obtained as clear well formed needles by slow evaporation from acetone solution.

Unit cell dimensions were obtained from rotation and precession photographs. The crystals are monoclinic. The values obtained compared with those found by Lonsdale, Robertson and Woodward (1941) are given in Table I.

Table 1

		LR + W
a	$20.0\overset{2}{1} \pm .02$Å	$20.00 \pm .05$Å
b	$4.020 \pm .005$Å	$4.03 \pm .02$Å
c	$15.82 \pm .02$Å	$15.83 \pm .03$Å
β	$102.5^\circ \pm .2^\circ$	102.5°

For eight molecules in the unit cell, the calculated density is 1.198 g./cc., compared to the observed value of 1.185 g./cc.

4. Space Groups

Reflections are systematically absent in the $h0\ell$ zone when either h or ℓ is odd and in OKO when k is odd. In the general case absences occur when (h+k) = 2n+1. Since these absences are found for both C2 and C2/c, the space group cannot be determined unequivocally without some other indication of the space group symmetry. It was assumed in the earlier work (Lonsdale et al, 1941) that the structure was centrosymmetric, the space group being thus C2/c. This postulate was in agreement with the general observations on mono-carboxylic acids, which tend to form centrosymmetrical dimers. No further proof was given.

5. Intensity Data

A crystal .15 mm x .2 mm x 1.0 mm mounted in a thin walled pyrex capillary was set about the unique b axis. A five-film $h0\ell$ Weissenberg series was recorded in a 32 hour exposure using the Robertson (1943) multiple film technique with Cu Kα radiation from a Phillips sealed tube. To obtain reflections with high values of sin θ, a larger crystal .5 mm x .55 mm x 3 mm also mounted in a sealed capillary was used for a second five-film series, exposed to unfiltered copper radiation for 10 hours.

Weissenberg series were also taken of crystals mounted about the a and c axes. For the HKO series a section cut from a long needle measuring .2 mm x .18 mm x .65 mm was used for a 10 hour exposure to Cu $K\alpha$ radiation. Another crystal section .22 mm x .31 mm x .30 mm mounted about the a axis was used in a 10 hour exposure to Cu $K\alpha$ radiation to collect OKℓ data.

Upper layer line data about the b axis were collected on an equi-inclination Weissenberg camera using a new crystal, .2 mm x .25 mm x 2 mm. Two 4-film series using 1 hour and 10 hour exposures were taken for each of the $h1\ell$ $h2\ell$ and $h3\ell$ nets. Inclination angles (μ) for these layers are $11^{\circ}20'$, $22^{\circ}32'$ and $36^{\circ}9'$ respectively. Although $h4\ell$ and $h5\ell$ nets both fall within the copper sphere these were not obtained because μ became too large for the permitted angular shift of the camera.

To obtain correlating series a crystal .18 mm x .26 mm x 3 mm sealed in a thin walled capillary was mounted in a precession camera. A PW 1010 stabilized X-ray generator with a molybdenum tube and zirconium fiter was used as a source of radiation for a series of timed exposures. With the camera set at a 30° precession angle and using an appropriate layer line screen, six films were exposed for each of the hk0 hk1 and hk2 zones, with graduated exposure times of $6\frac{2}{3}$ min., 20 min., 1, 3, 9 and 27 hours. All photographs were taken on Ilford Industrial G X-ray film.

Intensities were estimated visually using wedge and standard spot techniques. Data from Weissenberg series were corrected for Lorentz and polarization factors; the upper layer lines were corrected also by the Tunell rotation factor (1939). The film factor for the upper zones was increased to allow for the longer X-ray path length through the film (Rossmann 1956). The data from precession series were corrected for Lorentz and polarization factors by the use of charts prepared by Waser (1951) and Grenville-Wells and Abrahams (1952). The linear absorption coefficient for sorbic acid, for copper radiation is .851 mm.$^{-1}$. This is sufficiently small for errors due to absorption to be neglected.

The values of the structure factors obtained from the precession series and HK0 and OKℓ Weissenberg series were used to interrelate the data from the various b-axial zones. When more than one series was recorded for any one zone, scaling of the structure factors was based on data estimable in both series.

An estimate of the reliability of the intensities was obtained by the method of Ibers (1956), suitable for small numbers of observations:

$$\sigma(F_o) = C(F_{o_{max}} - F_{o_{min}}) \tag{38}$$

where C is a constant depending on the number of independent observations. For two observations, C = .89. The average σF_o for planes recorded more than once is

$$\sigma F_o = .067 F_o \tag{39}$$

The values of F_o are listed in Appendix Ia.

6. Determination of Centrosymmetry

A number of statistical tests have been devised for the detection of symmetry. Three of these have been applied to sorbic acid.

6.1 N(z) Test

The N(z) test, developed by Howells, Phillips and Rogers (1950) compares the fraction of reflections, N(z), having intensities less than certain fractions z of the average value, with theoretical distributions for centric and acentric structures. For the acentric case

$$N_o(z) = 1 - \exp(-z) \tag{40}$$

while for the centric distribution

$$N_1(z) = \operatorname{erf}(z/2)^{\frac{1}{2}} \tag{41}$$

These expressions apply for random distribution of scattering matter in a cell.

For sorbic acid, the corrected intensity, data were divided into three ranges of Sin Θ; .20 - .55, .55 - .75 and .75 - .90. Reflections having values of Sin Θ below .20 and above .90 were discarded. The total numbers of reflections in each range were 385, 265 and 161. N(z) was evaluated for each range for z = .1 to 1.0 (see app~~r~~endix). δ The average value of N(z) for the three ranges, weighted according to the number of reflections in the range, is given in Table (II).

Table II

z	=	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0
N(z)	=	.293	.456	.555	.700	.734	.753	.783	.797	.829	.829

Comparison of these values with the theoretical curves for the acentric and centric cases (Fig. I) indicates that the structure is centrosymmetric.

6.2 Variance Test

The variance of a set of observations is defined as the mean square deviation from the average value. Wilson (1951) observed that the variance of observed intensities may be used as a method for detecting centrosymmetry. For an acentric structure, the distribution of intensities is

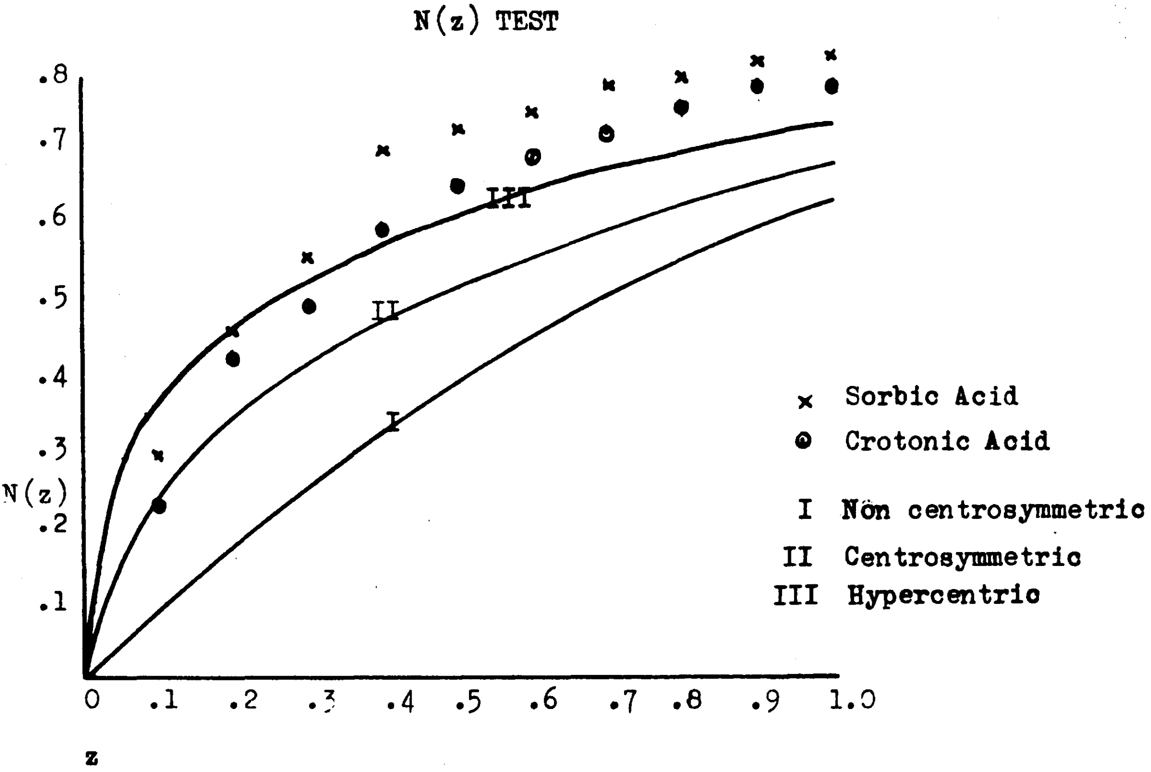

N(z) TEST
.8
.7
.6
.5
.4
.3
N(z)
.2
.1
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
z
III
II
I
× Sorbic Acid
● Crotonic Acid
I Non centrosymmetric
II Centrosymmetric
III Hypercentric

FIG. I

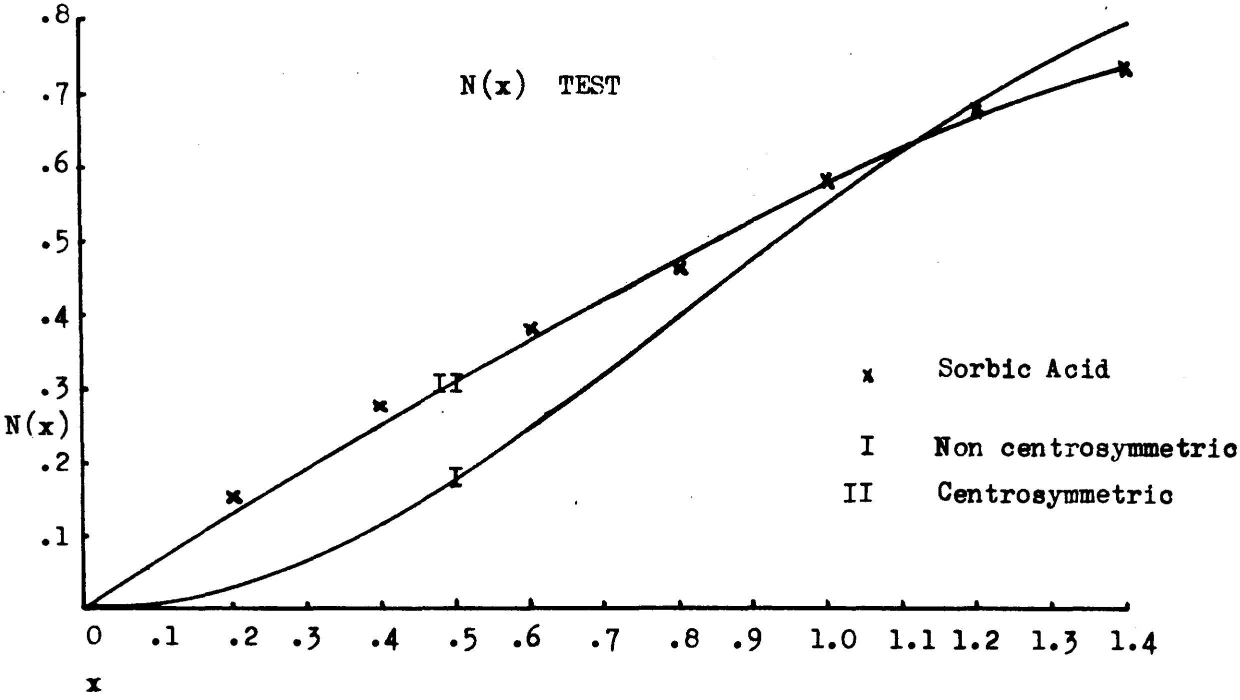

N(x) TEST
.8
.7
.6
.5
.4
.3
N(x)
.2
.1
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
x
II
I
× Sorbic Acid
I Non centrosymmetric
II Centrosymmetric

FIG. II

such that for a structure containing N atoms, of which the ith atom has a scattering factor f_i

$$(1) \quad \langle(I - \Sigma^2)\rangle = \Sigma^2 - \sum_{i=1}^{N} f_i^4 \qquad (42)$$

where
$$\Sigma = \sum_{\substack{i \neq j \\ \neq k \neq \ell}}^{N} f_i f_j f_k f_\ell \ \exp\ i(\theta_i + \theta_k - \theta_j - \theta_\ell) \qquad (43)$$

in which $\theta = 2\pi(hx + ky + \ell z)$ and f_i, f_j, f_k, and f_ℓ represent the scattering factors of four non-identical atoms. The corresponding expression for the centric case is

$$(\bar{1}) \quad \langle(I - \Sigma)^2\rangle = 2\Sigma^2 - 3\sum_{i=1}^{N} f_i^4 \qquad (44)$$

The second term in both equations may be neglected if N is large because $\sum_{i=1}^{N} f_i^4 \approx \frac{\Sigma^2}{N}$, (45)

thus the expression may be written

$$\frac{\langle(I - \Sigma)^2\rangle}{\Sigma^2} = V \qquad (46)$$

For an acentric cell V = 1; for the centric case V = 2. As with the N(z) test, higher values may be obtained if there are subsidiary non crystallogrphic symmetry elements (Rogers and Wilson 1953).

For sorbic acid, the weighted average variance taken over the same ranges as the N(z) test, is 2.987 (see appendix). The higher value is possibly attributable to parallelism within the sorbic acid molecule.

6.3 The N(x) Test

A method developed by Sim (1960) utilizes the structure amplitudes rather than the intensities to determine a function N(x), which is the fraction of reflections with $|F|$ /average $|F|$ less than or equal to x. For a structure containing only light atoms, the cumulative distribution for an acentric structure is given by

$$ {}_1N(x) = 1 - \exp\left[-\tfrac{1}{4}\pi x^2\right] \qquad (47) $$

For the centric case, the expression is

$$ {}_{\bar{1}}N(x) = 2\,\varphi\left[2(2\pi)^{-\frac{1}{2}}x\right] \qquad (48) $$

where φ represents a Gaussian distribution function.

The curves for the two cases, compared with that obtained from the $h0\ell$ zone of sorbic acid are shown in Fig. II. The values obtained for sorbic acid are listed in Table III (Sim 1960).

Table III

x	0	.2	.4	.6	.8	1.0	1.2	1.4	1.6
N(x)	0	.147	.275	.376	.459	.587	.670	.725	.826

7. The (010) Projection.

7.1 Fourier Transform

From the axial dimensions (a = 20.01Å, b = 4.02Å, c = 15.82Å) it seemed probable that the sorbic acid molecules were lying in the unit cell roughly parallel to the (010) plane. The length of the b axis, which is only slightly greater than the carbon-carbon Van der Waals distance of 3.4Å indicates that there should be no overlap in a projection upon (010). Under these circumstances, it was thought possible to determine the signs of structure factors in the $h0\ell$ zone from analysis of the appropriate Fourier transform.

A simplified model of the molecule dimer was constructed, with C - C and C - O bonds taken as 1.4Å, and the hydrogen bonds linking the carboxyl groups as 2.8Å (Fig. III).

A Fourier transform

$$T(X^*Y^*) = 2 \sum w \cos 2\pi (X^*\xi + Y^*\eta) \qquad (49)$$

was evaluated (Fig. IV). X^* and Y^* are the reciprocal

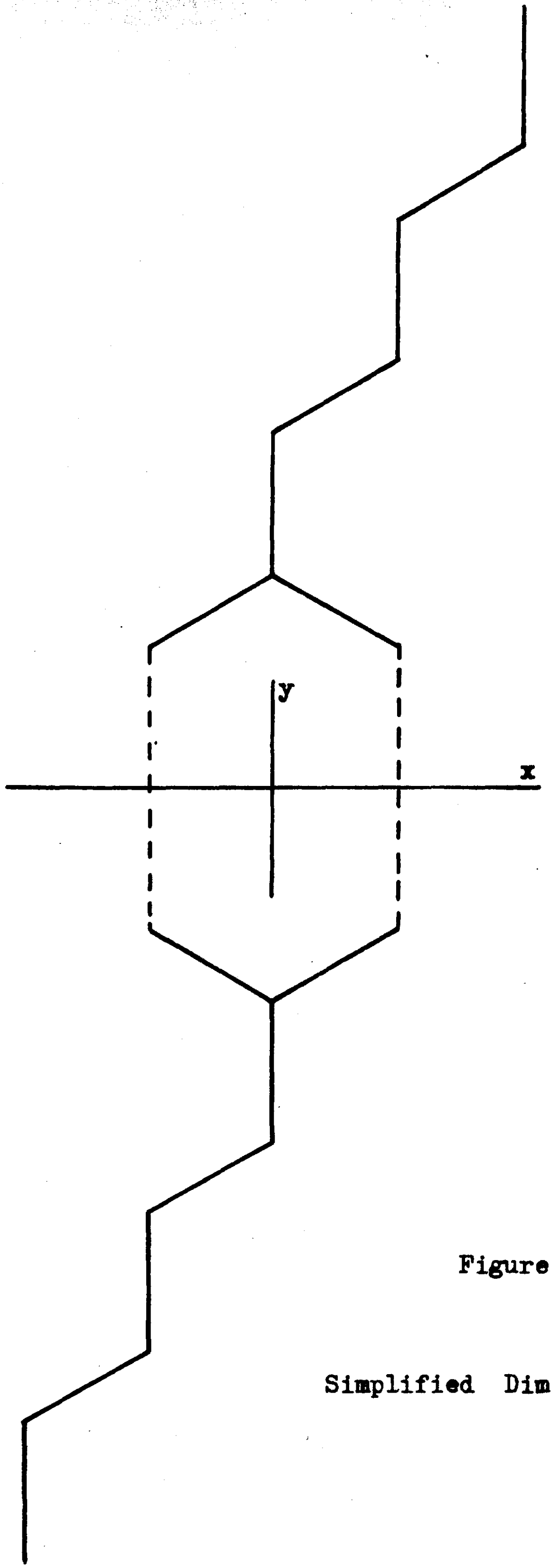
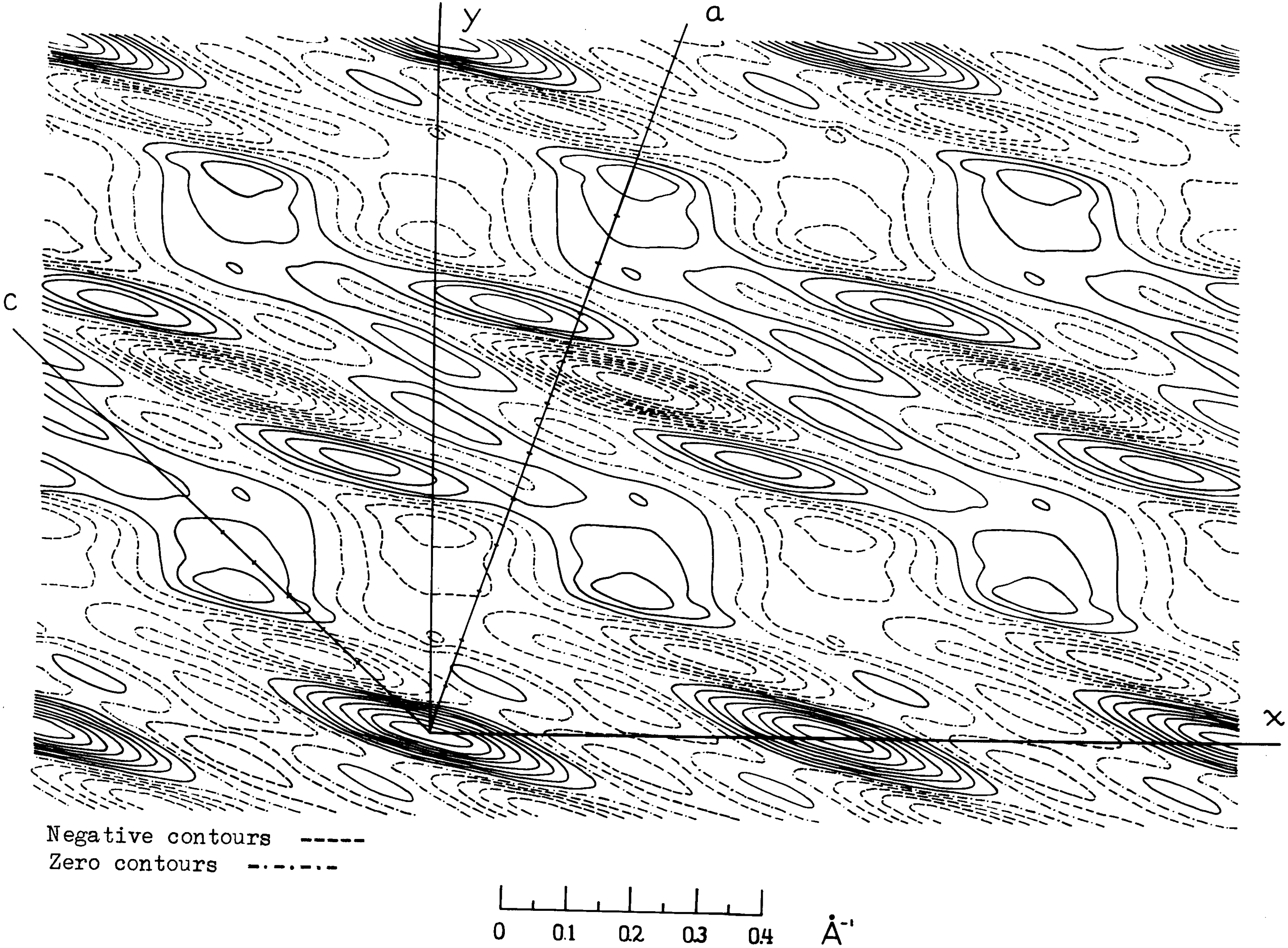


Figure III

Simplified Dimer for Transform



Fourier Transform for Sorbic Acid

Figure IV

dimensions, ξ and η, non integral distances in reciprocal space and w the weight given to each atom. The value of w was taken as 100 for carbon and 120 for oxygen. The summation was carried out using Beevers-Lipson strips (1934). The weighted reciprocal net was fitted to the transform as shown in Fig.IV. Signs were determined for eighty of the larger structure factors. Using the signs so obtained, with the corresponding values of the structure amplitudes obtained from the corrected intensities, the Fourier series (equation 50) for the $h0\ell$ zone was summed at intervals of $^1/60$th along each of the a and c axes. No attempt was made to put the structure factors on an absolute scale, therefore although the positions of the peak maxima could be determined, the actual values of the peak heights were not significant.

$$\rho(h0\ell) = \frac{2}{A} \sum F_o(h0\ell) \cos 2\pi(hx + \ell z) \qquad (50)$$

The map of the electron density showed resolution of all the atoms except the carbon of the carboxyl group. Atomic coordinates were chosen and structure factors determined, using an isotropic temperature factor $B_\theta = 3.5$. The agreement factor was 43%. This agreement factor, R, defined as

$$R = 100 \frac{\sum(|KF_o| - |F_c|)}{\sum |(KF_o)|} \qquad (51)$$

where F_o and F_c are the calculated and observed structure factors and K is a suitable scaling factor, is used as a rough check of the accuracy of the proposed structure.

All the signs shosen from the transform were later proven to be correct.

7.2 Refinement of the (010) Projection by Fourier Methods

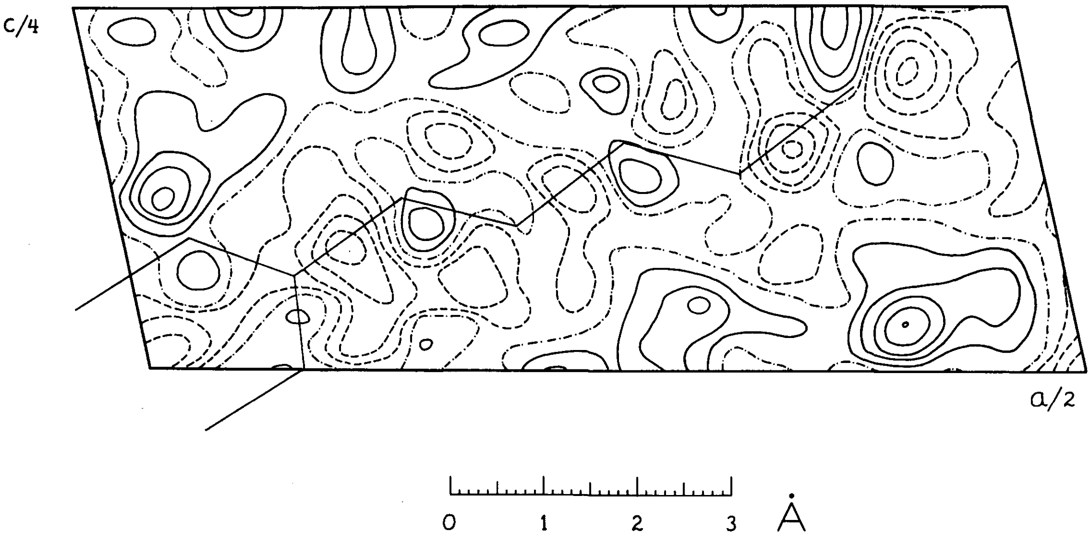
Structure factors for the $h0\ell$ zone were calculated from the contributions of the carbon and oxygen atoms using the equation:

$$F_c = 8 \sum_{i=1}^{8} f_i \cos 2\pi (hx + \ell z) \qquad (52)$$

where f_i is the scattering factor of an atom in the asymmetric unit. The scattering curves for carbon and oxygen were obtained from Hoerni and Ibers (1954). These were modified by the introduction of a temperature factor $B_\theta = 3.5$ (see section I. 3.1).

The signs from the first set of calculated structure factors (F_c) were applied to the observed structure amplitudes ($|F_o|$), which were then used as coefficients for a further Fourier summation. Terms for which the calculated value was less than one-third of the observed were omitted, as the signs of these structure factors were most liable to change during the refinement of the atomic coordinates. When after another cycle the agreement factor had fallen below 30%, difference syntheses were used. In the Fourier summation, the structure factor was replaced by a term $F_o - F_c$. As shown in section I. 6.1, the atomic positions may be refined by moving them up the slopes of the resulting difference density map. At this stage, the positions of the four hydrogen atoms along the unsaturated chain were determined geometrically. These were included in the structure factor calculations, using McWeeny's (1951) scattering curve for hydrogen.

When the agreement index had fallen to 17.5%, it was observed that the difference map showed marked evidence of thermal anisotropy (Fig. V), indicating that further refinement of the structure required application of anisotropic temperature factors. Although it was apparent that the terminal carbon atom had a much greater amplitude of vibration than the remainder of the atoms, it was decided, as a first approximation to treat the molecule as a vibrating unit.



Sorbic Acid (010) Projection

Difference map showing anisotropic thermal motion. Contours at intervals of 0.2e/A^2 ; negative contours dashed.

Figure V

The scattering factors corrected for anisotropic vibrations could be expressed as

$$f = f_c \exp\left(-\left[\alpha + \beta \sin^2(\varphi - \psi)\right] \sin^2 \theta\right) \qquad (53)$$

(Sim, 1955), where α and β are constants, 2 sin θ and φ are polar coordinates of a point in the reciprocal lattice and ψ is the angle between the direction of maximum vibration and the c axis. By plotting the observed structure factors against the calculated geometrical structure factors for various ranges of sin θ, a number of graphs were obtained. Straight lines were fitted to the points by the method of least squares. The slopes of the lines so obtained were then plotted against φ. A curve of the form:

$$B/\lambda^2 = \alpha + \beta \sin^2(\varphi - \psi), \qquad (54)$$

where B is the temperature factor, was fitted to the points by least squares methods. The curve so obtained (Fig. VI) agreed with the equation:

$$B/\lambda^2 = 1.450 + .688 \sin^2(\varphi - 22). \qquad (55)$$

i.e. the direction of maximum vibration is inclined at 22°

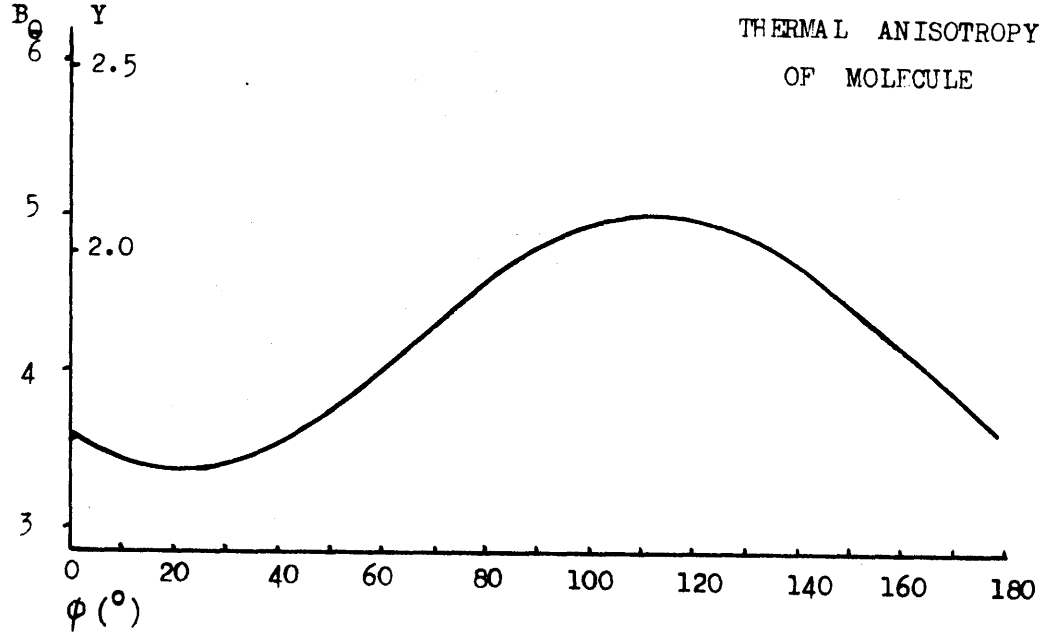


FIG. VI

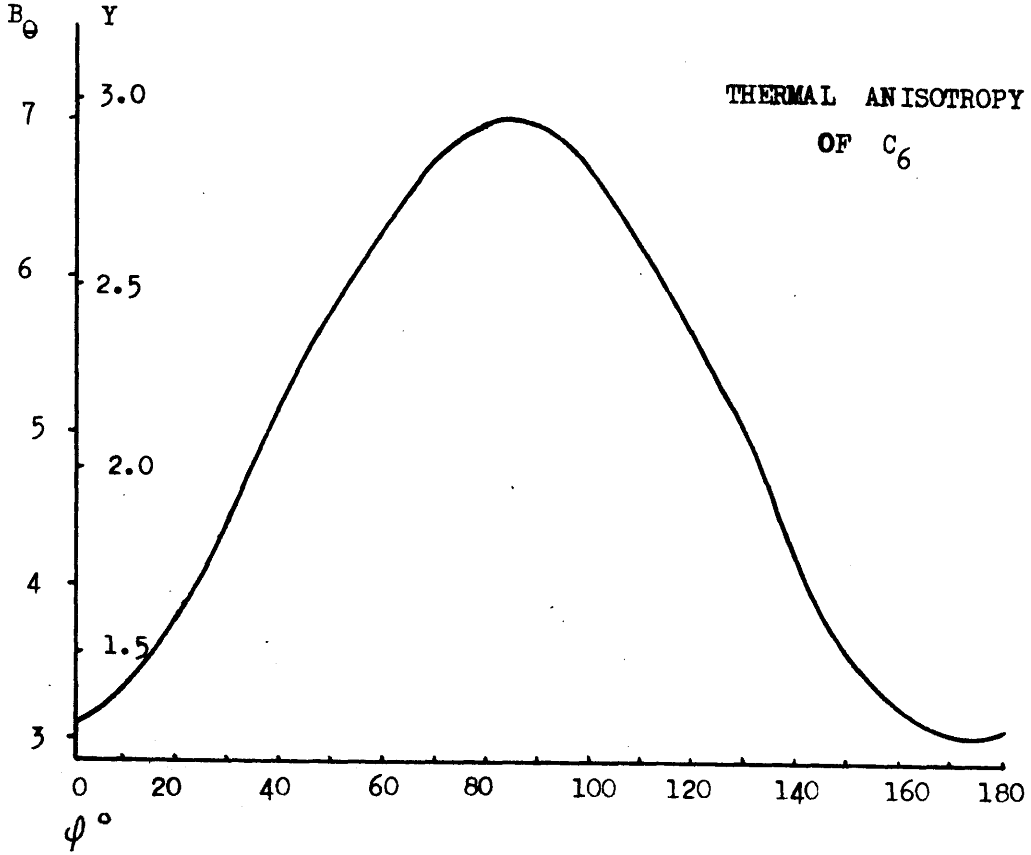


FIG. VII

from the c axis, and is therefore approximately at right angles to the chain length. The maximum value of B_θ was 5.08, and the minimum $3.45A^2$.

Structure factors were calculated using the values of B_θ from the graph, and including the hydrogen atoms of the methyl group. The introduction of anisotropic temperature factors improved the agreement to 15.5%. A difference map calculated at this stage showed that most of the anisotropic motion had been satisfied except for that about the terminal carbon atom where the gradients of the saddle were still steep. A similar treatment was therefore applied to C_6 alone, the rest of the molecule remaining unchanged except for slight positional corrections. For C_6 the curve obtained (Fig. VI) satisfied the equation.

$$B/\lambda^2 = 1.262 + 1.682 \sin^2(\varphi - 173). \qquad (56)$$

This gave to B_θ a maximum value of 7.0 at right angles to the $C_5 - C_6$ bond, and a minimum value of 3.0 in the direction of the bond. Application of these values to the next structure factor calculation lowered the discrepancy to 13.7%.

7.3 Least Squares Refinement

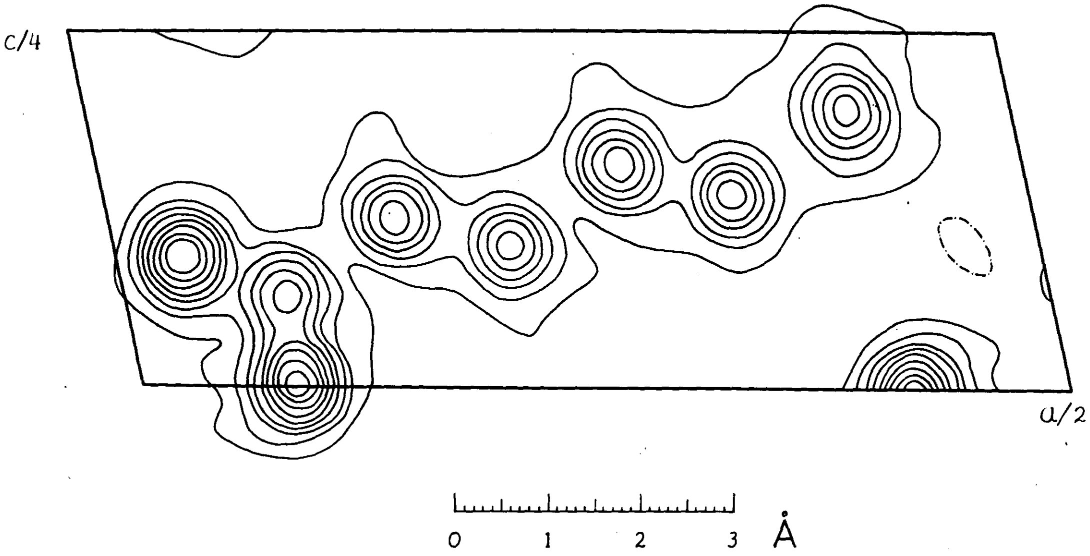
Further treatment of the $h0\ell$ zone was carried out later on the Deuce computer using a block diagonal least squares refinement (Rollett 1960). Coordinates were obtained from the final differences map, and an isotropic temperature factor $B_\theta = 4.2$ was introduced. This was the average value obtained from the graph (Fig. VI). The programme has facilities for the input of isotropic or anisotropic temperature factors, though the actual refinement is anisotropic (see section II.1). A weight, w, was applied to each structure factor such that for reflections for which $|F_0| > |F^*|$, where $|F^*| = 8\,|F_{min}|$, $\sqrt{w} = \frac{|F^*|}{|F_0|}$; while for reflections having $|F_0| \leq |F^*|$, $\sqrt{w} = \frac{|F_0|}{|F^*|}$. F^* was given the value of 64. The quantity minimized in the refinement was $\sum w\Delta^2$ where Δ is the modulus of the difference between the calculated and observed structure factors. Half shifts were employed (see section II.1). The positional, vibrational and scaling parameters were refined to an agreement factor of 10.9% after 9 cycles, the time for one cycle being approximately thirty minutes: the final x and z coordinates are listed in Table IV.

With the signs from the final $h0\ell$ structure factor

Table IV

Final Fractional Coordinates - 010 Projection

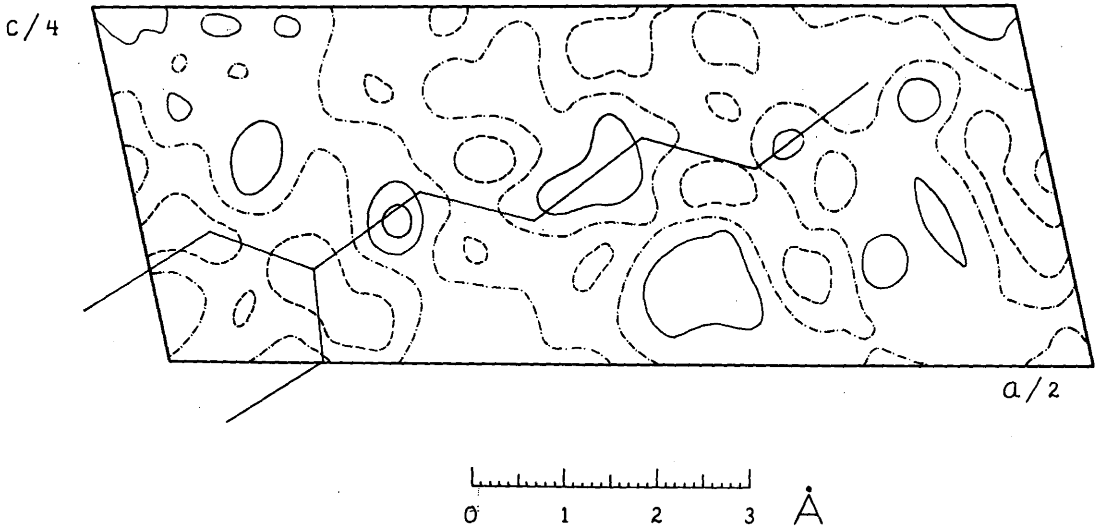
	x/a	z/c
O_1	.08421	.00284
O_2	.03611	.09166
C_1	.08923	.06539
C_2	.15822	.12073
C_3	.21500	.10042
C_4	.28415	.15591
C_5	.33998	.13681
C_6	.41195	.19340
H_1	.03658	-.03333
H_2	.15070	.18679
H_3	.22680	.04129
H_4	.28310	.21919
H_5	.34880	.07239
H_6	.38190	.20119
H_7	.42800	.22819
H_8	.45290	.15999



Sorbic Acid (010) Projection

Electron density map. Contours at intervals of $1e/A^2$; zero contour broken.

Figure VIII



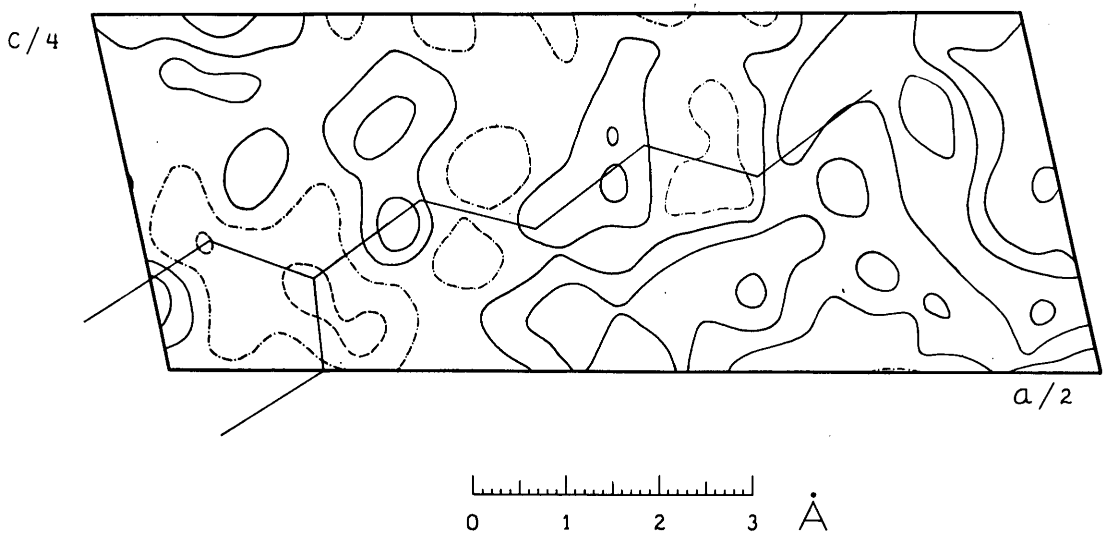
Sorbic Acid (010) Projection

$(F_o - F_c)$ map. Contours at intervals of 0.2e/A^2.

Negative contours ------

Zero contours -·-·-·-

Figure IX



Sorbic Acid (010) Projection

Hydrogen map. Carbon and oxygen contributions subtracted out. Contours at intervals of 0.2e/A^2.

Negative contours -----

Zero contours -·-·-·-

Figure X

calculation and the observed structure factors, a Fourier synthesis was computed to show the electron density of the sorbic acid molecule in projection on to (010) (Fig. VIII). A difference synthesis (Fig. IX) shows no outstanding features, indicating that reasonable values have been obtained for all parameters. The standard deviation of electron density, $\sigma\rho$, (Cruickshank 1949) is $.29e\text{Å}^{-2}$.

A further set of structure factors was calculated, including only carbon and oxygen atoms. Summation of a Fourier series using as coefficients $(F_o - F_c)$ where F_c was based on carbon and oxygen alone, would yield a map showing the positions of the hydrogens. These appear (Fig. IX) as diffuse positive regions with peak heights up to .7 electrons. The hydrogens in the methyl group in particular appear as a smear of electron density from which individual atomic positions cannot be resolved.

8. The (001) Projection

From the (010) projection in which the molecule is well resolved, it was possible to obtain accurate values for the x and z coordinates. From these, the projected bond lengths were calculated. If the molecule were approximately planar, then comparison of the projected bond lengths with the expected values should determine the tilt of the molecule. In this manner, a set of relative Y coordinates was obtained. There were two possible configurations in the hk0 projection, one in which the bonds in the carbon chain were directed alternately up and down, and a second in which they were all tilted upward. Considering the molecules to exist in centrosymmetric pairs about the origin, and assuming a hydrogen bond distance of 2.65Å, absolute Y coordinates could be obtained for the oxygen atoms, to which the rest of the molecule could be related. In the space group C 2/c, the origin for the hk0 zone could be chosen at either 0, 0, 0 or $\frac{1}{4}, \frac{1}{4}, 0$ with relation to $h0\ell$. This gave a total of four possibilities. Structure factor calculations for all four structures gave very poor agreement, the best being nearly 50%.

The paucity of data in this zone, however, 24 observed reflections out of 42 within the copper sphere, made attempts at refinement in projection difficult. It was therefore decided to collect full three dimensional data.

9. The Structure in Three Dimensions

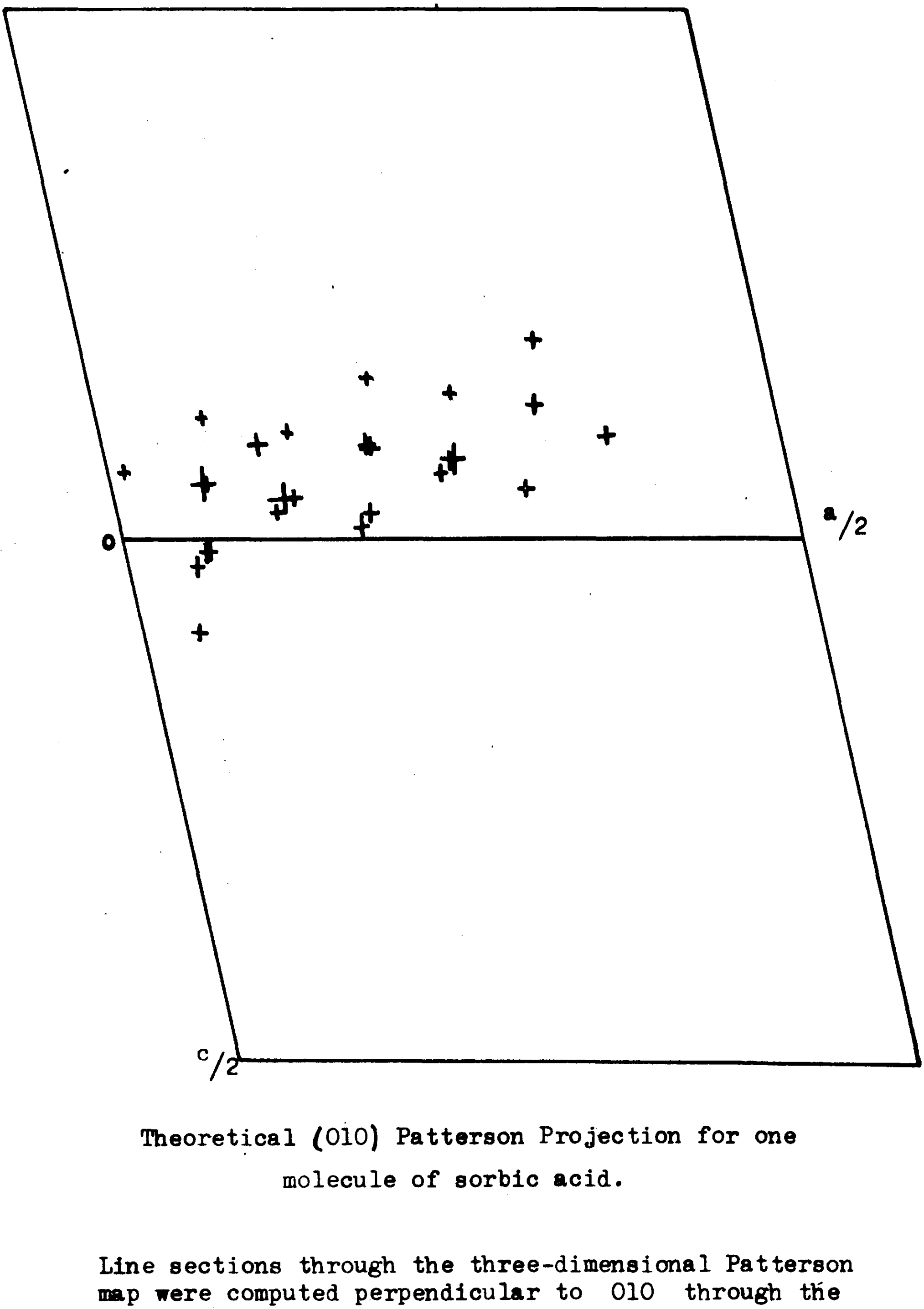
9.1 Trial Structures

Structure factors were calculated on Deuce for the $hl\ell$ net, for the four possible structures examined in the (001) projection. In all cases, the R factor was greater than 60%. This result was not entirely unexpected. Because the b axis is very short (4.02Å), a small aberration in the y coordinates of any atom would result in a comparatively larger shift in y, thus any error between theoretical and actual bond lengths would be magnified. It was thus apparent that the problem would have to be solved by some other method.

9.2 Three-Dimensional Patterson Synthesis

Since the projected atomic coordinates were known with some accuracy, it was possible to construct a theoretical Patterson map for the (010) projection (Fig. XI). Peaks in this map would thus correspond to the projections of the interatomic vectors. In order to find the Y coordinate of the vector peak, it was therefore only necessary to compute the vector density along a line through and perpendicular to the projected vector peak.

Sections through the three-dimensional Patterson map were computed, using as coefficients the squared structure



Theoretical (010) Patterson Projection for one molecule of sorbic acid.

Line sections through the three-dimensional Patterson map were computed perpendicular to 010 through the points marked.

FIG. XI

amplitudes for the 837 observed terms. For better definition, the peaks were sharpened using the modification function shown in Fig. XII. This function was chosen to give mild sharpening while avoiding appreciable diffraction ripples. The effect on a simple model structure is shown in Fig. XIIa. Graph A represents an unsharpened Patterson peak for a theoretical one dimensional cell containing one atom at the origin. Graph B shows the modified peak. Using the Fourier programme for the Deuce computer, line sections were calculated at intervals of $^1/240$th of the cell edge up the y axis. Fig. XIII.

Analysis of the positions of the peaks yielded a self-consistent set of Y coordinates for the carbon and oxygen atoms which were used for the subsequent three-dimensional refinement. Coordinates used are listed in table V.

Table V

$^Y/b$ coordinates from Patterson sections

o_1	-.06250	c_3	.10410
o_2	.23720	c_4	.17500
c_1	.16660	c_5	.06670
c_2	.20000	c_6	.12920

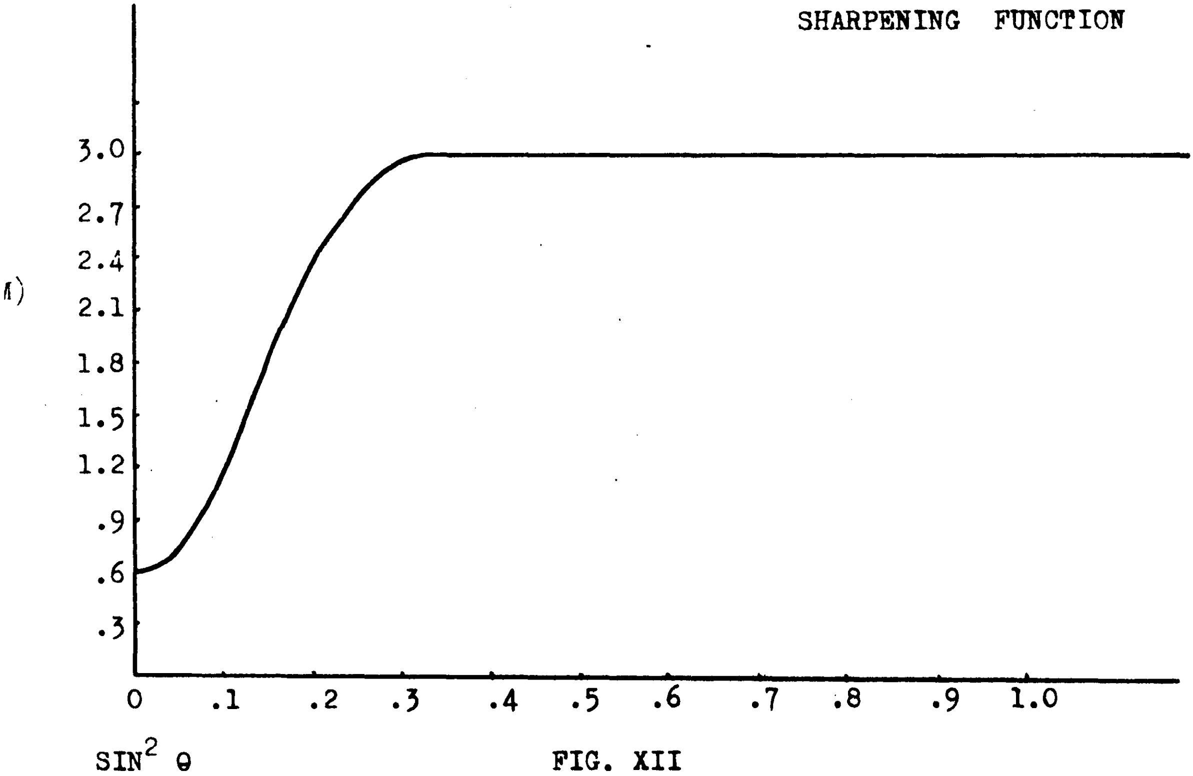


FIG. XII

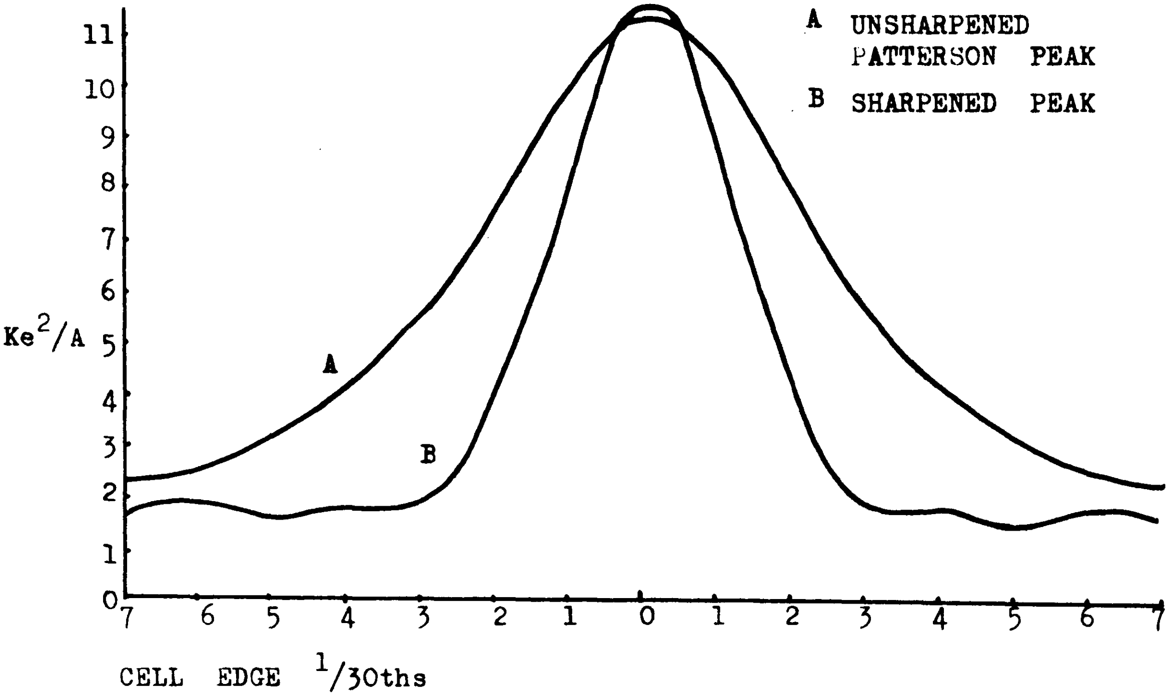
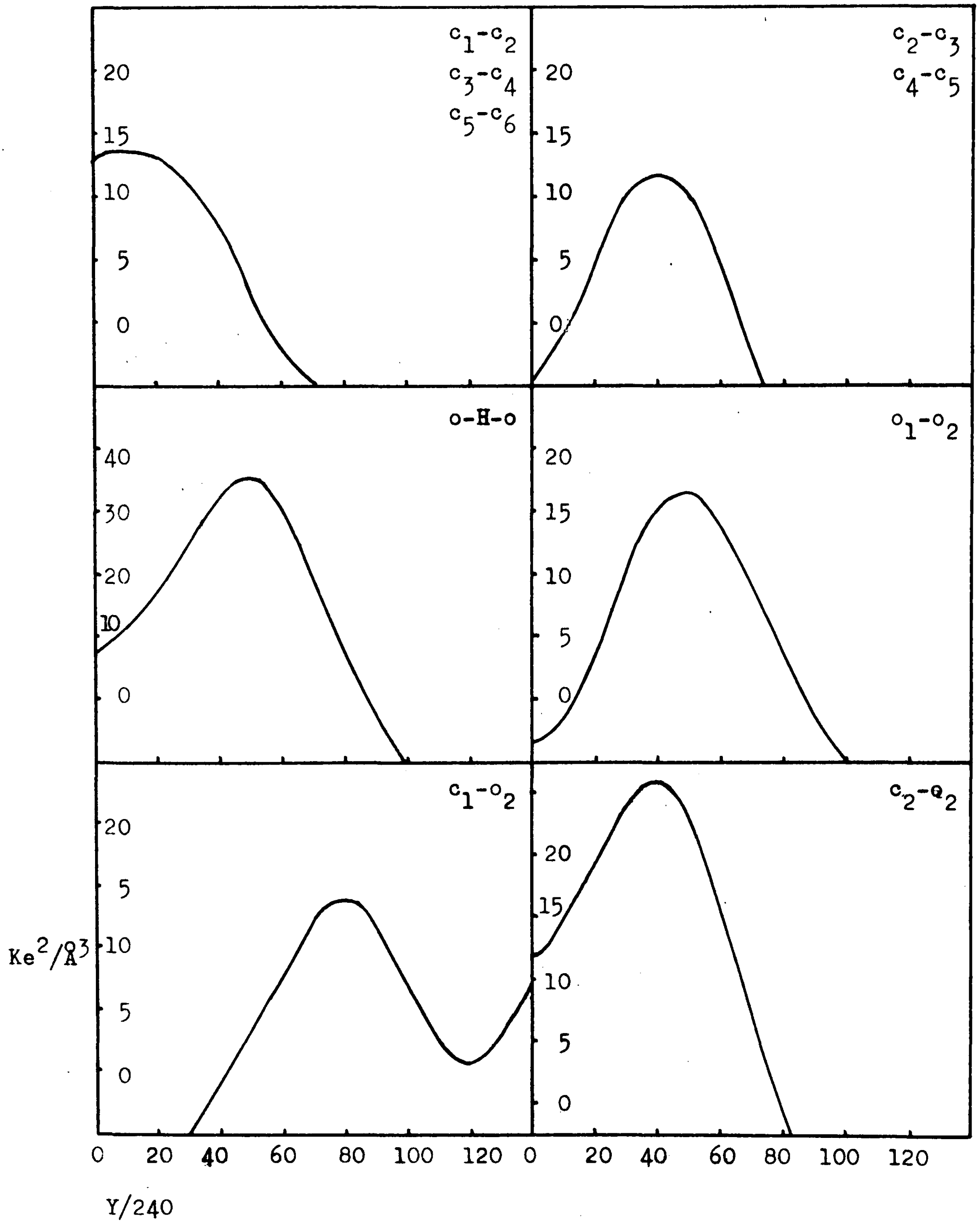
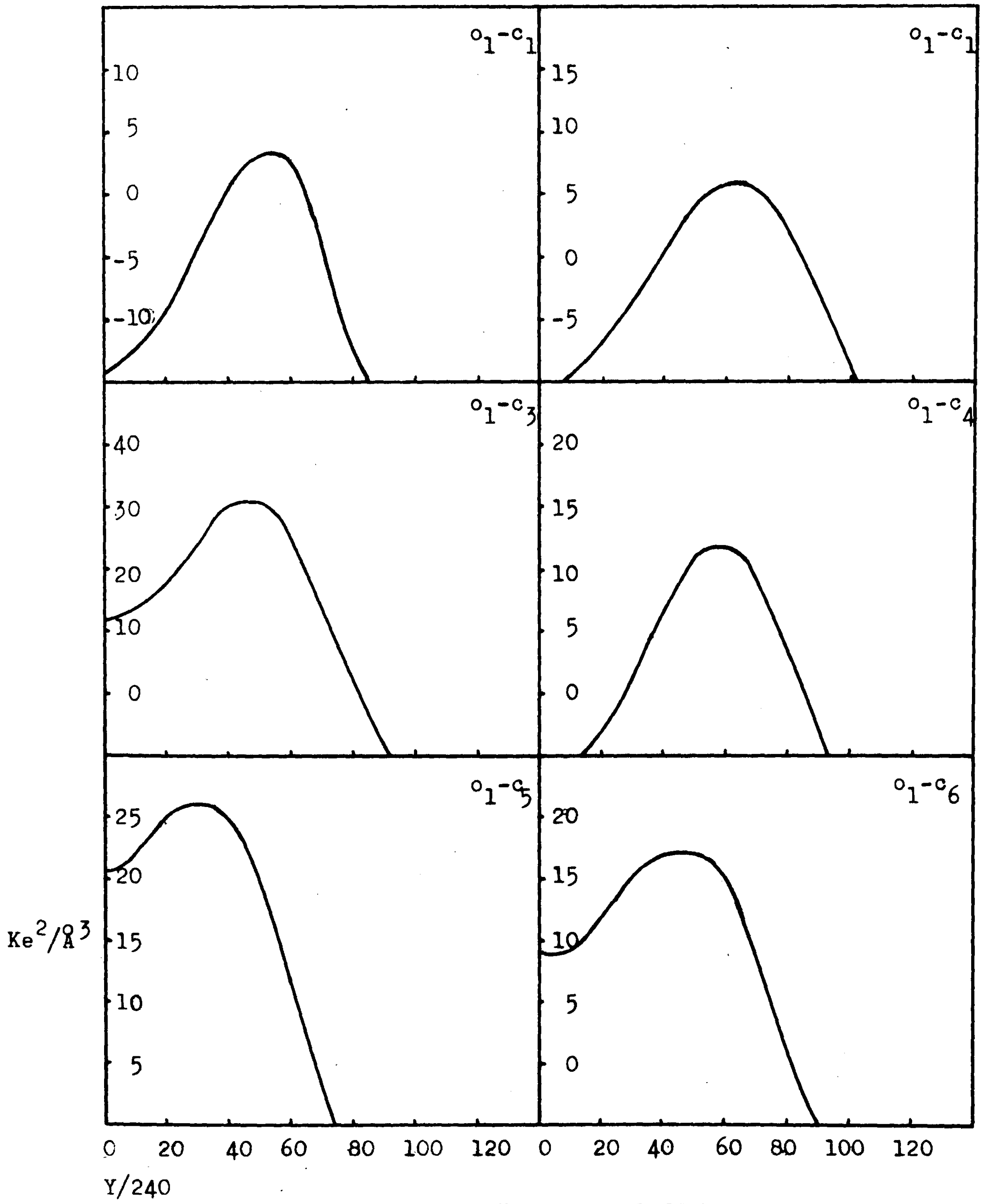


FIG. XIIa



PATTERSON LINE SECTIONS

FIG. XIII$_a$



PATTERSON LINE SECTION

FIG. $XIII_b$

9.3 Structure Refinement

Using the Y coordinates obtained from the Patterson synthesis, structure factors were calculated for the $h1\ell$ zone. An isotropic temperature factor was used with $B_\theta = 4.2Å^2$, the average value obtained from the graph (Fig. VI). Agreement seemed good, being 23% on the scaled structure factors. Two cycles of least squares refinement, however, did not lower the discrepancy materially, and solve failures occured when r the temperature factors became too high (see section II. 1).

Structure factors calculated for the same coordinates for the $h3\ell$ zone did not give such good initial agreement (35%), however, two least squares cycles on half shift (see section II.1) lowered the discrepancy to 24%. Coordinates and temperature factors from the second cycle were used for structure factor calculations for the $h2\ell$ zone. The predicted scale factor, which appeared to be too high, was altered to a more reasonable value from comparison of ΣF_o and ΣF_c for the second $h3\ell$ cycle.

The first structure factor calculation for the $h2\ell$ zone gave an agreement factor of 31%, falling to 23% after one cycle. Coordinates and anisotropic temperature factors from the $h2\ell$ cycle were then applied to a recalculation of the $h1\ell$ zone structure factors. The new R factor for this zone was 24.5%.

Since it was apparent from these results that the structure would probably refine further calculations were carried out on the full three-dimensional data. The coordinates used were those obtained from the last $h1\ell$ cycle. The scale factor for the second $h2\ell$ calculation was retained, but the $h0\ell$ zone data were rescaled before inclusion with the upper zones. Throughout the course of the refinement it was observed that the predicted scale factor tended to be too high. It was altered at the beginning of each cycle to correspond to the value found by comparison of $\sum F_o$ and $\sum F_c$.

For the first full three-dimensional least squares cycle, only the observed terms were included. The overall agreement was 21.7%. For the next cycle, the original scale factor was retained but the coordinates and temperature factors were allowed to shift (see section II.1). Half shifts were used throughout.

All the unobserved reflections in the copper sphere were included for the second cycle, increasing the time per cycle from 2 to 2½ hours. For these unobserved terms, the intensity was assumed to be half the lowest observed value. As this meant the inclusion of 370 unobserved terms, it was expected that the R factor would rise slightly. This was indeed the case. However, after two more complete cycles, the discrepancy fell to 18.5%. At this stage the individual zones were rescaled to the calculated values. The scale factors used are listed in Table VI.

Table VI

$h0\ell$	1.0886
$h1\ell$	.9419
$h2\ell$	.8916
$h3\ell$	1.0420
$h4\ell$	unchanged
$h5\ell$	unchanged

For scaling, $h4\ell$ and $h5\ell$ were considered together, as both contain very few reflections.

The rescaled data were used as input for the sixth structure factor calculation. For this cycle, five of the eight hydrogen atoms were included. The positions of the hydrogen of the Carboxyl group and those joined to the unsaturated chain could be determined approximately as they were assumed to be coplanar with the carbon skeleton. The mean plane of the carbon atoms was calculated using the method of least squares. Using the x and z coordinates of the hydrogen atoms from the (010) projection, Y coordinates were found by substitution in the equation of the plane:

$$X + 4.8658\,Y - 3.4277\,Z - .6356 = 0 \qquad (57)$$

calculated with respect to the orthogonal axes <u>a</u> <u>b</u> and <u>c</u>'. In this equation $X = x + z\cos\beta$ $Y = y$ and $Z_1 = z\sin\beta$ where x,y and z are the atomic coordinates in angstroms and β is the cell angle. The coordinates so determined are listed in Table VII. The methyl group hydrogens were not included.

Table VII

	x/a	y/b	z/c
H_1	.03658	.09109	-.03332
H_2	.15070	.41648	.18679
H_3	.22680	-.08040	.04129
H_4	.28310	.37448	.21919
H_5	.34880	-.11550	.07239

The agreement factor for the sixth cycle with rescaled data and including five hydrogens was 16.3%. As the R factor fell by less than one per cent in a further cycle, there seemed little point in continuing without the addition of the remainder of the hydrogen atoms.

The values of $(F_o - F_c)$ obtained from the seventh cycle were used as coefficients for a three-dimensional difference Fourier synthesis. Sections were computed for the regions around the carboxyl group and the methyl group. Nine sections through c were calculated parallel to (001), at intervals of $^1/60$ of the cell edge (.2637Å) from $^8/60$ to $^{16}/60$ inclusive. The sections were taken from y = 0 to $^{30}/30$, (.134Å intervals) and from x = $^{56}/120$ to $^{66}/120$ in $^1/120$ths (.1667Å). The three hydrogens of the methyl group were fitted on to the contours obtained. As expected, they were staggered with respect to the planar hydrogen atoms of the unsaturated chain. Four sections were taken through the hydrogen bond parallel to (001) from z = $^2/60$ to z = $^5/60$ inclusive. The summation was carried out over the full length of the y axis at intervals of $^1/30$th and from x = $^{55}/120$ to $^{62}/120$. Coordinates obtained from these sections were related to those of the parent molecule by the symmetry $\frac{1}{2}$, $\frac{1}{2}$, 0. Examination of the hydrogen coordinates showed that the hydrogen was associated with O_2 rather than O_1. From this, it follows that C_1-O_1 was doubly bonded and C_1-O_2 singly.

The coordinates obtained are listed in Table VIII.

Table VIII

	x/a	y/b	z/c
H_1	-.00420	.17000	.05420
H_6	.43300	.36445	.21250
H_7	.44200	.29000	.16230
H_8	.40200	-.03555	.25000

When these atoms were introduced into the structure factor calculations, very little change in discrepancy resulted. The R factor after the eighth cycle was 15.5 % for the total data in the copper sphere and 13.9% for the observed reflections. At this point hydrogen coordinates for H_2 - H_5, the hydrogen atoms of the unsaturated chain, were revised using the equation of the plane for the eighth cycle.

$$X + 4.972\,Y - 3.464\,Z - .5980 = 0 \qquad (57)$$

The coordinates are listed in Table IX.

Table IX

	x/a	y/b	z/c
H_2	.17208	.27909	.19066
H_3	.21344	-.07699	.06567
H_4	.28555	.37298	.21258
H_5	.34780	-.10550	.09239

A calculation of standard deviation of positional parameters after the tenth cycle indicated that the mean atomic shifts were less than the standard deviations of the coordinates (Table X), therefore the refinement was terminated. The progressive decrease of R and $\Sigma w\Delta^2$ during the course of the refinement is given in Table XI. The agreement factor for the final observed structure factors is 13.3%. The coordinates used for this calculation are listed in Table XII. A Fourier projection upon (100) based on the final coordinates is given in Figure XIV. The overlap and lack of detail in this projection is manifest.

Table X

Coordinate Shift, Final Cycle

	$\Delta x/a$	$\sigma x/a$	$\Delta y/b$	$\sigma y/b$	$\Delta z/c$	$\sigma z/c$
O_1	.00004	.00012	.00036	.00007	.00004	.00014
O_2	.00004	.00016	.00012	.00112	.00010	.00021
C_1	.00004	.00022	.00002	.00126	.00002	.00027
C_2	.00005	.00023	.00021	.00131	.00014	.00027
C_3	.00005	.00019	.00055	.00016	.00000	.00023
C_4	.00002	.00023	.00025	.00059	.00008	.00028
C_5	.00007	.00023	.00080	.00135	.00001	.00030
C_6	.00000	.00026	.00017	.00149	.00005	.00035

Table XI

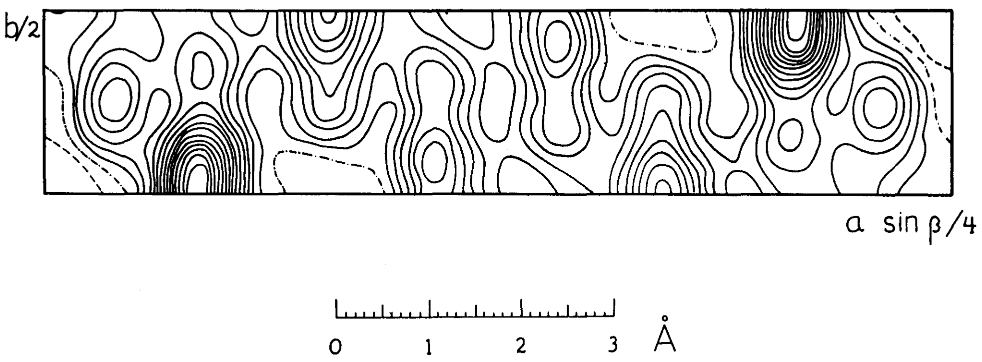
R and $\Sigma w\Delta^2$

Cycle	R	$\Sigma w\Delta^2$	Cycle	R	$\Sigma w\Delta^2$
1	21.7% (obs. only)	124	6	16.3	64
2	21.3	104	7	15.7	61
3	19.5 (all terms)	93	8	15.6	58
4	18.5	84	9	15.5	58
5	17.3	73	10	15.5 13.8 obs.	57

Table XII

Final Fractional Coordinates

	x/a	y/b	z/c
O_1	.08439	- .06441	.00261
O_2	.03662	.23966	.09174
C_1	.09000	.12368	.06591
C_2	.15599	.21923	.11810
C_3	.21602	.11212	.10389
C_4	.28320	.19980	.15427
C_5	.34176	.07961	.13983
C_6	.41225	.16330	.19203



Sorbic Acid (001) Projection

Electron density map. Contours at intervals of 1e/A^2.

Negative contours -----

Zero contours -·-·-·-

Figure XIV

10. Standard Deviation

The standard deviations of atomic positions were calculated using the expression (Dunitz and Rollett 1956):

$$\sigma \xi = \left[\frac{\sum w \Delta^2}{(n-s) \sum w (\frac{\partial F}{\partial \xi})^2} \right]^{\frac{1}{2}} \qquad (58)$$

where $\sum w \Delta^2$ is the sum of the weighted discrepancies for each reflection, n is the number of reflections, s, the number of parameters to be refined and ξ is an atomic parameter, positional or thermal.

The values of $\sum w \Delta^2$ and of the weighted derivatives were obtained from the output of the least squares refinement programme (see appendix). The total number of reflections considered, n, was 1207. The number of parameters, 9a + 1, where a is the number of atoms in the asymmetric unit, was 73. The values obtained were increased by 1.025 to allow for the monoclinic angle of 102.5° (Templeton 1959). The standard deviations of atomic coordinates are listed in Table XIII. The standard deviation of electron density (Cruickshank 1949) is .24 $e\text{Å}^{-3}$.

11. Molecular Geometry

The bond lengths within the sorbic acid molecule, calculated from the orthogonalized coordinates (Table XIV), are listed in Table XV. The corresponding bond angles are given in Table XVI. These values are not corrected for errors caused by thermal oscillation of the molecule (see sections I. 3.2; II. 1.4).

12. Hydrogen Positions

The final hydrogen positions are listed in Table XVII, with the lengths of bonds involving hydrogen given in Table XVIII. The mean value of the C - H bond lengths is 1.063 ± .027Å (Crumpler and Yoe 1940). The standard deviation of any single C - H bond, .07Å, may be considered to be due to errors in position of the hydrogen atoms, as these could not be located accurately.

Table XIV

Orthogonal Coordinates (Å)

	X	Y	Z
O_1	1.67886	-.25892	.04031
O_2	.41822	.96343	1.41691
C_1	1.57428	.49719	1.01797
C_2	2.71535	.88130	1.82404
C_3	3.96461	.45072	1.60457
C_4	5.13568	.80320	2.38268
C_5	6.35633	.32003	2.15966
C_6	7.58736	.65647	2.96588

Table XV

Bond Lengths (Å)

$O_1 - C_1$	1.240 ± .0051	$C_3 - C_4$	1.450 ± .006
$O_2 - C_1$	1.309 ± .006	$C_4 - C_5$	1.332 ± .007
$C_1 - C_2$	1.449 ± .007	$C_5 - C_6$	1.510 ± .007
$C_2 - C_3$	1.340 ± .006	O - H - O	2.650 ± .004

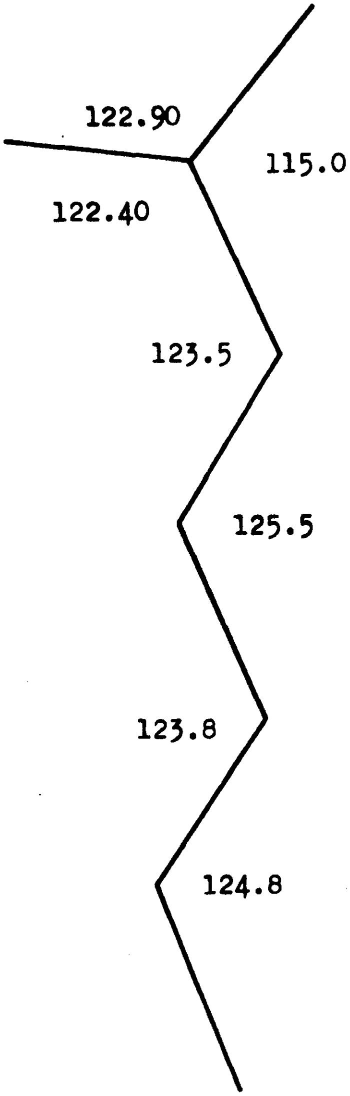
Table XVI

Bond Angles

$O_1 - C_1 - O_2$	122.1 ± .5	$C_2 - C_3 - C_4$	126.0 ± .5
$O_1 - C_1 - C_2$	122.3 ± .5	$C_3 - C_4 - C_5$	124.2 ± .5
$O_2 - C_1 - C_2$	115.7 ± .5	$C_4 - C_5 - C_6$	125.3 ± .5
$C_1 - C_2 - C_3$	123.9 ± .5		

SORBIC ACID
BOND LENGTHS (Å)

FIG. XIX



SORBIC ACID
BOND ANGLES (DEG.)

FIG. XX

Table XVII

Final Fractional Coordinates - Hydrogen Atoms

	x/a	y/b	z/c
H_1	- .00609	.12584	.04325
H_2	.17208	.27909	.19066
H_3	.21344	- .07699	.06567
H_4	.28555	.37298	.21258
H_5	.34780	- .10550	.09239
H_6	.42500	.28332	.25416
H_7	.41677	.41320	.19882
H_8	.40858	- .08333	.20297

Table XVIII

Bond Distances Involving Hydrogen (Å)

$O_2 - H_1$	1.116 Å	$C_5 - H_5$	1.082 Å
$C_2 - H_2$	1.148	$C_6 - H_6$	1.075
$C_3 - H_3$	.966	$C_6 - H_7$	1.012
$C_4 - H_4$	1.148	$C_6 - H_8$	1.012

Average C - H distance 1.063 Å

13. Molecular Plane

The mean plane of the molecule was determined in two ways; first using a method which minimized preferentially the X component of the deviation from the plane, A, and later by a least squares minimization of the perpendicular distances of atoms from the plane, B, (Shomaker et. al. 1959). The plane A given by the first method is:

$$X + 4.926\,Y - 3.400\,Z - .7167 = 0 \qquad (59)$$

Plane B through the molecule is given by

$$.1626\,X + .7950\,Y - .5844\,Z - .0476 = 0 \qquad (60)$$

The deviations from the plane B, which are listed in Table XIX are slightly smaller than those for plane A, the root mean square deviations being .0346Å for A and .0250Å for B. The interplanar angle is 1.7°.

The planarity of the molecule may be determined by the χ^2 test (Fisher and Yates 1957).

$$\chi^2 = \frac{\sum \Delta^2}{\sigma \xi^2} \qquad (61)$$

where Δ is the deviation of an atom from the plane and $\sigma \xi$ is the standard deviation of position of the atom.

The probability of the atom lying on the plane, which, for any χ^2, varies with the number of degrees of freedom, may be determined by consulting tabulated values of χ^2. The number of degrees of freedom is n - 3 where n is the number of atomic parameters.

For plane B through the molecule, $n - 3 = 5$

$$\chi^2 = .004996/25 \times 10 = 200 \qquad (62)$$

Another plane was calculated through the carbon atoms alone.

$$.17261\,X + .75538\,Y - .59642\,Z - .05249 = 0 \qquad (63)$$

For this plane $\chi^2 = 42$. For $n - 3 = 3$ degrees of freedom, the probability that all the carbon atoms are coplanar is still very low, however they appear to lie more closely on the plane than do the oxygen atoms. The root mean square deviation of the carbon atoms from the carbon plane is .0133Å. Deviations of carbons and oxygens are listed in Table XX. The plane of the carboxyl group is given by

$$.18680\,X + 1.31885\,Y - Z + .06818 = 0 \qquad (64)$$

The angle between the carbon plane and the carboxyl group is 3.6°.

Table XIX

Deviations from the Plane of the Molecule (Å)

O_1	+ .0038 Å	C_3	- .0182 Å
O_2	+ .0416	C_4	- .0343
C_1	- .0090	C_5	+ .0209
C_2	- .0290	C_6	+ .0242

Table XX

Deviations from the Plane of the Carbon Atoms (Å)

O_1	+ .0181 Å	C_3	+ .0158 Å
O_2	- .0999	C_4	+ .0202
C_1	- .0126	C_5	- .0014
C_2	+ .0060	C_6	- .0159

An electron density section evaluated in plane A is shown in Figure XV. This is plotted with respect to the axes f and g in the molecular plane (Broadley et. al 1959). To determine these axes the plane was recalculated with respect to a set of orthogonal axes a', b, c to give

$$.1926\,X' + 4.9260\,Y' - 3.5358\,Z' - .7167 = 0 \qquad (65)$$

where $X' = x \sin\beta$ $\;Y' = y$ and $Z' = z + x \cos\beta$ and the coefficients of X' Y' and Z' are A' B' and C'.

The angle between the b crystal axis and f is given by

$$\tan^{-1} \frac{A'}{C'} = -3.1^{\circ} = \varphi \qquad (66)$$

The angle between the a' crystal axis and g is given by

$$\tan^{-1} \frac{B'}{C'} = -54.3^{\circ} = \theta \qquad (67)$$

The lengths of f and g are obtained from

$$f = \frac{b}{\cos 54.3^{\circ}} = 6.894\ \text{Å} \qquad (68)$$

$$g = \frac{a'}{\cos 3.1^{\circ}} = 19.565\ \text{Å} \qquad (69)$$

The angle between f and g is given by

$$\cos^{-1}\left[(-\sin\theta)(-\sin\phi)\right] = \psi = 87.6^{\circ} \qquad (70)$$

Contours are plotted at intervals of $1e\text{Å}^{-3}$. The mean plane Fourier map shows clearly the high degree of anisotropic motion of the atoms, which is masked in the projection by the fact that the molecule is fore shortened along the direction of maximum anisotropy.

14. Thermal Motion

It was observed from difference maps at an early stage of the refinement that the atoms of the sorbic acid molecule were vibrating anisotropically. For the difference maps, the molecule was considered as a vibrating unit (see section II. 7.2), however, in the least squares refinement the vibration parameters of each atom were treated separately. Isotropic B values were assigned to the atoms for original input (see section II. 9.3), but these were converted to the corresponding β ij's (equations 15, 16) which were then refined in conjunction with the atomic coordinates.

In the refinement programme, correction is made for the variation in scattering factor of symmetry-related atoms. When an atom vibrates anisotropically, the motion may be described in terms of an ellipsoid of vibration.

If the atoms are related by a centre of symmetry there is no change in scattering factor as is also the case if the ellipsoid of vibration is directed along the principal axes of the crystal. For atoms related by two fold axes or mirror planes, however, the axes of their ellipsoids are not parallel, and a correction must be made.

For sorbic acid, this corresponds to a change in sign of the terms β_{12} and β_{23} (Rollett and Davies 1955).

The final values of the anisotropic temperature factors are listed in Table XXI. The standard deviations of th β_{ij}'s, also listed in Table XXI, were calculated as in equation 58 (see appendix); the values of $\left(\frac{\partial F}{\partial \beta_{ij}}\right)^2$ being obtained from the least squares output.

In their paper, Rollett and Davies described a method for the determination of the axes of the ellipsoids of vibration. This method was used to compute the directions of the axes of the ellipsoids of the atoms of sorbic acid with respect to the crystal axes (Table XXII). The root mean square deviations, $\bar{U}$, from the axes, with the corresponding

Table XXI

Anisotropic Temperature Factors (x10^{-2})

	β_{11}	β_{22}	β_{33}
O_1	.271 ± .005	10.396 ± .132	.485 ± .008
O_2	.265 ± .005	11.910 ± .217	.635 ± .009
C_1	.265 ± .006	7.720 ± .232	.442 ± .010
C_2	.292 ± .008	7.560 ± .236	.466 ± .011
C_3	.270 ± .007	7.071 ± .218	.434 ± .010
C_4	.290 ± .008	7.066 ± .221	.466 ± .011
C_5	.259 ± .007	9.025 ± .185	.531 ± .012
C_6	.191 ± .008	8.810 ± .273	.683 ± .016

	β_{12}	β_{23}	β_{13}
O_1	.150 ± .055	-1.566 ± .067	.137 ± .010
O_2	.240 ± .057	-1.696 ± .079	.242 ± .012
C_1	.338 ± .071	- .227 ± .090	.173 ± .014
C_2	.128 ± .074	- .619 ± .088	.136 ± .015
C_3	- .033 ± .069	- .139 ± .086	.141 ± .013
C_4	- .132 ± .073	- .414 ± .090	.142 ± .015
C_5	.311 ± .077	- .012 ± .100	.137 ± .015
C_6	- .150 ± .086	.191 ± .115	.113 ± .019

Table XXII

Orientation of the Axes of Ellipsoids of Vibration with respect to Crystal Axes

	a	b	c
O_1	1. 93.6°	1. 95.3°	1. 6.4°
	2. 148.5	2. 58.5	2. 90.3
	3. 60.5	3. 36.1	3. 71.1
O_2	1. 89.8	1. 141.5	1. 51.5
	2. 145.9	2. 69.8	2. 63.9
	3. 56.8	3. 70.4	3. 40.0
C_1	1. 110.1	1. 135.9	1. 52.7
	2. 154.3	2. 64.3	2. 89.9
	3. 79.4	3. 67.9	3. 24.8
C_2	1. 102.2	1. 91.1	1. 12.3
	2. 139.8	2. 51.1	2. 98.9
	3. 56.6	3. 40.9	3. 69.2
C_3	1. 86.2	1. 48.0	1. 137.7
	2. 160.6	2. 73.5	2. 80.1
	3. 70.6	3. 35.4	3. 61.6
C_4	1. 65.2	1. 81.7	1. 153.6
	2. 50.1	2. 138.2	2. 79.9
	3. 44.1	3. 48.2	3. 78.3
C_5	1. 13.8	1. 103.6	1. 87.9
	2. 103.7	2. 163.8	2. 81.7
	3. 77.9	3. 84.5	3. 13.3
C_6	1. 98.5	1. 11.1	1. 82.9
	2. 74.6	2. 80.8	2. 161.9
	3. 26.1	3. 71.4	3. 72.2

Table XXIII

R.M.S. Deviations from the Principal Axes (Å)

	a	β_{11}	b	β_{22}	c	β_{33}
O_1	.457	7.9 Å^2	.303	3.5 Å^2	.330	4.1 Å^2
O_2	.492	9.2	.303	3.5	.361	4.9
C_1	.374	5.3	.308	3.6	.336	4.3
C_2	.384	5.6	.319	3.8	.341	4.4
C_3	.349	4.6	.327	4.0	.331	4.2
C_4	.323	3.9	.364	5.0	.345	4.6
C_5	.318	3.8	.397	6.0	.367	5.1
C_6	.426	6.9	.342	4.4	.386	5.6

values of B are given in Table XXIII.

The value of $\bar{\bar{U}}$ is compounded from the interval normal modes of vibration of each atom and the rigid body vibrations of the molecule as a whole. These rigid body motions may be resolved into vibrational and rotational components ($T + \omega$) with respect to a set of molecular axes (Cruickshank 1956) (see section I. 3.2).

For further analysis of the molecular motions, the atomic coordinates were transformed to molecular axes (Table XXIV). These were chosen with the origin at the centre of mass of the sorbic acid molecule. The axis of minimum inertia, determined by least squares, was taken as the x axis. The molecule being planar, the x and y axes were at right angles in the plane, with the z axis perpendicular (Figure XVI).

It was observed by Higgs (1955) that there is a linear relationship between $\bar{\bar{U}}^2$ and the square of the distance of the atom from the centre of mass. This would, of course, hold only for atoms of one chemical type. When this was applied to the carbon atoms of sorbic acid (Figure XVIII) $\bar{\bar{U}}^2$ for the atoms C_2 to C_6 lay along a straight line, though the value of $\bar{\bar{U}}^2$ for C_2 is high, indicating possibly that the centre of vibration of the molecule does not quite coincide with the centre of mass

MOLECULAR AXES

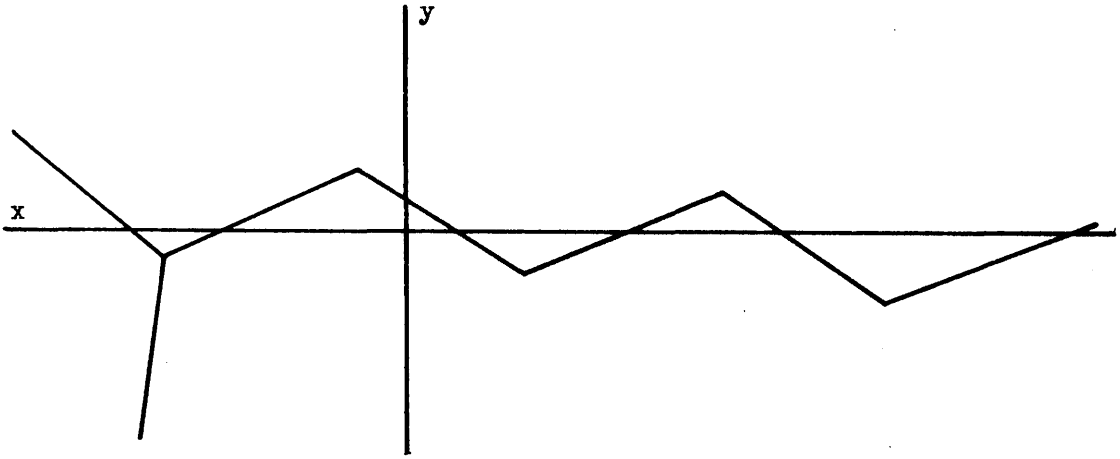
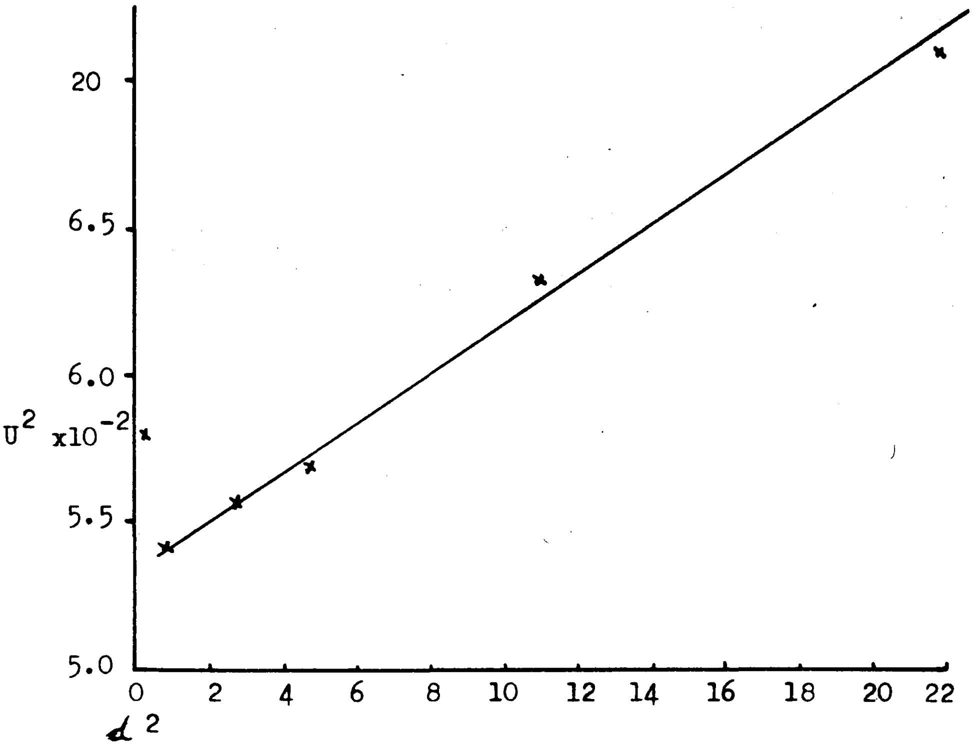


FIG. XVI



Variation of Atomic Vibration Amplitude
with distance of the atom from the
molecular centre of mass.

FIG. XVII

of the monomer. The linearity of the graph does, however, lend confirmation to the validity of application of Cruickshank's treatment to the molecule.

The root mean square displacements of the atoms in the direction of the molecular axes are related to T and ω by the equations (1. 19). In the case of a planar molecule, coordinates may be chosen such that $z = 0$ The formulae 1.19 are thus considerably simplified, and the normal equations which in the general case are of the twelfth order, may be reduced to three fourth order equations

$$\begin{bmatrix} 1 & 0 & 0 & y^2 \\ & 1 & 0 & x^2 \\ & & 1 & -xy \\ & & & x^4+y^4+x^2y^2 \end{bmatrix} \begin{bmatrix} T_{11} \\ T_{22} \\ T_{12} \\ \omega_{33} \end{bmatrix} = \begin{bmatrix} U_{11} \\ U_{22} \\ U_{12} \\ y^2U_{11}+x^2U_{22}-xyU_{12} \end{bmatrix}$$

$$\begin{bmatrix} 1 & y^2 & x^2 & -2xy \\ & y^4 & x^2y^2 & -2xy^3 \\ & & x^4 & -2x^3y \\ & & & 4x^2y^2 \end{bmatrix} \begin{bmatrix} T_{33} \\ \omega_{11} \\ \omega_{22} \\ \omega_{12} \end{bmatrix} = \begin{bmatrix} U_{33} \\ y^2U_{33} \\ x^2U_{33} \\ -2xyU_{33} \end{bmatrix} \tag{71}$$

$$\begin{bmatrix} 1 & 0 & -x^2 & xy \\ & 1 & xy & -y^2 \\ & & x^4+x^2y^2 & -xy^3-x^3y \\ & & & y^4+x^2y^2 \end{bmatrix} \begin{bmatrix} T_{23} \\ T_{13} \\ \omega_{23} \\ \omega_{13} \end{bmatrix} = \begin{bmatrix} U_{23} \\ U_{13} \\ -x^2U_{23}+xyU_{13} \\ xyU_{23}-y^2U_{13} \end{bmatrix}$$

The values of T_{ij} and ω_{ij} obtained from the solution of the normal equations, together with their standard deviations, are listed in Table XXV. The estimation of the accuracy of determination of T + ω was derived from the expression

$$\sigma^2 (A_p) = C_{pp}^{-1} \sigma^2(U) \qquad (72)$$

where A_p represents only T_{ij} or ω_{ij} C_{pp}^{-1} is the appropriate diagonal element of the inverse of the left hand matrices in equations (71), and

$$\sigma^2(U) = \sum_n (U_n^{obs} - U_n^{calc})^2 /(t - n) \qquad (73)$$

where t is the total number of observed U_{ij} and n the number of parameters to be determined. The values of U^{calc} were obtained by the solution of the equations 1.19 using the predetermined T_{ij} and ω_{ij}. The calculated and observed U_{ij} are compared in Table XXVI.

From the U_{ij} it appears that there is no preferred direction of vibration, the mean displacements being .22A, .21Å and .26Å along the x y and z molecular axes. The cross terms are all small, on the order of one tenth the value of the diagonal terms. This serves to indicate that the

Table XXV

T_{ij} $(x10^{-2}\ \text{Å}^2)$

4.916±.212	.796 ± .212	- .322 ± .219
	4.334 ± .290	.438 ± .291
		6.005 ± .352

ω_{ij}. (deg.^{2})

110.42 ± 14.55	17.31 ± 3.51	1.85 ± 4.97
	1.61 ± 1.06	.65 ± 1.03
		5.39 ± 1.02

Table XXVI

Atomic Vibration Amplitudes (x10^{-2} Å^{2})

	$U_{11}^{(obs.)}$	$U_{11}^{(calc.)}$	$U_{22}^{(obs.)}$	$U_{22}^{(calc.)}$	$U_{33}^{(obs.)}$	$U_{33}^{(calc.)}$
O_1	5.140	5.232	4.182	4.882	9.879	10.036
O_2	4.920	4.994	5.100	5.475	11.466	9.789
C_1	4.927	4.921	4.823	4.776	6.351	5.941
C_2	5.516	4.945	4.631	4.354	6.923	6.750
C_3	5.063	4.930	5.020	4.443	5.687	6.562
C_4	5.458	4.926	4.926	5.095	6.190	5.872
C_5	4.958	4.954	6.331	6.095	7.129	8.976
C_6	3.836	4.917	8.028	7.921	7.073	6.789

	$U_{12}^{(obs.)}$	$U_{12}^{(calc.)}$	$U_{23}^{(obs.)}$	$U_{23}^{(calc.)}$	$U_{13}^{(obs.)}$	$U_{13}^{(calc.)}$
O_1	.590	.384	.605	.242	-.197	-.335
O_2	1.668	1.089	.478	.423	-.772	-.413
C_1	1.093	.751	.515	.408	.041	-.318
C_2	.490	.818	.049	.392	-.081	-.329
C_3	.419	.834	.346	.416	-.359	-.332
C_4	.259	.707	.026	.391	-.517	-.314
C_5	1.000	1.052	.559	.737	.079	-.358
C_6	.866	.749	-.199	.346	-.913	-.318

molecular axes chosen coincide closely with the principal axes of vibration.

The main component of molecular motion is an oscillation of 10.5° about the axis of minimum inertia. The oscillations about the y and z axes, 1.27 and 2.32 are comparatively small. The standard deviations found for ω_{22} and ω_{33} are sufficiently large that only oscillations about the long x axis need be considered significant with respect to alterations in bond lengths. The cross terms ω_{13} and ω_{23} are small, indicating that the axes of oscillation tend to coincide with the molecular axes. The large value of ω_{12} may be accounted for by the fact that the atoms in the chain are all close to the long x axis, thus giving large standard deviations to the values of ω_{11}, ω_{12} and ω_{13} (Cruickshank 1956 c). The large standard deviations may also be accounted for by the effects of interval vibrations of the atoms which cannot be resolved from the rigid body motions (Higgs 1955).

The considerable oscillation about the long axis of the molecule would have the effect of shortening the apparent distance of the atoms from the axis (Cruickshank 1956 b) (Figure XVIII).

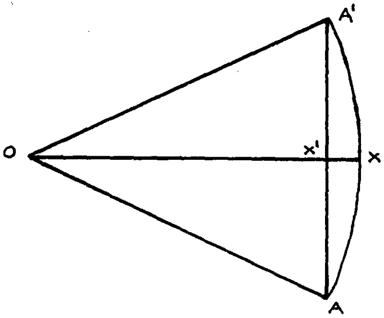


Figure XVIII

Whereas the true atomic position would be represented in the diagram by x, the measured coordinate would be x' where Ox is perpendicular to the axis of rotation and OA and OA' are the limits of oscillation. Knowing the amplitude of the oscillation it is thus possible to calculate the true coordinate. Since all the atoms in sorbic acid except O_1 lie close to the axis (Fig. XVI) the shifts are small, being for the most part within the limits of accuracy of the coordinates. The C_1-O_1 bond is, however, considerably lengthened. The revised bond lengths are given in Table XXVI. The bond angles along the chain are all slightly decreased with the exceptions of $O_1 - C_1 - O_2$, which is increased. The corrected bond angles are given in Table XXVIII. These, and the bond lengths are shown diagrammatically in Figures XIX and XX.

Table XXVII

Revised Bond Lengths (Å)

$O_1 - C_1$	1.260 Å	$C_3 - C_4$	1.454 Å
$O_2 - C_1$	1.318	$C_4 - C_5$	1.339
$C_1 - C_2$	1.454	$C_5 - C_6$	1.513
$C_2 - C_3$	1.346		

Table XXVIII

Revised Bond Angles

$O_1 - C_1 - O_2$	122.9°	$C_2 - C_3 - C_4$	125.5°
$O_1 - C_1 - C_2$	122.4°	$C_3 - C_4 - C_5$	123.8°
$O_2 - C_1 - C_2$	115.0°	$C_4 - C_5 - C_6$	124.8°
$C_1 - C_2 - C_3$	123.5°		

15. Intermolecular Contacts

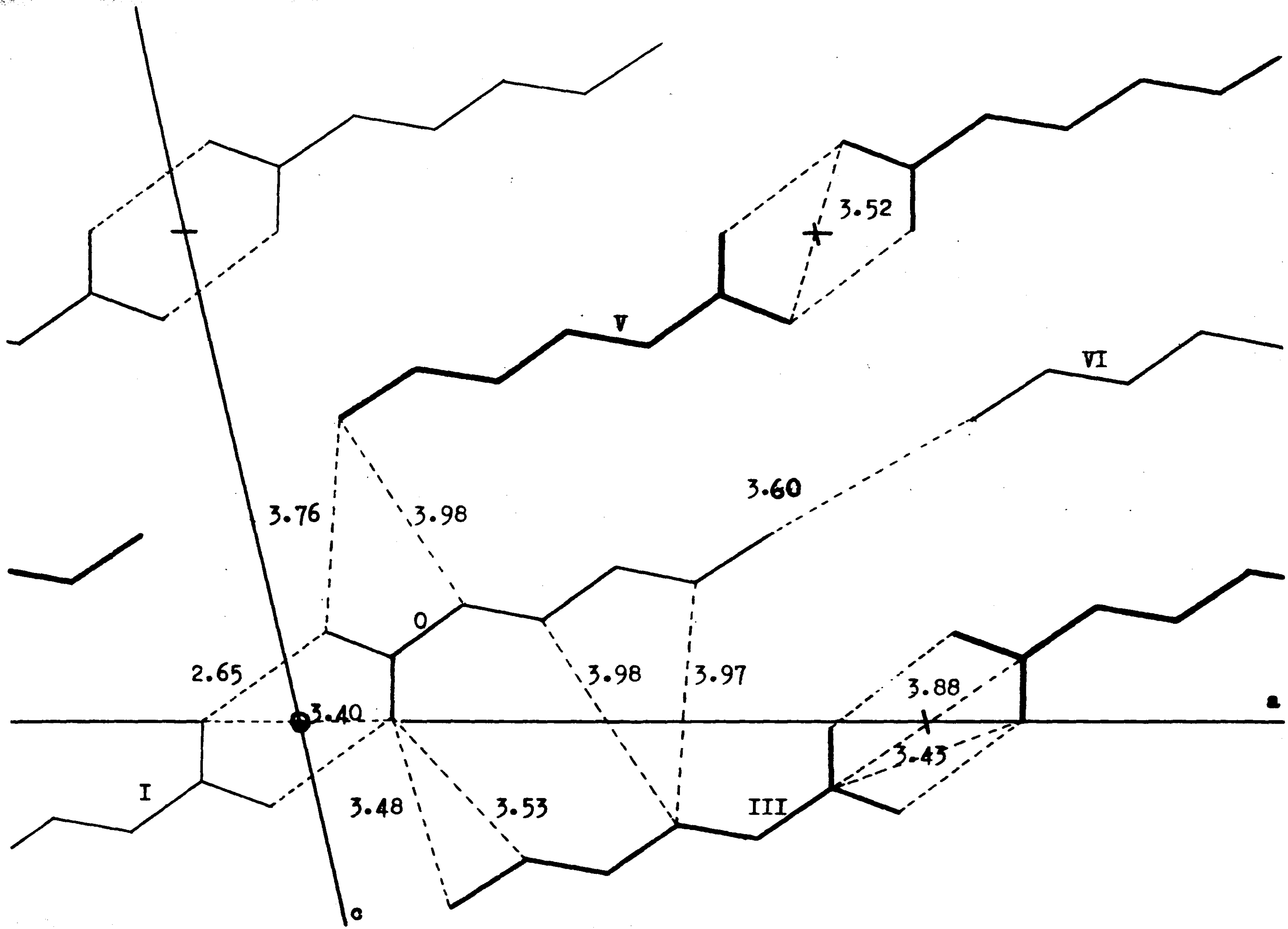
The closest approaches to neighbouring molecules are listed in increasing order of length up to a distance of 4 Å (Table XXIX). The equivalent positions of the molecules concerned are: molecule 0; x, y, z; molecule 1; $\bar{x}$ $\bar{y}$ $\bar{z}$; molecule 2; x, 1+y, z ; molecule 3; $\frac{1}{2}-x$ $\frac{1}{2}-y$ $-z$; molecule 4; $\bar{x}$, 1-y, -z; molecule 5; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; and molecule 6; 1-x, y, $\frac{1}{2}-z$. These intermolecular contacts are also shown diagrammatically in Figures XXI and XXII.

The shortest distance is the hydrogen bond between O_2 of molecule 0 and O_1 of molecule 1, related to the first by a centre of symmetry. Of the non-hydrogen bonded contacts, the shortest is that between O_2 of molecule 0 and O_1 of molecule 4. This is 3.36Å, which is greater than the sum of the Van der Waals radii for oxygen, 2.8Å. The carbon carbon distances are all greater than 3.4Å.

Table XXIX

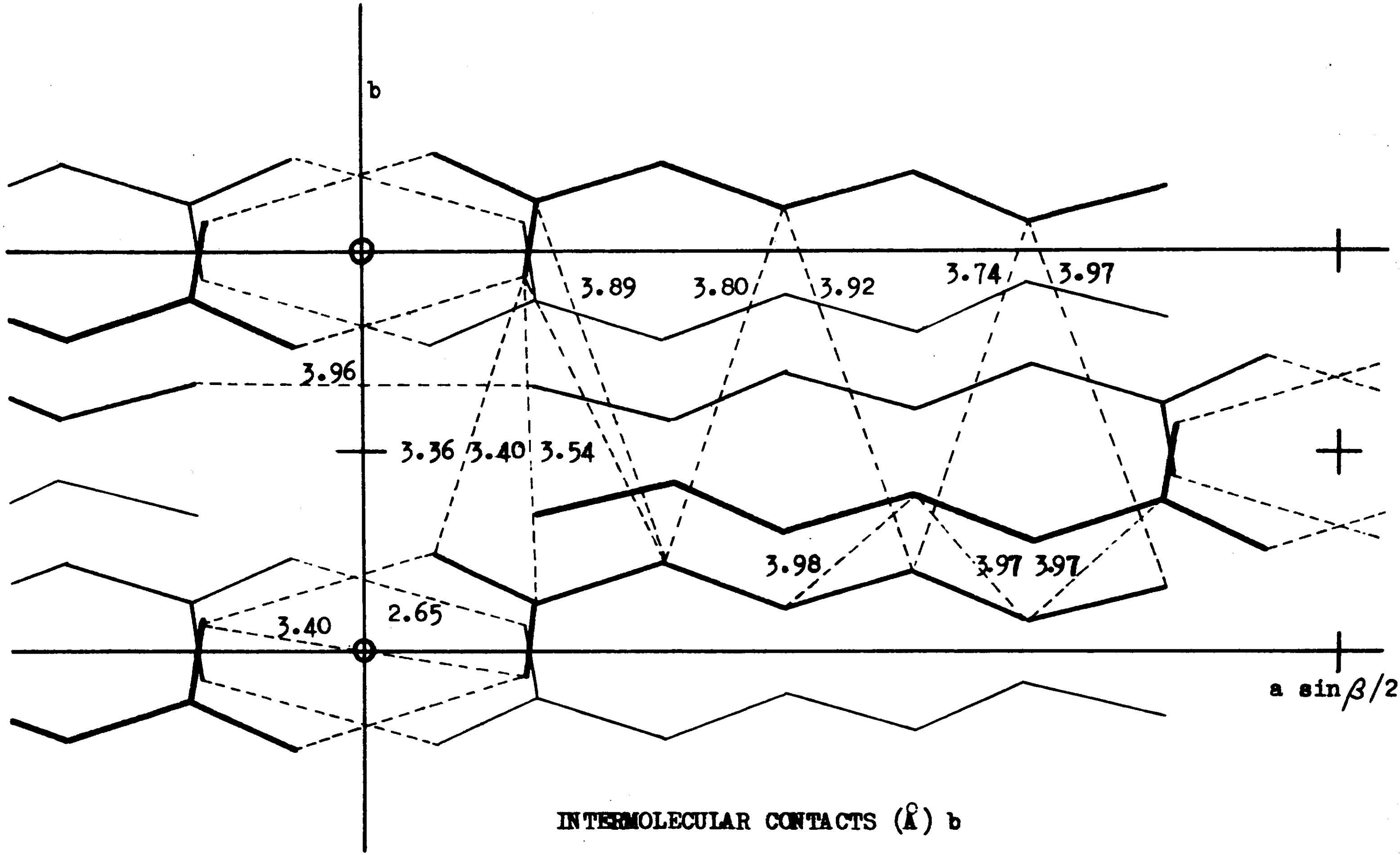
Intermolecular Distances less than 4Å

$O_2 - O_1^{I}$	2.65 Å	$O_2 - C_1^{II}$	3.76 Å
$O_2 - O_1^{II}$	3.36	$O_2 - C_6^{V}$	3.76
$O_1 - O_1^{I}$	3.40	$C_2 - C_3^{IV}$	3.81
$C_1 - O_1^{II}$	3.41	$C_1 - C_1^{I}$	3.88
$C_1 - O_1^{I}$	3.43	$C_2 - C_1^{II}$	3.90
$O_2 - C_1^{I}$	3.47	$C_4 - C_3^{II}$	3.93
$O_1 - C_6^{III}$	3.49	$C_6 - C_6^{VI}$	3.96
$O_2 - O_2^{I}$	3.53	$C_6 - C_5^{II}$	3.97
$O_1 - C_5^{III}$	3.54	$C_5 - C_1^{III}$	3.98
$C_2 - O_1^{II}$	3.54	$C_5 - C_3^{III}$	3.98
$O_2 - O_2^{IV}$	3.62	$C_3 - C_3^{III}$	3.98
$C_4 - C_5^{II}$	3.75	$C_2 - C_6^{V}$	3.98



INTERMOLECULAR CONTACTS (Å) a

FIG. XXI



INTERMOLECULAR CONTACTS (Å) b

FIG. XXII

16. Analysis of Molecular Dimensions

The lengths of the carbon-oxygen bonds in the carboxyl group confirm the earlier conclusion (see section 7.3) that the hydrogen is associated with O_2, C_1-O_2 being considerably longer than the doubly-bonded $C_1=O_1$. The carbon-oxygen bond lengths are within the normal limits for single and double bonds as found in free acids (Table XXX), though they vary slightly from the average values.

Table XXX

	C_1-O_1	C_1-O_2	
Sorbic Acid	1.256 Å	1.318 Å	
β-Ionylidene Crotonic	1.244	1.325	(Eichhorn and MacGillavry 1959)
Succinic	1.249	1.311	(Broadley et al 1959)
Average values	1.23	1.36	(Tables 1958)

It is noteworthy that the carbon-oxygen double bond is a not p~~r~~allel to the carbon-carbon double bonds as might have been expected. Other conjugated acids also show this effect (Crotonic, β-Ionylidene crotonic), which may be explained by the steric effect of the hydrogen on C_3 whose presence would cause slight overcrowding if the hydroxyl group which has a smaller C - C - O angle was directed on the same side of the molecule.

The double bonds $C_2 - C_3$ and $C_4 - C_5$ are of normal length, averaging 1.342Å. This compares with the normal ethylenic bond length of 1.337Å (Tables 1958).

The C - C bond of the terminal methyl group appears to be a pure single bond, however the $C_1 - C_2$ and $C_3 - C_4$ bonds are significantly shorter than normal single bonds. Dewar and Schmeising (1959) give a minimum value of 1.479 for an $Sp^2 - Sp^2$ hybrid single bond, whereas the lengths of both bonds in sorbic acid are 1.454Å. This could indicate some degree of conjugation both with the carbon-carbon double bonds and with the doubly-bonded oxygen of the carboxyl group. The near-planarity of the entire molecule (section 13) lends support to the possibility of such conjugation throughout the molecule.

The bond angles along the carbon chain are all slightly larger than the theoretical Sp^2 bond angle of 120°, the average value being 124.4°. Crotonic acid and β-Ionylidene crotonic acid also have bond angles slightly greater than 120°. This is probably due to the steric effect of the hydrogen atoms along the chain which would tend to force the carbon atoms apart by increasing the bond angles. The sum of the Van der Waals distances for two hydrogens is 2.4Å (Pauling 1960) compared with the values of 2.46 - 2.49Å for the hydrogen-hydrogen distances along the planar chain. Slight deviations from planarity would also serve to increase the distance somewhat.

IIb Crotonic Acid

1. Crystal Data

Crotonic acid $C_4H_6O_2$, m.p. 71 - 72°, was crystallized by slow evaporation from aqueous solution as thick clear needles. Unit cell dimensions were determined from measurements of rotation and Weissenberg photographs corrected for film shrinkage.

Crotonic acid is monoclinic.

Table XXXI

<u>a</u>	15.32 ± .02	Å
<u>b</u>	4.021 ± .005	
<u>c</u>	16.17 ± .02	
β	107.6 ± .1°	

It may be noted that in the axial system chosen, <u>c</u> is longer than <u>a</u>, whereas it is custumary in monoclinic systems to consider <u>a</u> to be the longer of the two non-unique axes. The choice was made in order to preserve the analogy with the structure of sorbic acid. It was immediately apparent from the Weissenberg photographs of the $h0\ell$ zone that the structure of the two acids were very similar. In sorbic acid, the unique axis is 4.02Å and the c axis is 15.82Å, both comparable to the b and c axes of crotonic acid. The a axis is longer, 20.01Å as compared to 15.32Å, corresponding to the greater chain length of sorbic acid.

2. Space Group

From Weissenberg photographs of the h0ℓ and hIℓ nets of crotonic acid, it was apparent that all odd reflections with indices were absent from the h0ℓ zone, whereas for the upper layer absences occured when $h + k = 2n + 1$. A precession photograph of the hk0 zone indicated that 0k0 reflections were absent for odd values of k. These absences correspond to either of the space groups C_2 or $C_{2/c}$. From consideration of the cell dimensions it was apparent that there were eight molecules per unit cell, corresponding to a density of 1.204 g/cc (found 1.192 g/cc at 22°c). If the structure were non-centrosymmetric then the asymmetric unit would contain two molecules / C_2 has only four equivalent positions. From the close resemblance of the structure to sorbic acid it was highly probable that $C_{2/c}$ was the correct choice.

This was confirmed after the collection of the three-dimensional data by the application of statistical tests.

3. Intensity Data

A large clear needle of crotonic acid which showed good extinction when examined under polarized light was cut to a size suitable for X-ray examination. As the substance had a high vapour pressure, the crystal section, .2 mm. x .4 mm. x 2 mm., was sealed in a thin-walled pyrex capillary.

Using four-film packs (Robertson 1943), in a Nonius camera, equi-inclination Weissenberg series were taken about the short b axis using CuKα radiation. Three h0ℓ series were recorded, with 1 hr., 6 hr. and 24 hr. exposures; two of each of h1ℓ and h2ℓ ; exposed for 3 hrs. and 24 hrs. respectively; and one h3ℓ series with a 48 hr. exposure. The h4ℓ net was not obtained because the equi-inclination angle was too large for the camera.

The intensities were estimated visually using a step wedge. The film factor for the h0ℓ series was 3.3. This was increased for the upper layers to compensate for the longer path length through the film (Rossmann 1956).

The data were corrected by the application of Lorentz and polarization factors, and, for the upper layers, the Tunell factor (1939).

4. Statistical Tests

4.1 Variance

The corrected $h0\ell$ $h1\ell$ and $h2\ell$ intensity data were divided into three ranges of sin θ; .20 - .55, .55 - .75 and .75 - .90. Any reflections lying outside the scope of these ranges were discarded. The total number of reflections considered in each range was 149, 194, and 288.

The weighted average variance calculated over the three ranges is 2.43.

4.2 N(z) Test

N(z) was evaluated for each range for z = .1(.1)1.0. The weighted average values for the three ranges are listed in Table XXVI.

Table XXXII

z =	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0
N(z) =	.232	.425	.497	.598	.653	.692	.723	.756	.780	.780

As both tests indicate that the structure is centrosymmetric the space group was confirmed as $C_{2/c}$.

5. The 010 Projection

By analogy with sorbic acid, crotonic acid was assumed to have the eight molecules in the unit cell arranged as four pairs linked through their carboxyl group as hydrogen bonded dimers, the centre of the dimer coinciding with a crystallographic centre of symmetry. A set of coordinates was chosen, based on the final sorbic acid parameters, but altered slightly to compensate for the difference in the monoclinic angle. A temperature factor of $B_\theta = 5$ was applied for the calculation of a set of structure factors, whose discrepancy between observed and calculated values was 66%. Although this value was not encouraging, the signs of 54 terms were combined with the corresponding observed structure factors for an (010) Fourier projection. Calculations were carried out on the Deuce computer, requiring five minutes for the 90 structure factors and 4½ minutes for a 30 x 30 $h0\ell$ Fourier. The atoms, apart from the terminal carbon atom were poorly resolved in the first Fourier projection, however, it was possible to obtain a new set of coordinates.

Structure factors calculated from coordinates obtained from the Fourier projection gave a discrepancy of 57%. When a third structure factor calculation failed to better the agreement (this was later discovered to be caused by a computer failure), an error synthesis was computed.

The coefficients $(F_o - F_c)$ for the 96 observed reflections, were used for the Fourier summation. The resulting error map indicated, as expected, that there was no gross misplacement of the atoms, although certain large shifts were indicated, particularly for C_3. The carbon atoms of the double bond, C_2 and C_3, were shifted so as to decrease the angle between the double bond and the single bond of the methyl group. A further set of structure factors gave an agreement of 41% for the observed terms.

A second error synthesis was computed to examine the effects of the coordinate shifts. The second map was similar to the first indicating that the shifts, though in the right direction, were not large enough. A further cycle indicated that shifts were again too small, and examination of the third error synthesis showed that the angle of the molecule to the a axis must be increased. Accordingly, the values of the z coordinates for C_2, C_3 and C_4 were increased by up to .2Å. Smaller shifts were applied to the atoms of the carboxyl group.

After the sixth structure factor calculation, the discrepancy had fallen to 25%. Further refinement of the projection was carried out by least squares procedures. Coordinates taken from the fifth difference map, combined with an initial isotropic temperature factor of 4.5 were used as input to the least squares programme. The initial

R factor, with the lowered value of B_θ was 22%. After three cycles on half shift the discrepancy had fallen to 14.6%.

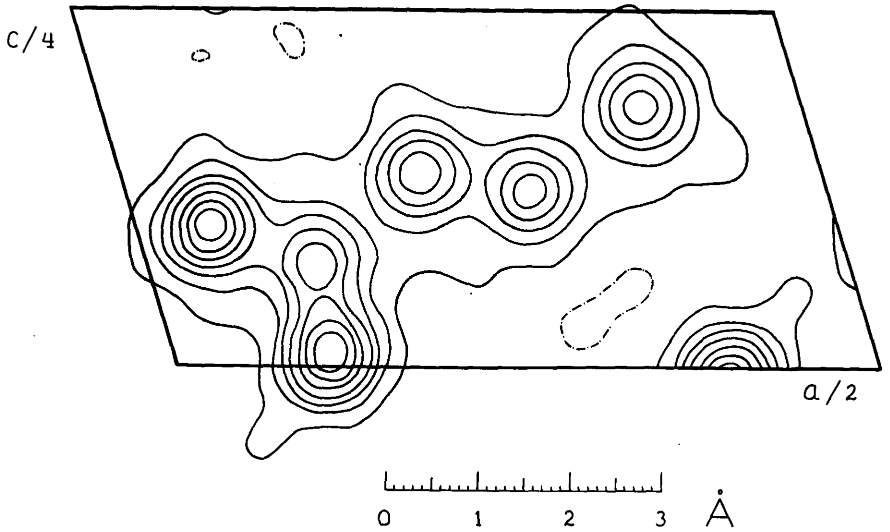
At this stage, the positions of the six hydrogen atoms were calculated from their probable location with respect to the carbon and oxygen atoms. Introduction of these hydrogens increased the time for a structure factor calculation from eight to fifteen minutes. After five more cycles, in which the R factor and $\sum w \Delta^2$ (see section IIa 1.) fell increasingly slowly, the refinement was terminated at a discrepancy of 12.9%. The final coordinates are listed in Table XXXIII.

The signs obtained from the last structure factor calculation were assigned to the corresponding observed structure amplitudes for the computation of the final electron density map Fig. XXIII. Contours are plotted at intervals of 1e/Å^2. This shows good resolution of the carbon and oxygen atoms. The differences between observed and calculated values of the signed structure factors were used as coefficients for a second Fourier summation to show the residual errors (Fig. XXIV). A further set of structure factors was calculated, based on the coordinates of the carbon and oxygen atoms alone. The values of $F_o - F_c$ resulting from this calculation, when used as Fourier coefficients, yielded a map showing the hydrogen positions (Fig. XXV). Contours on both $F_o - F_c$ maps are at intervals of .2e/Å with negative

Table XXXIII

Final Fractional Coordinates - 010 Projection

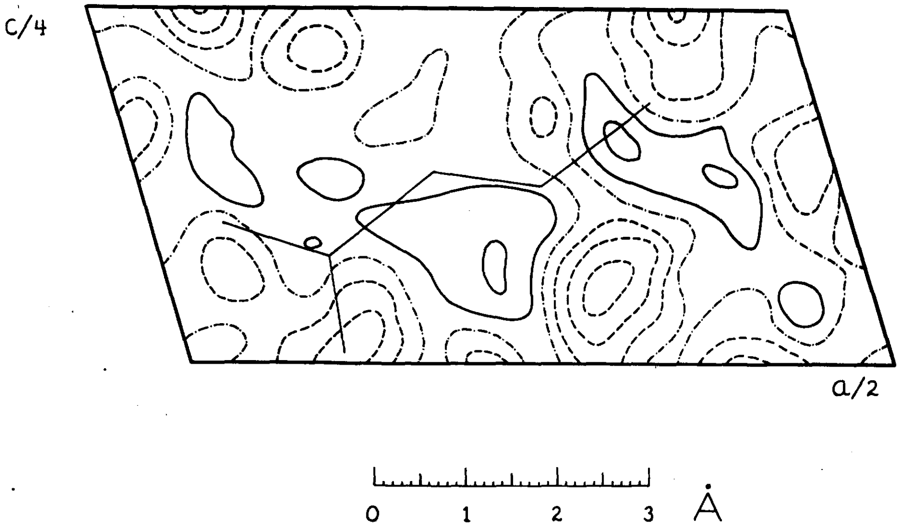
	x/a	z/c
O_1	.11049	.00716
O_2	.05456	.09598
C_1	.12365	.07262
C_2	.21146	.13491
C_3	.28952	.12517
C_4	.38709	.18248
H_1	-.00654	.05679
H_2	.20900	.19759
H_3	.29400	.06179
H_4	.39800	.23249
H_5	.41800	.23699
H_6	.46100	.15449



Crotonic Acid (010) Projection.

Electron density map. Contours at intervals of 1e/A^2 ; zero contour broken.

Figure XXIII



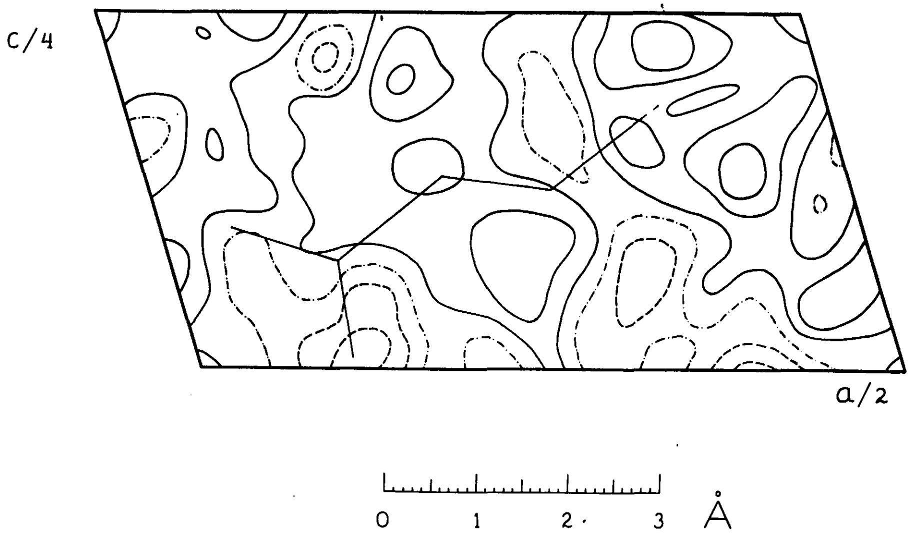
Crotonic Acid (010) Projection

$(F_o - F_c)$ map. Contours at intervals of $0.2e/A^2$.

Negative contours -----

Zero contours -.-.-.-

Figure XXIV



Crotonic Acid (010) Projection

Hydrogen map. Carbon and oxygen contributions subtracted out. Contours at intervals of 0.2e/A^2.

Negative contours -----

Zero contours -·-·-·-

Figure XXV

contours dashed. The hydrogen atoms appear as diffuse regions of electron density superimposed on the residual errors. These are relatively small, indicating that the majority of parameters have been successfully determined.

6. The Structure in Three Dimensions

It had already been determined by comparison of the $h0\ell$ zone structure factors that the structures of sorbic and crotonic acids were closely allied. Upper layer reflections also showed this similarity. The b-axial lengths of both compounds being virtually identical, a set of Y coordinates were chosen based on the sorbic acid coordinates (Table XXVIII).

Table XXXIV

Y-coordinates for three-dimensional refinement

	y/b		y/b
O_1	-.06421	C_2	.23000
O_2	.23688	C_3	.07500
C_1	.10424	C_4	.21500

These, combined with x and z values from the 010 projection were used for the calculation of structure factors for the 137 observed $h2\ell$ reflections. The agreement was 39%.

Following a method described by Rossmann, (Rossmann et. al. 1959) a few rapid least squares cycles were computed (time ~ 8 min./cycle). This method is useful for structures in which most of the atoms are close to their correct positions, particularly when two of the positional parameters for each atom are known. The magnitude of the shifts in the thermal parameters indicates which atoms are misplaced. The coordinates of these atoms may then be altered by hand from consideration of bond lengths. Three cycles of refinement on the $h2\ell$ zone lowered the discrepancy to 29%. None of the atoms were showing the large shifts of thermal parameters characteristic of wrongly placed atoms, however an isotropic temperature factor of $B_\theta = 4.5$ was reintroduced and three more cycles completed to bring the agreement for $h2\ell$ to 24% and lower the value of $\sum w\Delta^2$ from 51 to 18. The coordinates so obtained were used for a calculation of the $h1\ell$ reflections, for which R = 27%. A second calculation gave R = 23.5%. After a single calculation of the $h3\ell$ net structure factors for scaling purposes, all the observed data were included in a structure factor calculation using coordinates from the final $h1\ell$ cycle. The overall agreement was 33.6%. This fell slowly on refinement to a value of 20%. At this point, twelve of the strongest low order reflections whose calculated values were consistently higher than the observed, were removed from the refinement. The planes removed were those which would most likely suffer from extinction. Hydrogen atoms were included. The refinement then proceeded without incident to a discrepancy of 13.4% for the observed reflections. The progress of the three dimensional refinement is shown in Table XXXV. Refinement was terminated at 13.4% at which point the mean atomic shifts were less than the standard deviation of atomic position (Table XXXVI). The final coordinates are listed in Table XXXVII.

6a Standard Deviation

The standard deviations were calculated from the least squares output by the method described in section IIa 1 (see appendix II). The final value of $\sum w\Delta^2$ for crotonic acid was 42. The total number of reflections included was 848, therefore (n-s), the number of reflections less the number of parameters was 793. The standard deviation of atomic positions is given in Table XXXVIII. The values obtained from the least squares output were multiplied by 1.05 to allow for the monoclinic angle (Templeton 1959).

Table XXXV

R and $\sum w\Delta^2$

Cycle	R	$\sum w\Delta^2$	Cycle	R	$\sum w\Delta^2$	
1	33.6%	197	7	21.9	77	
2	31.8	191	8	21.3	66	
3	29.1	161	9	20.9	63	Extinction corr.
4	26.6	134	10	18.9	45	
5	26.3	122	11	18.7 13.9 obs.	42	
6	23.8	104				

Table XXXVI

Coordinate Shift Final Cycle

	$\Delta x/a$	$\sigma x/a$	$\Delta y/b$	$\sigma y/b$	$\Delta z/c$	$\sigma z/c$
O_1	.00015	.00025	.00005	.00115	.00012	.00023
O_2	.00000	.00024	.00014	.00111	.00007	.00024
C_1	.00014	.00034	.00003	.00013	.00000	.00032
C_2	.00018	.00038	.00012	.00134	.00003	.00033
C_3	.00044	.00038	.00025	.00137	.00004	.00322
C_4	.00018	.00038	.00010	.00157	.00006	.00039

Table XXXVIII

Final Fractional Coordinates

	x/a	y/b	z/c
O_1	.11113	- .07010	.00703
O_2	.05270	.21225	.09833
C_1	.11960	.09379	.07373
C_2	.21103	.17140	.13465
C_3	.28855	.06175	.12416
C_4	.38281	.13052	.18348

Table XXXVIII

Standard Deviation of Atomic Position (Å)

	x	σ x	y	σ y	z	σ z
O_1	1.7025	.0038	- .2819	.0042	.1137	.0039
O_2	.8073	.0039	.8535	.0047	1.5900	.0042
C_1	1.8323	.0056	.3771	.0057	1.1922	.0057
C_2	3.2330	.0062	.6892	.0057	2.1773	.0055
C_3	4.4206	.0061	.2483	.0058	2.0077	.0055
C_4	5.8646	.0061	.5248	.0067	2.9669	.0065

Table XXXIX

Orthogonal Coordinates (Å)

	X	Y	Z
O_1	1.6682	- .2819	.1084
O_2	..3280	.8535	1.5160
C_1	1.4729	.3771	1.1368
C_2	2.5766	.6892	2.0760
C_3	3.8153	.2483	1.9143
C_4	4.9703	.5248	2.8289

7. Molecular Geometry

The uncorrected bond lengths for crotonic acid, calculated from the orthogonalized coordinates (Table XXXIX) are listed in Table XL. These, and the bond angles given in Table XLI, are, even more than the dimensions of the sorbic acid molecule, subject to correction to allow for thermal motion (see section IIa 14). The standard deviation of bond length σd, calculated from the expression

$$\sigma d = (\sigma A_1^2 + \sigma B_2^2)^{\frac{1}{2}} \qquad (74)$$

where σA_1 and σB_2 are the mean standard deviations of position of two atoms, are given in Table XXXIV. The standard deviation of bond angles ($\sigma\theta$) was calculated from the expression

$$\sigma^2(\theta) = \frac{\sigma^2(A)}{d^2{}_{AB}} + \sigma^2(B)\left(\frac{1}{d^2{}_{AB}} - \frac{2\cos\theta}{d_{AB}\,d_{BC}} + \frac{1}{d^2{}_{BC}}\right) + \frac{\sigma^2 C}{d^2{}_{BC}} \qquad (75)$$

where σA, σB and σC are the mean standard deviations of position of three atoms and d is the distance between two atoms (Cruickshank and Robertson 1953). The values obtained are listed in Table XXXV.

Table XL

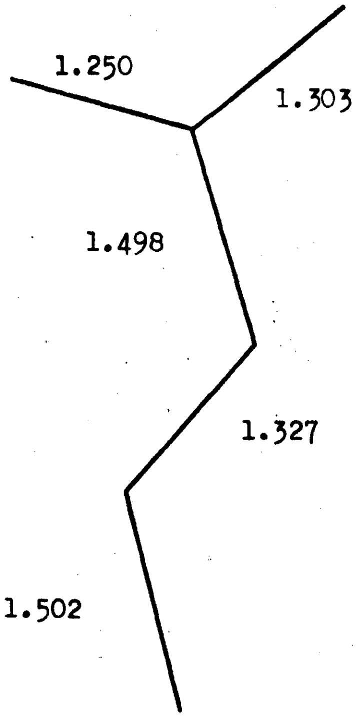
Bond Lengths (Å)

$O_1 - C_1$	1.237 ± .006 Å	$C_2 - C_3$	1.325 ± .008 Å
$O_2 - C_1$	1.297 ± .007	$C_3 - C_4$	1.498 ± .009
$C_1 - C_2$	1.482 ± .008	O - H - O	2.635 ± .006

Table XLI

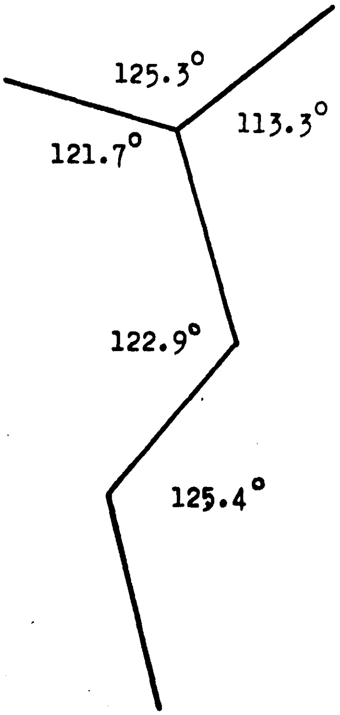
Bond Angles

$O_1 - C_1 - O_2$	124.4 ± .5°
$OO_1 - C_1 - C_2$	121.4 ± .5°
$O_2 - C_1 - C_2$	113.2 ± .5°
$C_1 - C_2 - C_3$	123.3 ± .5°
$C_2 - C_3 - C_4$	125.8 ± .6°



CROTONIC ACID
BOND LENGTHS (Å)

FIG. XXVIII



CROTONIC ACID
BOND ANGLES (DEG.)

FIG. XXIX

8. Hydrogen Positions

Hydrogens could not be located with accuracy. The final positions are listed in Table XLII. The bond lengths involving hydrogen, given in Table XLIII are thus subject to considerable error, the standard deviation of each individual C-H bond being .13Å. The mean value of the C-H bond distance is 1.06Å ± .05 (Crumpler and Yoe 1940).

9. Molecular Plane

Planes were calculated (Shomaker et al. 1959) through the molecule as a whole, and also separately through the carbon atoms and the carboxyl group. Application of the χ^2 test (sectn. IIa13) to the plane through the molecule yielded a value of

$$\chi^2 = \Sigma \Delta^2/\sigma(x)^2 = 59 \qquad (76)$$

For 6 atoms, for which the number of degrees of freedom is $6 - 3 = 3$, the probability that the atoms lie strictly on a plane is thus very low (Fisher and Yates 1957). For deviations of the four carbon atoms from the carbon plane, however, $\chi^2 = .059$ for $4 - 3 = 1$ degree of freedom. This corresponds to a probability of 80% that the carbon atoms

Table XLII

Final Fractional Coordinates - Hydrogen Atoms

	x/a	y/b	z/c
H_1	-.00657	.15354	.05676
H_2	.20910	.35784	.18461
H_3	.28533	-.01134	.07172
H_4	.42815	.14799	.13238
H_5	.38581	.39669	.19401
H_6	.42574	-.03104	.22713

Table XLIII

Bond Distances Involving Hydrogen (Å)

$O_2 - H_1$	.981 Å	$C_4 - H_4$	1.231 Å
$C_2 - H_2$	1.109	$C_4 - H_5$	1.082
$C_3 - H_3$	.884	$C_4 - H_6$	1.035

Average C - H distance 1.06Å

are coplanar. The equation of the plane of the carbon atoms with respect to the orthogonal axes $\underline{a}\ \underline{b}\ \underline{c}'$ is given by:

$$.22424X - .81360Y - .53645Z - .02463 = 0 \qquad (77)$$

where $X = x + z\cos\beta$; $Y = y$ and $Z = z\sin\beta$. The deviations of carbons and oxygens from this plane are listed in Table XLIV.

Table XLIV

Deviations from the carbon plane (Å)

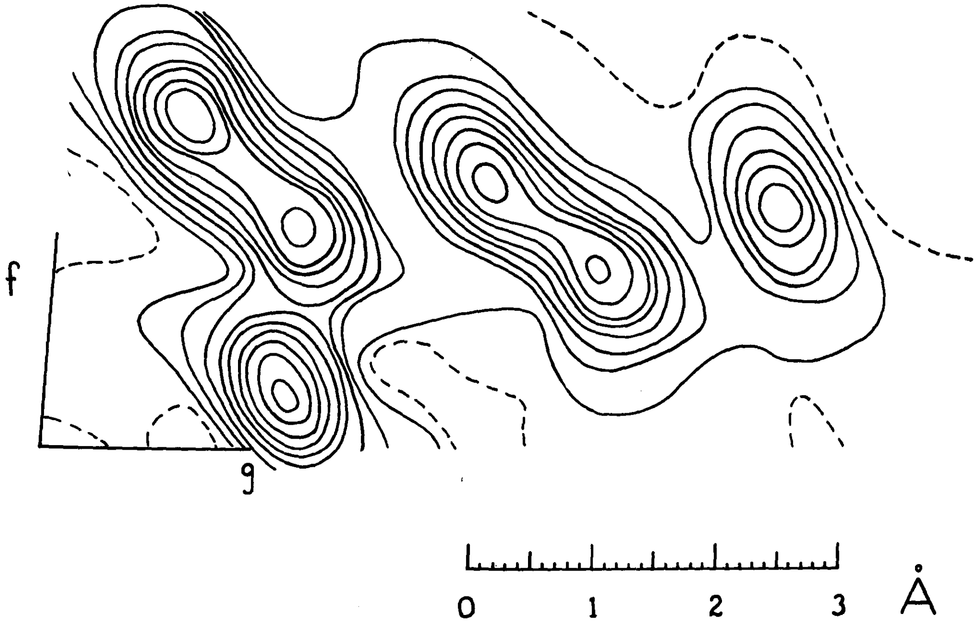
O_1	+.0291 Å	C_2	+.0006
O_2	-.0400	C_3	+.0007
C_1	-.0007	C_4	-.0007

The plane of the carboxyl group with respect to the same axial system is

$$.36301x + 1.66836y - z - .02694 = 0 \qquad (78)$$

This forms an angle of 5.75° with the carbon plane.

The electron density was determined in the plane of the carbon atoms (Fig. XXV). This is plotted with respect to the axes f + g in the plane (Broadley et al 1959). The plane was recalculated in terms of another set of orthogonal axes $\underline{a}'\ \underline{b}\ \underline{c}$



Crotonic Acid

Electron density map in the plane of the molecule. Contours at intervals of 1e/A^3; one electron contour dashed.

Figure XXVI

$$.05151X' + .81360Y' - .57915Z' - .02463 = 0 \qquad (79)$$

where $X' = x \sin\beta$ $Y' = y$ and $Z = z + x\cos\beta$ and A' B' and C' are the coefficients. The angle between the b crystal axis and f, $\tan^{-1} A'/C'$ is 54° 33'. The angle between a' and g, $\tan^{-1} B'/C'$ is 5° 5'. The lengths of f and g are 6.933 Å and 14.660 Å respectively. The angle between f and g is $\cos^{-1}(\sin 54^\circ\ 33' \sin 5^\circ\ 5') = 85^\circ\ 52'$.

This map reveals an even higher degree of anisotropy than was displayed in sorbic acid (Fig. XV). This is in agreement with the results of calculations on thermal motion.

10. Thermal Motion

The values of the anisotropic temperature factors obtained from the least squares refinement, with their standard deviations (see section IIb .6) are given in Table XLV. The axes of the ellipsoids of vibration of the atoms of crotonic acid were determined by the method of Rollett and Davies (1955) (Table XLVI). The root mean square amplitudes of vibrations along these axes are listed in Table XLVII. The eccentricities of the ellipsoids so described are slightly greater than those for sorbic acid (Table XXIII) though the lengths of the major axes are comparable.

If, as a first approximation, the molecule may be

Table XLV

Anisotropic Temperature Factors $(\times 10^{-2})$

	β_{11}	β_{22}	β_{33}
O_1	.553 ± .012	6.967 ± .021	.580 ± .012
O_2	.475 ± .013	9.983 ± .025	.667 ± .014
C_1	.442 ± .018	2.910 ± .026	.521 ± .018
C_2	.649 ± .021	3.526 ± .029	.467 ± .017
C_3	.708 ± .021	3.905 ± .029	.505 ± .018
C_4	.431 ± .020	6.653 ± .039	.751 ± .024

	β_{12}	β_{23}	β_{13}
O_1	.574 ± .010	-1.946 ± .008	.526 ± .018
O_2	.620 ± .011	-2.533 ± .010	.424 ± .021
C_1	- .376 ± .013	..130 ± .014	.214 ± .030
C_2	.578 ± .014	.001 ± .012	.464 ± .029
C_3	.634 ± .015	.613 ± .013	.638 ± .030
C_4	- .302 ± .016	.521 ± .018	.065 ± .039

Table XLVI

Orientation of the Axes of Ellipsoids of Vibration with respect to Crystal Axes

	a	b	c
O_1	1. 110.3°	1. 83.8°	1. 21.3°
	2. 47.2	2. 131.0	2. 70.8
	3. 59.2	3. 41.8	3. 64.7
O_2	1. 90.3	1. 118.8	1. 28.8
	2. 136.4	2. 52.7	2. 70.8
	3. 49.0	3. 62.7	3. 53.2
C_1	1. 102.0	1. 98.7	1. 14.8
	2. 167.2	2. 83.7	2. 101.1
	3. 89.4	3. 26.9	3. 63.1
C_2	1. 102.1	1. 16.4	1. 100.9
	2. 15.1	2. 80.0	2. 101.2
	3. 85.2	3. 59.9	3. 30.6
C_3	1. 27.1	1. 83.1	1. 116.0
	2. 77.8	2. 164.3	2. 80.3
	3. 49.3	3. 74.5	3. 44.8
C_4	1. 101.2	1. 17.9	1. 76.3
	2. 78.0	2. 74.0	2. 159.8
	3. 31.2	3. 65.6	3. 71.8

Table XLVII

R.M.S. Deviations from the Principal Axes (Å)

	a	B_{11}	b	B_{22}	c	B_{33}
O_1	.140	1.6 Å^2	.309	7.5 Å^2	.255	5.1 Å^2
O_2	.352	9.8	.167	2.2	.242	4.6
C_1	.149	1.8	.258	5.2	.220	3.8
C_2	.163	2.1	.270	5.8	.225	4.0
C_3	.292	6.7	.170	2.3	.216	3.5
C_4	.324	8.3	.209	3.5	.230	4.2

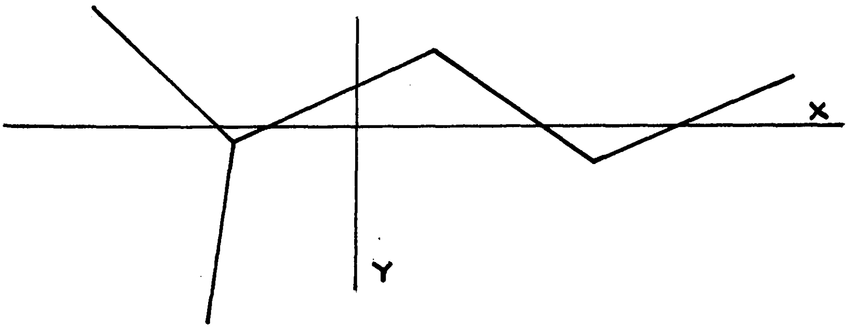
Table XLVIII

Coordinates with respect to Molecular Axes (Å)

	X	Y	Z
O_1	- .98571	-1.32162	.04799
O_2	-1.77257	.78418	-.06673
C_1	- .82300	- .09641	-.00127
C_2	.53256	.50391	.00125
C_3	1.64572	- .21476	.00150
C_4	3.04138	.33246	-.00092

assumed to move as a rigid body, the vibrations of the atoms may be resolved into translational and rotational motion of the molecule as a whole (Cruickshank 1956a). The positions of the atoms were calculated with respect to molecular axes whose origin was taken at the molecular centre of mass (Table XLVIII). The x axis is directed along the long axis of the molecule, with the y axis at right angles in the plane and the z axis perpendicular (Fig. XXVII).

Figure XVII



From the observed root mean square displacements (U_{ij}) of the atoms with respect to the molecular axes, least squares normal equations may be derived (sections I 3.3 and IIa 14) for the determination of $T + \omega$, the translational and rotational components of the molecular motion. The values of $T + W$ so obtained, with their standard deviations are listed in Table XLIX. Using these values, the equations (I (19)) were then solved for U_{ij}. The observed and calculated values of U_{ij} are compared in Table L. The fair correlation of these values indicate that the treatment of the crotonic acid molecule as a vibrating unit is probably valid.

Table XLIX

T_{ij} (x10^{-2} A^{2})

5.087 ± .440	1.830 ± .435	- .704 ± .474
	2.941 ± .579	- .925 ± .584
		2.121 ±.780

ω_{ij} (deg.^{2})

186.3 ± 27.0	44.3 ± 9.0	1.0 ± 13.5
	18.9 ± 5.1	1.1 ± 4.6
		18.0 ± 4.4

Table L

Atomic Vibration Amplitudes $(x10^{-2}\ A^{2})$

	$U_{11}^{(obs.)}$	$U_{11}^{(calc.)}$	$U_{22}^{(obs.)}$	$U_{22}^{(calc.)}$	$U_{33}^{(obs.)}$	$U_{33}^{(calc.)}$
O_1	5.068	6.056	2.126	3.493	8.795	9.074
O_2	4.640	5.433	2.956	4.691	11.855	11.178
C_1	4.724	5.093	5.100	3.315	3.085	2.350
C_2	6.078	5.228	3.567	3.098	3.627	3.000
C_3	6.267	5.113	4.412	4.434	2.797	4.900
C_4	5.294	5.149	8.909	8.039	5.695	5.352

	$U_{12}^{(obs.)}$	$U_{12}^{(calc.)}$	$U_{23}^{(obs.)}$	$U_{23}^{(calc.)}$	$U_{13}^{(obs.)}$	$U_{13}^{(calc.)}$
O_1	2.699	1.105	- .908	- .622	-1.101	- .771
O_2	2.502	2.595	- .755	- .619	-1.036	- .910
C_1	.438	1.786	-1.480	- .945	- .892	- .702
C_2	1.925	1.682	- .716	- .929	- .219	- .712
C_3	2.859	2.024	- .084	-1.024	- .712	- .719
C_4	.039	1.272	-1.410	-1.214	- .515	- .671

The cross terms of the T_{ij}'s are small with respect to the diagonal terms, indicating that the molecular axes chosen are closely coincident to the true axes of vibration of the molecule. The values of ω_{11} ω_{12} + ω_{13} are larger because the atoms are close to the x axis, resulting in a large error for these terms (Cruickshank 1956c). The effects of internal vibrations, which cannot be determined accurately, also contribute to the error (Lonsdale 1961)

The vibrational movements are fairly uniform, though, as expected, slightly larger along the chain length. The mean displacements are .22Å, .18Å and .13Å in the x,y and z molecular directions respectively. The oscillations about the x axis are exceptionally large; approximately 13.5°, which would have considerable effect on the bond lengths (Cruickshank 1956b). Oscillations about the other axes are 4.1° and 4.2° respectively. The molecular dimensions were revised to include the effects of oscillation about the molecular axes. (Cruickshank 1956b). The values obtained for bond lengths and angles are given in Tables LI and LII.. These are shown diagrammatically in Figures XXVIII and XXIX.

Table LI

Revised Bond Lengths (Å)

$O_1 - C_1$	1.250 Å
$O_2 - C_1$	1.303
$C_1 - C_2$	1.498
$C_2 - C_3$	1.327
$C_3 - C_4$	1.502

Table LII

Revised Bond Angles

$O_1 - C_1 - O_2$	125.3°
$O_1 - C_1 - C_2$	121.7°
$O_2 - C_1 - C_2$	113.1°
$C_1 - C_2 - C_3$	122.9°
$C_2 - C_3 - C_4$	125.4°

11. Intermolecular Contacts

The closest approaches to the surrounding molecules are given in Table LIV. They are listed in increasing order of length up to a distance of 4.0Å. The equivalent positions of the molecules included are listed in Table LIII.

Table LIII

Equivalent positions of neighbouring molecules

Molecule 0	x, y, z
Molecule 1	$\bar{x}, \bar{y}, \bar{z}$
Molecule 2	$x, 1+y, z$
Molecule 3	$\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$
Molecule 4	$\bar{x}, 1-y, \bar{z}$
Molecule 5	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
Molecule 6	$1-x, y, \frac{1}{2}-z$

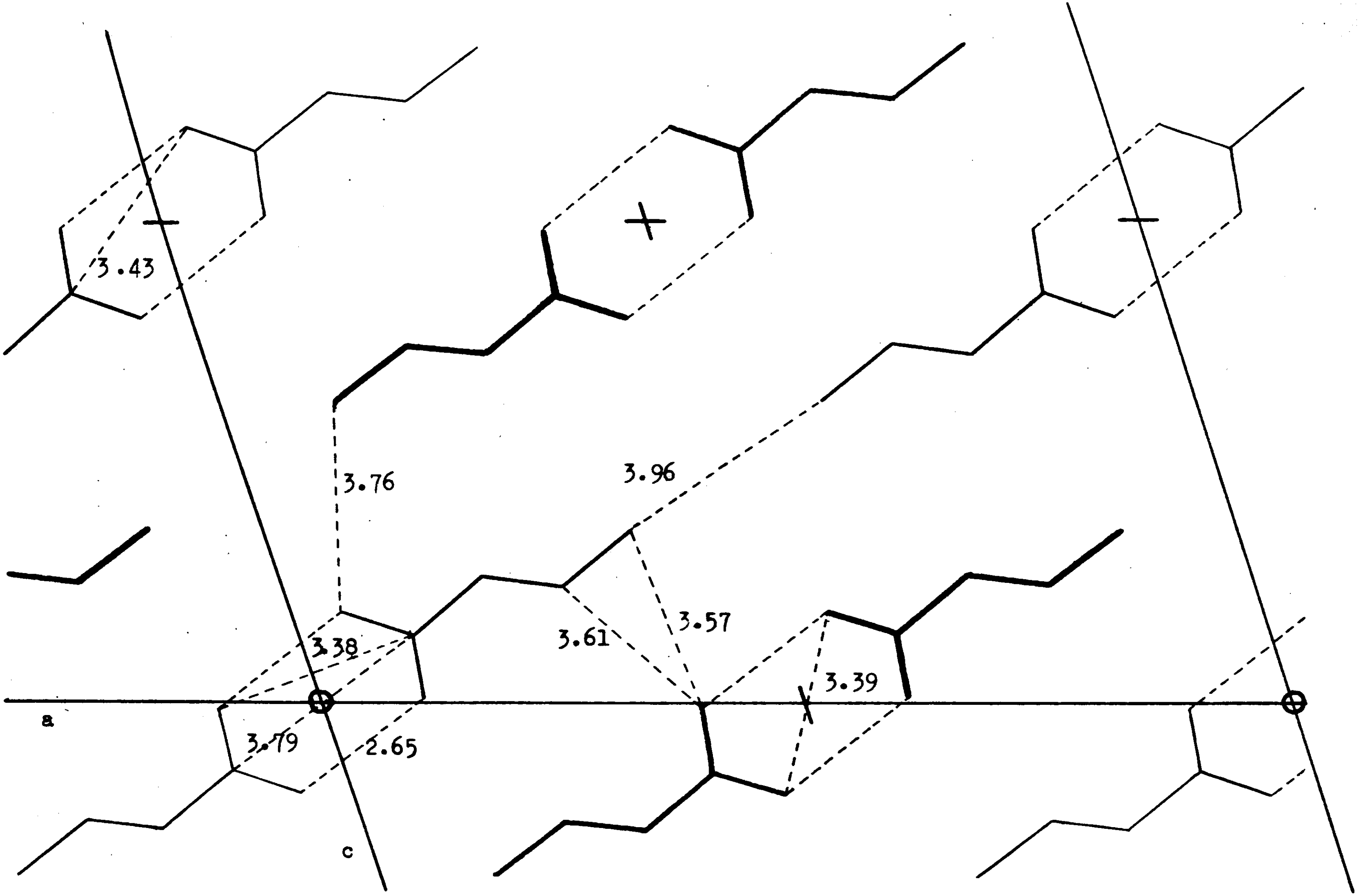
The closest approaches are shown diagrammatically in Figures XXX and XXXI.

The shortest distance between neighbouring molecules occurs in the hydrogen bonded carboxyl group; between O_2 of molecule 0 and O_1 of molecule 1 which is related to molecule 0 by a centre of symmetry. The distance between C_1 of molecule 0 and O_1 of molecule 1 is 3.38Å. This is slightly greater than the sum of the Van der Waals radii for carbon and oxygen (3.1Å Pauling 1960).

Table LIII

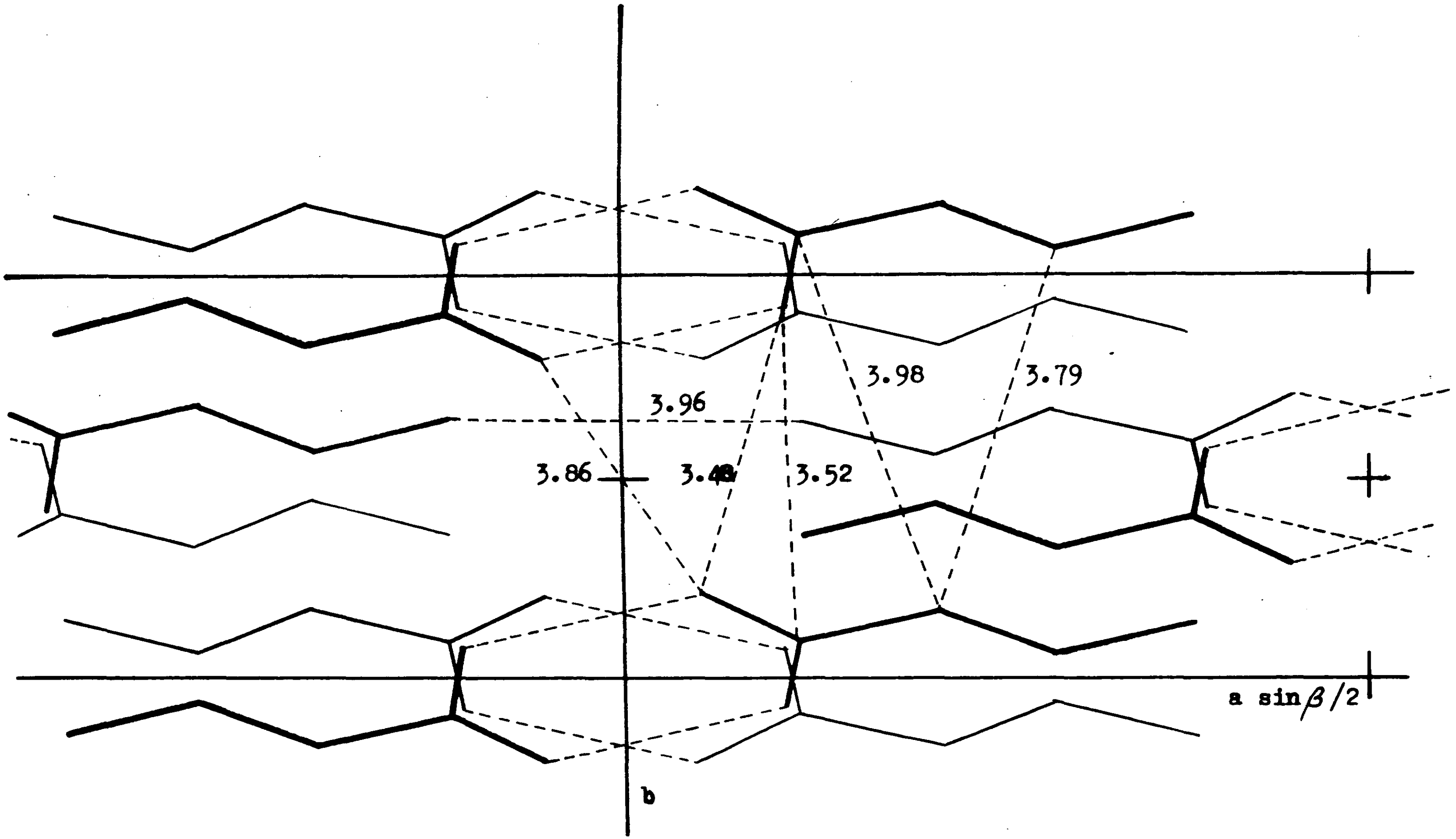
Intermolecular Distances less than 4 Å

$O_1 - O_2^{I}$	2.63 A	$C_3 - O_1^{III}$	3.61 A
$C_1 - O_1^{I}$	3.38	$O_2 - C_1^{II}$	3.74
$O_1 - O_1^{I}$	3.39	$C_2 - O_1^{II}$	3.74
$C_1 - O_2^{I}$	3.43	$O_2 - C_4^{V}$	3.76
$O_2 - O_1^{II}$	3.48	$C_1 - C_1^{I}$	3.79
$C_1 - O_1^{II}$	3.52	$C_2 - C_3^{II}$	3.79
$O_2 - O_2^{I}$	3.54	$O_2 - O_2^{IV}$	3.87
$C_4 - C_4^{VI}$	3.56	$C_2 - C_1^{II}$	3.98
$C_4 - O_1^{III}$	3.58		



INTERMOLECULAR CONTACTS (A)a

Figure XXX



INTERMOLECULAR CONTACTS (Å) b
Figure XXXI

12. Analysis of Molecular Dimensions

The revised bond lengths found for the carboxyl group of crotonic acid (Table LI) are not inconsistent with those found for other carboxylic acids. The shortening of the single carbon-oxygen bond (1.303A) from the average value of 1.36Å and corresponding slight lengthening of the double bond (1.250Å , average 1.23Å) possibly indicate that a certain degree of hybridization occurs, or that a fraction of the dimers is packed with carboxyl groups arranged in the opposite sense. The latter would, however, tend to be prevented by the steric effect of the hydrogen atom on C_2.

The length of 1.498Å found for the C_1-C_2 bond, which corresponds to the normal Sp^2 - sp^2 single bond distance, coupled with the value of 1.327Å found for the double bond seems to indicate that conjugation does not play a large part in the determination of the molecular dimensions. The oxygens of the carboxyl group are not, of course, coplanar with the carbon skeleton, though the angle of tilt, 5.7°, is sufficiently small that some orbital overlap could still occur.

The revised bond angles found for crotonic acid (Table LII) are consistent with those obtained for sorbic acid and ionylidene crotonic acid, both around the carboxyl group and along the carbon chain.

IIc Discussion

1. Bond Length

The bond lengths of the two acids, studied compare favourably with each other and with those found for other similar carboxylic acids. The main point of difference occurs in the $C_1 - C_2$ bond; that is, the carbon-carbon bond to the carboxyl group. The value obtained for sorbic acid is 1.45Å while that for crotonic is 1.50Å. As the standard deviations of these bonds is less than .01Å, these differences are possibly significant. The sorbic acid molecule has a longer double bond system which may result in some conjugation along the chain.

A survey of a number of unsaturated acids shows that, in general, the $C_1 - C_2$ bond is shortened (Table LV).

Table LV

$C_1 - C_2$ Bond length of some unsaturated acids

	Bond length (Å)	
Tiglic acid	1.44	(Porte and Robertson 1959)
Chlorocrotonic	1.44	(Mammi et. al. 1960)
Maleic	1.44	(Shahat 1952)
Sorbic	1.45	
Salicylic	1.458	(Cochran 1953)

Acrylic	1.46	(Nitta 1960)
β-Ionylidene crotonic	1.46	(Eichhorn and MacGillavry 1959)
Furoic	1.47	(Goodwin and Thompson 1954)
Benzoic	1.48	(Sim et. al. 1955)
Crotonic	1.50	

This shortening may be sufficient to indicate a certain amount of hybridization in some of these compounds, particularly in those molecules with a $C_1 - C_2$ bond length less than 1.45Å. It must be noted, however, that for cyclooctatetraene which is sufficiently non planar to preclude overlap of the orbitals, electron diffraction studies show a C - C bond distance of 1.462 ± .001Å (Bastiansen et. al. 1957). This distance, though shorter than Dewar's (1959) calculated value of 1.479Å must thus be included as a lower limiting value for pure $Sp^2 - Sp^2$ single bonds. Thus in crotonic acid, as in the other instances in which the $C_1 - C_2$ bond has been found to be greater than 1.46Å resonance must play a limited role.

2. Molecular Motion

Most of the organic structures investigated by X-ray analysis are studied at room temperature, that is, relatively close to their melting points. Sorbic and crotonic acids present two interesting examples of structures with relatively loose intermolecular forces and correspondingly great freedom of motion for the individual molecule. Crotonic and sorbic acids melt at 72°C and 134°C respectively, thus crotonic acid in particular would be expected to show a high degree of thermal motion. This has been confirmed. Crotonic acid has been found to have an oscillation of amplitude 13.5° about the long axis of the molecule, compared with the smaller but still considerable value of 10.5° for the higher melting point of sorbic acid. These results are consistent with those obtained for β-Succinic acid which is a dibasic acid melting at 189-90°C. This acid crystallizes in infinite chains linked by hydrogen bonding through the carboxyl groups at each end of the molecule. This structure, which would still have little resistance to rotation about the chain axis has been found to have an oscillation about this axis of approximately 9° (Broadley et al 1959). Though the values of the individual temperature factors obtained from the refinement of crotonic and sorbic acids may be subject to error (Lonsdale 1961), nevertheless the syntheses of these values in the determination of the motion of the molecule as a whole should yield a result whose order of magnitude, at least, is significant. The correlation of the values obtained for these three acids with their molecular size and melting point appears to confirm this conclusion. Some of the observed effects of oscillation about the long axis may be accounted for by internal twisting vibrations however these should have a comparatively small influence at room temperature (Cruickshank 1960).

These results also agree with those predicted from observation of the thermal diffuse reflections for sorbic acid (Lonsdale et. al. 1941). Laue photographs of sorbic acid exhibit a pattern of broad diffuse reflections corresponding to planes parallel to the chain length, and thin diffuse streaks in directions perpendicular to the chain.

These streaks indicate the existence of transverse waves travelling through the crystal normal to the chain direction, resulting in a movement of chain against chain (Amorós and Canut 1957). The observed oscillation of the molecules about the chain axis appears to confirm this.

The apparent slight deviation from planarity may result from these thermal vibrations of the molecule. Allene, butatriene and dimethylacetylene which would be expected to be strictly linear have been observed in investigations by electron diffraction to exhibit slight bending due to thermal motion (Bastiansen and Traetteberg 1960).

APPENDIX I

STRUCTURE FACTORS

Appendix Ia

Structure Factors for Sorbic Acid

h	k	l	F(calc)	F(meas)
0	0	2	56.0	46.2
0	0	4	- 94.0	71.1
0	0	6	1.2	5.1
0	0	8	84.5	84.1
0	0	10	80.0	77.4
0	0	12	13.7	14.6
0	0	14	9.4	8.2
0	0	16	5.0	4.6
0	0	18	3.8	3.2
0	0	20	4.2	< 1.0
			.	.
2	0	- 20	5.4	2.5
2	0	- 18	2.0	2.3
2	0	- 16	0.5	< 1.9
2	0	- 14	5.6	6.3
2	0	- 12	19.4	19.9
2	0	- 10	21.2	19.3
2	0	- 8	- 50.2	49.7
2	0	- 6	- 38.5	37.1
2	0	- 4	188.3	171.4
2	0	- 2	71.4	60.0
2	0	2	29.8	25.3
2	0	4	- 37.0	33.1
2	0	6	- 5.7	5.1
2	0	8	10.2	11.0
2	0	10	80.4	81.0
2	0	12	3.9	4.0
2	0	14	4.7	5.7
2	0	16	11.5	13.3
2	0	18	- 6.2	6.9
			.	.
4	0	- 20	2.0	2.3
4	0	- 18	- 1.0	< 1.6
4	0	- 16	- 5.8	7.5
4	0	- 14	2.8	< 1.9
4	0	- 12	- 15.1	15.4
4	0	- 10	- 15.0	16.7
4	0	- 8	8.8	8.3
4	0	- 6	- 43.6	48.1
4	0	- 4	10.9	10.0
4	0	- 2	29.1	29.0
4	0	0	- 40.3	41.3
4	0	2	- 36.3	35.9
4	0	4	- 66.7	63.1
4	0	6	- 28.9	25.3
4	0	8	- 24.0	26.0
4	0	10	9.1	10.7
4	0	12	27.5	33.5
4	0	14	- 18.8	21.8
4	0	16	- 20.6	21.1
4	0	18	0.3	< 1.0
			.	.
6	0	- 20	- 5.9	5.4
6	0	- 18	- 7.2	7.7
6	0	- 16	- 8.7	8.9
6	0	- 14	- 5.2	5.7
6	0	- 12	- 1.6	2.5
6	0	- 10	- 23.7	21.3
6	0	- 8	- 22.3	25.6
6	0	- 6	- 40.7	43.2
6	0	- 4	- 36.6	34.3
6	0	- 2	18.9	3.1
6	0	0	- 61.4	60.9
6	0	2	- 64.6	62.9
6	0	4	-111.5	116.2
6	0	6	- 12.0	13.9
6	0	8	50.7	62.1
6	0	10	- 13.0	12.4
6	0	12	- 29.7	35.7
6	0	14	- 9.8	10.6
6	0	16	- 3.5	3.1
6	0	18	- 1.2	< 1.0
			.	.
8	0	- 20	- 3.0	< 1.7
8	0	- 18	- 4.4	4.6
8	0	- 16	- 4.0	4.8
8	0	- 14	- 0.7	< 2.0
8	0	- 12	5.4	5.4
8	0	- 10	- 16.2	17.0
8	0	- 8	- 16.9	15.8
8	0	- 6	- 7.3	11.6
8	0	- 4	- 49.6	44.4
8	0	- 2	18.3	14.1
8	0	0	- 50.6	54.6
8	0	2	- 34.6	46.5
8	0	4	30.6	30.9
8	0	6	- 4.3	< 1.6
8	0	8	3.3	< 1.8
8	0	10	- 4.9	4.8
8	0	12	- 12.7	13.3
8	0	14	- 3.4	3.7
8	0	16	- 0.1	< 1.4
			.	.
10	0	- 20	- 1.3	< 1.0
10	0	- 18	0.2	< 1.5
10	0	- 16	2.3	2.5
10	0	- 14	6.3	7.4
10	0	- 12	24.8	25.8
10	0	- 10	1.2	2.5
10	0	- 8	- 86.4	53.3
10	0	- 6	11.2	8.3
10	0	- 4	50.9	51.9
10	0	- 2	29.4	29.9
10	0	0	14.8	8.7
10	0	2	- 11.9	10.8
10	0	4	30.1	30.3
10	0	6	20.5	18.3
10	0	8	4.1	5.4
10	0	10	3.3	3.8
10	0	12	- 3.8	2.5
10	0	14	5.1	< 1.6
10	0	16	2.5	2.3
			.	.
12	0	- 18	0.1	< 1.4
12	0	- 16	23.5	21.6
12	0	- 14	17.7	16.7
12	0	- 12	- 18.9	20.1
12	0	- 10	- 6.3	6.6
12	0	- 8	15.5	18.1
12	0	- 6	34.3	31.5
12	0	- 4	35.7	33.7
12	0	- 2	17.7	16.3
12	0	0	27.7	25.1
12	0	2	1.2	< 1.7
12	0	4	23.4	23.0
12	0	6	21.0	22.2
12	0	8	- 4.0	2.5
12	0	10	6.9	5.7
12	0	12	5.3	5.4
12	0	14	3.6	3.5
			.	.
14	0	- 18	8.7	6.9
14	0	- 16	- 2.4	2.3
14	0	- 14	- 0.7	2.0
14	0	- 12	- 1.9	2.0
14	0	- 10	- 3.2	4.1
14	0	- 8	7.0	6.0
14	0	- 6	19.1	20.5
14	0	- 4	22.9	20.2
14	0	- 2	- 4.3	< 2.5
14	0	0	20.0	21.2
14	0	2	0.4	< 1.0
14	0	4	- 24.5	24.1
14	0	6	12.9	17.0
14	0	8	13.9	13.3
14	0	10	- 1.1	2.5
14	0	12	- 0.5	< 1.0
14	0	14	0.6	< 1.0
			.	.
16	0	- 18	0.1	< 1.0
16	0	- 16	- 1.2	< 1.5
16	0	- 14	- 5.2	5.1
16	0	- 12	- 8.0	8.9
16	0	- 10	- 5.6	5.7
16	0	- 8	- 2.5	< 2.0
16	0	- 6	1.4	< 1.9
16	0	- 4	30.7	30.5
16	0	- 2	- 13.7	11.4
16	0	0	- 61.9	66.3
16	0	2	- 4.4	5.4
16	0	4	15.7	16.4
16	0	6	2.0	< 1.9
16	0	8	- 6.9	8.9
16	0	10	- 6.0	5.4
16	0	12	- 0.8	< 1.0
			.	.
18	0	- 16	- 2.2	< 1.7
18	0	- 14	- 4.9	4.6
18	0	- 12	- 13.2	12.8
18	0	- 10	- 8.6	8.6
18	0	- 8	21.6	22.8
18	0	- 6	3.2	2.9
18	0	- 4	- 37.2	37.7
18	0	- 2	- 18.0	20.6
18	0	0	- 7.5	5.7
18	0	2	- 1.5	< 2.0
18	0	4	0.5	< 1.0
18	0	6	- 3.3	3.7
18	0	8	- 4.3	4.1
18	0	10	- 5.5	6.3
20	0	- 16	- 2.7	< 1.0
20	0	- 14	- 4.6	3.7
20	0	- 12	4.0	5.1
20	0	- 10	2.1	2.5
20	0	- 8	- 4.8	5.7
20	0	- 6	- 1.5	< 2.0
20	0	- 4	- 11.5	12.2
20	0	- 2	- 8.2	9.2
20	0	2	4.8	4.6
20	0	4	1.8	2.3
20	0	6	- 2.5	2.3
20	0	8	3.9	4.8
			.	.
22	0	- 14	- 0.3	< 1.0
22	0	- 12	0.6	< 1.0
22	0	- 10	4.7	6.9
22	0	- 8	0.6	2.3
22	0	- 6	0.8	3.5
22	0	- 4	- 1.6	< 1.8
22	0	- 2	0.0	< 1.0
22	0	0	4.7	4.8
22	0	2	6.2	7.4
22	0	4	12.6	16.4
22	0	6	- 1.3	< 1.0
			.	.
24	0	- 10	4.3	4.0
24	0	- 8	1.1	< 1.0
24	0	- 6	1.1	< 1.0
24	0	- 4	2.8	4.0
24	0	- 2	2.7	< 1.9
24	0	0	11.3	13.9
24	0	2	3.6	7.4
			.	.
			.	.
1	1	- 19	- 0.8	< 1.2
1	1	- 18	4.2	4.3
1	1	- 17	- 1.4	< 2.6
1	1	- 16	5.1	5.8
1	1	- 15	0.3	< 1.0
1	1	- 14	4.4	4.1
1	1	- 13	5.1	4.2
1	1	- 12	6.0	9.5
1	1	- 11	1.3	< 1.7
1	1	- 10	15.9	16.0
1	1	- 9	- 17.7	19.6
1	1	- 8	11.0	13.6
1	1	- 7	- 41.1	34.9
1	1	- 6	- 20.2	21.6
1	1	- 5	53.6	56.5
1	1	- 4	51.0	41.7
1	1	- 3	105.4	136.1
1	1	- 2	144.6	129.5
1	1	- 1	- 56.9	74.7
1	1	1	- 90.4	71.0
1	1	2	- 13.6	11.1
1	1	3	- 0.4	4.0
1	1	4	25.3	21.9
1	1	5	9.6	7.9
1	1	6	20.9	17.6
1	1	7	29.9	23.1
1	1	8	14.1	13.0

h	k	l	F(calc)	F(meas)
1	1	9	15.4	15.0
1	1	10	10.3	9.6
1	1	11	4.2	4.4
1	1	12	10.0	9.8
1	1	13	0.5	<1.0
1	1	14	4.8	5.2
1	1	15	3.0	<1.0
1	1	16	4.4	4.9
1	1	17	2.7	2.8
1	1	18	5.6	5.5
1	1	19	-3.6	3.0
			.	.
3	1	-20	0.8	<1.0
3	1	-19	-0.3	<1.2
3	1	-18	1.4	<1.3
3	1	-17	-0.8	<1.6
3	1	-16	3.0	3.2
3	1	-15	5.4	5.6
3	1	-14	0.7	3.2
3	1	-13	7.6	9.7
3	1	-12	-5.5	4.2
3	1	-11	-18.9	20.9
3	1	-10	-16.4	19.6
3	1	-9	4.9	5.6
3	1	-8	8.7	7.5
3	1	-7	56.4	46.5
3	1	-6	43.5	36.8
3	1	-5	19.2	20.1
3	1	-4	-13.1	18.1
3	1	-3	15.9	20.2
3	1	-2	-1.1	4.0
3	1	-1	1.1	2.5
3	1	0	16.6	16.6
3	1	1	-28.2	31.1
3	1	2	-19.1	17.5
3	1	3	3.2	8.5
3	1	4	-10.5	11.3
3	1	5	20.2	17.5
3	1	6	-3.8	3.3
3	1	7	28.8	25.2
3	1	8	2.6	4.2
3	1	9	9.3	9.9
3	1	10	-5.9	6.1
3	1	11	10.1	9.9
3	1	12	3.0	3.4
3	1	13	4.6	4.1
3	1	14	8.6	10.2
3	1	15	-13.9	14.6
3	1	16	-4.6	8.5
3	1	17	-1.0	<1.3
3	1	18	-5.9	6.2
			.	.
5	1	-20	1.8	<1.0
5	1	-19	-2.5	3.1
5	1	-18	-2.5	2.9
5	1	-17	5.4	5.2
5	1	-16	-9.2	9.8
5	1	-15	1.5	<1.3
5	1	-14	-12.4	13.7
5	1	-13	4.1	5.1
5	1	-12	-4.0	6.1
5	1	-11	8.0	8.2
5	1	-10	-1.1	<1.7
5	1	-9	-6.3	6.6
5	1	-8	-20.7	20.6
5	1	-7	14.8	15.3
5	1	-6	-10.2	10.7
5	1	-5	22.7	22.9
5	1	-4	-18.6	24.5
5	1	-3	5.7	12.6
5	1	-2	-44.0	43.1
5	1	-1	-3.8	3.3
5	1	0	-24.3	29.4
5	1	1	-33.1	30.9
5	1	2	-34.3	31.1
5	1	3	4.4	4.0
5	1	4	-35.2	28.9
5	1	5	7.6	6.7
5	1	6	-32.8	30.0
5	1	7	36.9	35.1
5	1	8	-1.0	3.4
5	1	9	19.8	20.4
5	1	10	11.0	11.2
5	1	11	-30.8	28.6
5	1	12	-16.1	14.3
5	1	13	-14.7	13.3
5	1	14	-14.1	13.2
5	1	15	8.2	9.7
5	1	16	-1.6	<1.4
5	1	17	3.9	4.0
5	1	18	-0.8	<1.0
			.	.
7	1	-20	-3.8	<1.0
7	1	-19	0.4	<1.0
7	1	-18	-4.7	4.4
7	1	-17	2.1	<1.6
7	1	-16	-4.0	3.7
7	1	-15	4.3	4.8
7	1	-14	-6.2	6.1
7	1	-13	0.0	<1.8
7	1	-12	-7.5	8.3
7	1	-11	-4.4	4.2
7	1	-10	-2.4	<1.8
7	1	-9	-12.1	12.0
7	1	-8	-16.1	16.7
7	1	-7	4.4	5.6
7	1	-6	-19.2	23.2
7	1	-5	10.5	9.5
7	1	-4	-10.8	10.3
7	1	-3	-10.6	10.7
7	1	-2	-37.7	38.0
7	1	-1	-3.7	<1.1
7	1	0	-55.0	53.7
7	1	1	-57.5	54.3
7	1	2	-38.5	38.0
7	1	3	14.6	11.9
7	1	4	2.6	3.9
7	1	5	40.3	41.5
7	1	6	16.6	14.1
7	1	7	-17.6	16.9
7	1	8	-20.9	14.7
7	1	9	-21.7	19.6
7	1	10	-15.4	15.2
7	1	11	-7.3	7.3
7	1	12	-4.6	3.8
7	1	13	-1.6	<1.9
7	1	14	-5.2	5.2
7	1	15	1.8	<1.5
7	1	16	-2.4	2.7
			.	.
9	1	-19	0.0	<1.0
9	1	-18	-2.0	<1.3
9	1	-17	1.6	<1.5
9	1	-16	-8.3	2.7
9	1	-15	1.2	2.9
9	1	-14	1.9	3.0
9	1	-13	-4.8	5.1
9	1	-12	-1.1	<1.8
9	1	-11	-6.4	6.8
9	1	-10	9.5	10.1
9	1	-9	-19.4	21.1
9	1	-8	6.2	6.7
9	1	-7	-12.9	14.5
9	1	-6	-24.0	22.1
9	1	-5	33.8	37.1
9	1	-4	-19.5	21.3
9	1	-3	-19.9	17.4
9	1	-2	-2.1	4.1
9	1	-1	-35.5	30.1
9	1	0	25.2	31.9
9	1	1	2.8	5.1
9	1	2	17.9	16.5
9	1	3	-4.7	5.5
9	1	4	-5.1	5.1
9	1	5	4.3	6.0
9	1	6	6.2	6.5
9	1	7	-10.4	10.1
9	1	8	1.7	<1.7
9	1	9	-14.0	11.6
9	1	10	-5.1	6.1
9	1	11	-2.9	3.5
9	1	12	-0.1	<1.0
9	1	13	-0.3	<1.8
9	1	14	0.6	<1.6
9	1	15	2.1	2.3
			.	.
11	1	-19	-0.7	<1.0
11	1	-18	-0.1	8.1
11	1	-17	3.9	4.5
11	1	-16	1.1	<1.6
11	1	-15	7.0	8.9
11	1	-14	14.7	17.1
11	1	-13	-18.6	17.6
11	1	-12	14.2	15.5
11	1	-11	-27.3	26.9
11	1	-10	-8.0	10.1
11	1	-9	13.9	14.9
11	1	-8	-1.6	2.9
11	1	-7	21.2	21.1
11	1	-6	14.2	15.4
11	1	-5	1.6	3.0
11	1	-4	24.6	24.9
11	1	-3	-13.7	15.4
11	1	-2	18.9	18.8
11	1	-1	-18.5	18.2
11	1	0	14.7	14.7
11	1	1	3.2	5.6
11	1	2	28.3	25.5
11	1	3	1.2	<1.6
11	1	4	11.2	11.3
11	1	5	2.7	3.5
11	1	6	6.8	7.9
11	1	7	-5.6	4.9
11	1	8	8.9	8.1
11	1	9	-7.0	7.6
11	1	10	0.1	<1.8
11	1	11	4.8	4.8
11	1	12	1.9	<1.8
11	1	13	0.9	<1.5
11	1	14	4.8	3.0
11	1	15	1.7	2.3
			.	.
13	1	-18	7.3	4.4
13	1	-17	-2.1	<1.3
13	1	-16	7.1	8.2
13	1	-15	-13.6	13.7
13	1	-14	-1.7	3.4
13	1	-13	2.5	<1.7
13	1	-12	1.2	<1.8
13	1	-11	4.4	4.6
13	1	-10	6.5	6.7
13	1	-9	10.5	11.0
13	1	-8	7.0	6.7
13	1	-7	12.1	11.4
13	1	-6	8.9	9.6
13	1	-5	1.8	<1.7
13	1	-4	15.5	16.6
13	1	-3	-2.2	6.1
13	1	-2	19.1	21.0
13	1	-1	-10.0	9.5
13	1	0	7.0	8.1
13	1	1	11.0	11.1
13	1	2	16.2	17.2
13	1	3	0.1	3.3
13	1	4	14.0	12.9
13	1	5	-2.3	2.8
13	1	6	-7.0	7.4
13	1	7	14.6	14.6
13	1	8	0.9	<1.9
13	1	9	0.4	<1.8
13	1	10	7.4	7.0
13	1	11	-2.3	2.6
13	1	12	6.5	9.0
13	1	13	4.4	5.5
13	1	14	2.9	3.6
			.	.
15	1	-18	-1.5	<1.0
15	1	-17	-0.2	<1.0
15	1	-16	0.0	<1.3
15	1	-15	-0.7	2.5

h	k	l	F(calc)	F(meas)
15	1	- 14	0.1	<1.6
15	1	- 13	- 0.1	<1.5
15	1	- 12	- 2.3	2.9
15	1	- 11	5.2	5.3
15	1	- 10	- 2.4	3.0
15	1	- 9	11.3	11.0
15	1	- 8	1.5	<1.9
15	1	- 7	9.1	11.0
15	1	- 6	0.4	<1.7
15	1	- 5	0.4	<1.9
15	1	- 4	- 0.1	<1.9
15	1	- 3	6.7	7.3
15	1	- 2	14.0	16.7
15	1	- 1	- 17.2	17.2
15	1	0	2.0	3.0
15	1	1	- 6.0	7.1
15	1	2	- 23.6	20.2
15	1	3	32.9	30.4
15	1	4	- 4.7	7.3
15	1	5	10.5	8.4
15	1	6	6.1	6.0
15	1	7	- 7.6	8.7
15	1	8	1.7	<1.8
15	1	9	- 1.7	<1.7
15	1	10	- 0.9	<1.5
15	1	11	2.2	2.4
15	1	12	- 0.9	<1.0
15	1	13	2.5	2.5
			.	.
17	1	- 17	0.3	<1.0
17	1	- 16	- 2.8	2.6
17	1	- 15	- 0.5	<1.3
17	1	- 14	- 2.7	3.2
17	1	- 13	0.6	<1.5
17	1	- 12	- 3.8	3.9
17	1	- 11	2.6	3.4
17	1	- 10	- 8.0	7.6
17	1	- 9	10.3	10.9
17	1	- 8	- 4.2	5.3
17	1	- 7	17.2	18.1
17	1	- 6	10.1	10.7
17	1	- 5	- 17.9	16.9
17	1	- 4	- 7.9	7.6
17	1	- 3	- 26.8	25.1
17	1	- 2	- 25.3	26.0
17	1	- 1	15.8	17.7
17	1	0	- 9.6	9.3
17	1	1	17.0	16.9
17	1	2	- 1.0	<2.0
17	1	3	3.6	3.4
17	1	4	- 4.3	4.3
17	1	5	- 3.5	4.0
17	1	6	- 4.0	4.8
17	1	7	- 4.2	4.3
17	1	8	- 2.7	3.0
17	1	9	0.3	<1.0
17	1	10	- 1.3	<1.0
17	1	11	0.0	<1.0
			.	.
19	1	- 16	- 2.6	<1.0

h	k	l	F(calc)	F(meas)
19	1	- 15	- 2.9	2.2
19	1	- 14	- 4.1	4.8
19	1	- 13	0.8	<1.0
19	1	- 12	- 1.2	2.4
19	1	- 11	11.4	10.9
19	1	- 10	5.0	5.8
19	1	- 9	- 1.6	<1.8
19	1	- 8	- 5.2	6.4
19	1	- 7	- 14.9	14.0
19	1	- 6	- 12.9	13.2
19	1	- 5	- 4.4	4.8
19	1	- 4	- 3.7	4.0
19	1	- 3	- 0.5	<1.5
19	1	- 2	- 5.2	6.6
19	1	- 1	5.3	6.3
19	1	0	- 6.5	6.8
19	1	1	4.6	5.0
19	1	2	- 2.6	3.4
19	1	3	- 1.3	2.9
19	1	4	- 1.1	2.4
19	1	5	- 4.4	3.4
19	1	6	- 1.9	2.5
19	1	7	- 3.6	4.0
19	1	8	- 2.9	2.5
19	1	9	0.7	<1.0
			.	.
21	1	- 14	3.3	4.1
21	1	- 13	- 0.5	<1.0
21	1	- 12	- 1.2	<1.0
21	1	- 11	- 1.6	<1.0
21	1	- 10	- 2.0	<1.0
21	1	- 9	- 1.2	<1.3
21	1	- 8	1.3	<1.4
21	1	- 7	- 6.3	6.6
21	1	- 6	- 2.0	3.0
21	1	- 5	- 2.9	3.1
21	1	- 4	- 1.3	<1.7
21	1	- 3	- 0.1	<1.7
21	1	- 2	1.2	<1.7
21	1	- 1	3.1	<1.3
21	1	0	1.1	1.6
21	1	1	0.7	<1.0
21	1	2	1.0	3.0
21	1	3	- 2.0	<1.4
21	1	4	1.9	<1.0
21	1	5	- 0.3	<1.0
21	1	6	4.7	<1.0
21	1	7	- 7.0	<1.0
			.	.
23	1	- 12	1.6	<1.0
23	1	- 11	- 0.2	<1.0
23	1	- 10	0.1	<1.0
23	1	- 9	- 0.5	2.5
23	1	- 8	2.2	4.1
23	1	- 7	- 3.4	<1.3
23	1	- 6	2.0	<1.3
23	1	- 5	- 0.3	<1.5
23	1	- 4	1.3	<1.5
23	1	- 3	1.3	<1.0
23	1	- 2	3.1	3.2

h	k	l	F(calc)	F(meas)
23	1	- 1	1.4	<1.3
23	1	0	6.0	6.7
23	1	2	7.1	7.9
23	1	3	- 5.8	6.1
23	1	4	- 0.6	<1.0
			.	.
25	1	- 7	0.4	<1.0
25	1	- 6	3.2	3.9
25	1	- 5	- 2.1	3.3
25	1	- 4	4.9	5.2
25	1	- 3	3.8	4.3
25	1	- 2	3.9	<1.0
25	1	- 1	1.1	<1.0
			.	.
			.	.
0	2	1	- 49.0	42.3
0	2	2	18.1	13.9
0	2	3	- 39.2	35.7
0	2	4	36.6	33.5
0	2	5	20.4	20.5
0	2	6	20.4	19.8
0	2	7	8.5	9.4
0	2	8	8.5	8.2
0	2	9	3.3	4.2
0	2	10	- 0.2	2.4
0	2	11	2.5	2.4
0	2	12	1.9	<1.2
0	2	13	4.2	3.7
0	2	14	6.5	4.9
0	2	15	3.7	2.4
0	2	16	4.3	3.9
0	2	17	1.9	<1.2
0	2	18	1.0	<0.7
			.	.
2	2	- 18	1.0	<0.7
2	2	- 17	0.0	<1.2
2	2	- 16	2.2	2.5
2	2	- 15	0.1	<1.2
2	2	- 14	4.6	4.5
2	2	- 13	0.0	<1.2
2	2	- 12	- 3.0	2.6
2	2	- 11	0.6	2.4
2	2	- 10	- 14.3	12.7
2	2	- 9	- 6.5	[illegible]
2	2	- 8	14.8	15.2
2	2	- 7	33.3	34.8
2	2	- 6	42.9	39.1
2	2	- 5	49.3	50.1
2	2	- 4	- 2.0	3.3
2	2	- 3	- 16.3	22.9
2	2	- 2	- 25.2	24.4
2	2	- 1	- 7.5	6.5
2	2	0	- 2.9	5.5
2	2	1	14.6	17.7
2	2	2	19.5	14.1
2	2	3	6.0	5.4
2	2	4	28.6	24.9
2	2	5	16.3	16.4
2	2	6	10.8	7.3
2	2	7	14.9	13.5

h	k	l	F(calc)	F(meas
2	2	8	2.0	[illegible]
2	2	9	10.6	9.6
2	2	10	0.9	<1.2
2	2	11	5.3	5.1
2	2	12	2.3	<1.2
2	2	13	8.1	6.8
2	2	14	1.8	<1.2
2	2	15	5.0	4.7
2	2	16	1.0	<1.8
2	2	17	- 4.4	4.6
2	2	18	3.5	2.7
			.	.
4	2	- 18	3.9	3.4
4	2	- 17	- 2.7	3.4
4	2	- 16	2.1	2.6
4	2	- 15	- 0.2	<1.3
4	2	- 14	- 14.7	13.3
4	2	- 13	3.3	2.6
4	2	- 12	- 8.5	9.2
4	2	- 11	19.1	17.4
4	2	- 10	10.3	9.4
4	2	- 9	21.8	21.8
4	2	- 8	0.8	2.3
4	2	- 7	- 3.3	7.4
4	2	- 6	- 7.8	8.8
4	2	- 5	10.6	11.2
4	2	- 4	- 9.7	10.5
4	2	- 3	10.7	12.4
4	2	- 2	- 16.2	16.9
4	2	- 1	0.8	<1.3
4	2	0	- 18.4	17.9
4	2	1	12.9	12.7
4	2	2	- 4.4	4.9
4	2	3	8.7	9.4
4	2	4	11.1	10.3
4	2	5	13.7	14.0
4	2	6	- 5.1	5.0
4	2	7	9.1	8.3
4	2	8	- 4.4	4.9
4	2	9	16.3	14.4
4	2	10	- 4.6	4.9
4	2	11	6.4	7.0
4	2	12	- 9.2	9.3
4	2	13	- 14.0	14.4
4	2	14	1.5	<1.2
4	2	15	- 2.7	3.2
4	2	16	3.4	3.0
4	2	17	6.1	5.6
			.	.
6	2	- 18	- 4.0	3.4
6	2	- 17	0.7	<1.2
6	2	- 16	- 4.5	5.4
6	2	- 15	6.6	7.4
6	2	- 14	- 1.5	<1.3
6	2	- 13	7.1	5.4
6	2	- 12	- 8.1	7.7
6	2	- 11	2.1	<1.2
6	2	- 10	- 7.9	9.0
6	2	- 9	4.5	4.7
6	2	- 8	2.7	2.6

h	k	l	F(calc)	F(meas)
6	2	- 7	- 4,9	7,1
6	2	- 6	- 5,5	4,8
6	2	- 5	- 2,9	3,4
6	2	- 4	- 20,4	21,4
6	2	- 3	0,2	2,7
6	2	- 2	- 19,6	19,4
6	2	- 1	- 10,1	11,4
6	2	0	- 15,0	13,6
6	2	1	0,7	< 1,2
6	2	2	- 23,7	21,5
6	2	3	5,7	7,3
6	2	4	7,4	6,7
6	2	5	19,0	15,7
6	2	6	6,7	8,2
6	2	7	6,2	8,6
6	2	8	- 23,1	21,2
6	2	9	- 28,1	24,5
6	2	10	- 15,6	13,9
6	2	11	- 9,6	9,9
6	2	12	2,1	< 1,2
6	2	13	4,7	5,5
6	2	14	1,7	2,3
6	2	15	0,2	< 0,7
6	2	16	- 2,4	2,2
			.	.
8	2	- 18	0,8	< 0,7
8	2	- 17	- 0,0	< 1,3
8	2	- 16	- 2,1	2,3
8	2	- 15	1,4	< 1,2
8	2	- 14	- 3,7	2,7
8	2	13	1,0	< 1,2
8	2	- 12	- 2,2	< 1,3
8	2	- 11	- 6,2	5,6
8	2	- 10	- 0,9	< 1,3
8	2	- 9	- 2,7	3,1
8	2	- 8	1,6	2,4
8	2	- 7	- 13,4	12,1
8	2	- 6	10,2	10,0
8	2	- 5	- 21,7	23,4
8	2	- 4	- 8,2	11,2
8	2	- 3	- 6,0	4,6
8	2	- 2	- 48,2	49,3
8	2	- 1	- 3,4	< 1,3
8	2	0	0,5	3,0
8	2	1	6,6	8,4
8	2	2	35,5	28,1
8	2	3	0,1	< 1,2
8	2	4	- 4,3	5,7
8	2	5	- 25,1	21,6
8	2	6	- 19,7	17,5
8	2	7	- 12,6	12,3
8	2	8	- 6,8	6,6
8	2	9	- 6,0	7,7
8	2	10	0,3	2,5
8	2	11	- 6,0	5,4
8	2	12	5,1	2,1
8	2	13	- 0,4	2,3
8	2	14	- 0,3	< 1,0
8	2	15	- 0,7	< 0,7
8	2	16	- 0,3	< 1,3
10	2	- 18	2,1	2,2
10	2	- 17	- 1,5	6,8
10	2	- 16	1,2	< 1,2
10	2	- 15	0,2	2,3
10	2	- 14	- 3,1	3,4
10	2	- 13	5,0	5,7
10	2	- 12	- 1,9	2,6
10	2	- 11	- 13,9	13,2
10	2	- 10	16,8	16,6
10	2	- 9	- 27,9	26,6
10	2	- 8	18,4	16,7
10	2	- 7	- 2,7	< 1,3
10	2	- 6	- 16,1	14,9
10	2	- 5	3,9	4,1
10	2	- 4	- 11,3	11,2
10	2	- 3	5,9	5,0
10	2	- 2	17,5	18,3
10	2	- 1	- 4,7	3,4
10	2	0	12,5	10,7
10	2	1	- 15,1	13,9
10	2	2	8,3	8,6
10	2	3	- 3,6	3,2
10	2	4	5,6	4,8
10	2	5	- 11,5	10,3
10	2	6	- 2,0	< 1,3
10	2	7	- 8,6	9,4
10	2	8	- 1,9	< 1,3
10	2	9	- 2,3	< 1,2
10	2	10	4,2	5,1
10	2	11	- 2,3	2,6
10	2	12	3,5	3,5
10	2	13	1,0	2,4
10	2	14	- 1,6	< 1,0
			.	.
12	2	- 18	1,5	< 1,1
12	2	- 17	6,0	5,1
12	2	- 16	- 3,3	3,3
12	2	- 15	- 4,2	4,9
12	2	- 14	1,0	< 1,2
12	2	- 13	- 15,0	14,7
12	2	- 12	11,3	9,9
12	2	- 11	- 2,5	< 1,3
12	2	- 10	6,7	5,6
12	2	- 9	4,0	3,6
12	2	- 8	4,5	3,9
12	2	- 7	5,6	5,4
12	2	- 6	2,2	3,3
12	2	- 5	2,9	4,6
12	2	- 4	- 2,8	2,7
12	2	- 3	0,8	< 1,2
12	2	- 2	10,4	9,9
12	2	- 1	3,8	3,2
12	2	0	16,2	15,1
12	2	1	- 6,2	6,2
12	2	2	10,1	9,2
12	2	3	1,0	< 1,2
12	2	4	0,9	< 1,2
12	2	5	- 2,9	2,7
12	2	6	6,2	6,8
12	2	7	- 6,8	7,8
12	2	8	4,2	3,3
12	2	9	7,7	7,4
12	2	10	- 3,5	4,0
12	2	11	6,7	6,9
12	2	12	4,7	5,4
12	2	13	2,9	3,6
			.	.
14	2	- 17	- 3,7	< 1,0
14	2	- 16	0,1	< 1,0
14	2	- 15	0,6	< 1,0
14	2	- 14	1,8	2,1
14	2	- 13	1,6	< 1,2
14	2	- 12	4,1	3,1
14	2	- 11	2,2	2,6
14	2	- 10	3,3	3,2
14	2	- 9	5,0	4,4
14	2	- 8	- 2,0	2,3
14	2	- 7	9,2	7,3
14	2	- 6	- 1,3	< 1,3
14	2	- 5	6,8	8,6
14	2	- 4	- 0,0	< 1,3
14	2	- 3	2,6	< 1,2
14	2	- 2	3,3	3,4
14	2	- 1	9,6	9,7
14	2	0	5,1	7,4
14	2	1	- 5,5	6,2
14	2	2	12,0	11,1
14	2	3	- 9,0	9,9
14	2	4	3,5	3,1
14	2	5	15,9	13,1
14	2	6	- 11,6	12,0
14	2	7	10,6	10,0
14	2	8	- 0,4	< 1,3
14	2	9	2,5	2,7
14	2	10	8,6	8,5
14	2	11	1,4	< 1,0
14	2	12	1,5	< 1,0
			.	.
16	2	- 16	- 1,6	< 1,0
16	2	- 15	1,0	< 1,0
16	2	- 14	- 1,6	< 1,3
16	2	- 13	2,3	2,0
16	2	- 12	0,4	< 1,2
16	2	- 11	3,0	3,1
16	2	- 10	- 0,3	< 1,3
16	2	- 9	3,6	4,1
16	2	- 8	- 4,2	3,4
16	2	- 7	8,3	6,7
16	2	- 6	- 5,4	5,6
16	2	- 5	13,5	11,9
16	2	- 4	- 0,7	7,4
16	2	- 3	- 10,3	9,7
16	2	- 2	3,0	1,8
16	2	- 1	- 11,7	10,8
16	2	0	9,1	8,9
16	2	1	16,0	13,6
16	2	2	- 7,5	8,0
16	2	3	11,0	9,3
16	2	4	- 8,6	7,7
16	2	5	1,2	< 1,2
16	2	6	- 2,2	< 1,0
16	2	7	0,6	< 1,0
16	2	8	- 7,2	< 1,0
16	2	9	0,7	< 1,0
16	2	10	1,2	< 1,0
16	2	11	1,1	< 1,0
			.	.
18	2	- 15	0,9	< 1,0
18	2	- 14	- 2,3	1,8
18	2	- 13	0,2	< 0,7
18	2	- 12	0,1	< 0,7
18	2	- 11	4,1	3,3
18	2	- 10	2,6	3,7
18	2	- 9	8,6	8,3
18	2	- 8	- 8,3	7,7
18	2	- 7	- 8,7	8,7
18	2	- 6	- 11,8	10,8
18	2	- 5	- 11,0	10,4
18	2	- 4	1,7	2,2
18	2	- 3	5,8	5,6
18	2	- 2	3,7	4,2
18	2	- 1	3,6	2,7
18	2	0	- 1,8	2,5
18	2	1	1,5	< 0,7
18	2	2	- 7,9	7,3
18	2	3	0,5	< 1,2
18	2	4	- 6,3	5,9
18	2	5	- 1,0	< 1,3
18	2	6	- 0,6	< 1,0
18	2	7	- 1,0	< 1,0
18	2	8	0,0	< 1,0
18	2	9	- 1,7	< 1,0
			.	.
20	2	- 13	0,9	< 1,0
20	2	- 12	1,4	< 1,0
20	2	- 11	- 5,9	4,1
20	2	- 10	- 5,9	6,0
20	2	- 9	- 5,3	4,7
20	2	- 8	- 3,1	2,7
20	2	- 7	0,3	< 0,7
20	2	- 6	0,9	< 0,7
20	2	- 5	- 3,2	2,7
20	2	- 4	2,4	< 1,2
20	2	- 3	- 0,9	2,2
20	2	- 2	- 0,3	< 0,7
20	2	- 1	0,0	< 0,7
20	2	0	- 1,1	< 0,7
20	2	1	- 1,1	< 0,7
20	2	2	- 2,5	2,2
20	2	3	- 1,8	2,1
20	2	4	- 2,3	2,7
20	2	5	- 2,5	2,4
20	2	6	0,7	< 1,0
			.	.
22	2	- 10	0,5	< 1,0
22	2	- 9	- 2,5	< 2,0
22	2	- 8	- 0,5	< 1,0
22	2	- 7	- 0,4	< 1,0
22	2	- 6	0,9	< 1,0
22	2	- 4	3,9	3,7

h	k	l	F(calc)	F(meas)
22	2	-3	-0.5	<1.0
22	2	-2	1.1	<1.0
22	2	-1	0.1	<1.0
22	2	0	-0.2	<1.0
22	2	1	-0.5	<1.0
22	2	2	2.0	<1.0
22	2	3	-0.5	<1.0
			.	.
			.	.
1	3	-16	0.5	<1.0
1	3	-15	-0.8	<1.3
1	3	-14	0.5	<1.3
1	3	-13	-1.3	<1.3
1	3	-12	1.1	<1.3
1	3	-11	-2.6	7.7
1	3	-10	2.6	<1.3
1	3	-9	0.4	2.3
1	3	-8	-3.0	2.8
1	3	-7	10.1	9.3
1	3	-6	14.2	15.6
1	3	-5	22.5	24.1
1	3	-4	0.3	9.4
1	3	-3	-3.9	2.6
1	3	-2	-23.4	25.0
1	3	-1	-5.3	7.1
1	3	1	8.6	6.6
1	3	2	13.8	13.9
1	3	3	10.1	10.5
1	3	4	6.1	4.8
1	3	5	1.4	2.4
1	3	6	6.8	5.3
1	3	7	0.7	<1.3
1	3	8	-0.7	<1.3
1	3	9	3.1	3.9
1	3	10	3.0	<1.3
1	3	11	6.5	6.0
1	3	12	3.5	<1.3
1	3	13	4.2	3.8
1	3	14	1.9	<1.3
1	3	15	1.8	<1.0
1	3	16	-0.3	<1.0
			.	.
3	3	-16	0.3	<1.0
3	3	-15	-3.9	4.2
3	3	-14	2.5	2.5
3	3	-13	-5.1	5.6
3	3	-12	-4.8	4.9
3	3	-11	10.9	8.9
3	3	-10	3.7	4.7
3	3	-9	23.5	27.9
3	3	-8	5.5	5.2
3	3	-7	5.0	4.4
3	3	-6	-14.9	21.0
3	3	-5	-7.3	9.9
3	3	-4	-3.8	5.8
3	3	-3	5.0	4.8
3	3	-2	0.1	<1.3
3	3	-1	11.3	12.0
3	3	0	1.2	<1.7
3	3	1	8.3	9.3

h	k	l	F(calc)	F(meas)
3	3	2	5.7	5.8
3	3	3	10.7	9.6
3	3	4	-0.8	<1.0
3	3	5	6.6	8.1
3	3	6	5.2	4.4
3	3	7	3.2	3.2
3	3	8	0.2	<1.3
3	3	9	6.5	5.1
3	3	10	2.7	<1.3
3	3	11	6.1	5.5
3	3	12	-0.2	<1.3
3	3	13	3.1	3.6
3	3	14	-3.4	3.5
3	3	15	0.4	<1.0
			.	.
5	3	-16	-1.1	<1.0
5	3	-15	2.2	2.0
5	3	-14	1.2	<1.3
5	3	-13	11.2	9.6
5	3	-12	0.7	<1.3
5	3	-11	4.7	4.6
5	3	-10	-9.2	7.7
5	3	-9	1.5	<1.3
5	3	-8	-4.7	4.7
5	3	-7	5.9	5.6
5	3	-6	-3.5	2.0
5	3	-5	-2.6	2.5
5	3	-4	-0.7	<1.3
5	3	-3	-1.2	3.6
5	3	-2	-3.1	3.5
5	3	-1	5.5	7.5
5	3	0	-4.3	1.8
5	3	1	5.4	6.0
5	3	2	6.6	6.9
5	3	3	2.8	1.9
5	3	4	-4.5	4.7
5	3	5	9.8	8.5
5	3	6	0.5	<1.3
5	3	7	5.6	6.2
5	3	8	-2.6	<1.3
5	3	9	-5.6	5.7
5	3	10	-11.7	11.7
5	3	11	-3.8	4.4
5	3	12	2.8	<1.3
5	3	13	2.3	<1.3
5	3	14	4.6	5.1
5	3	15	0.7	<1.0
			.	.
7	3	-16	1.5	<1.0
7	3	-15	-0.8	<1.3
7	3	-14	-1.9	<1.3
7	3	-13	0.2	<1.3
7	3	-12	-2.2	2.0
7	3	-11	3.5	3.8
7	3	-10	-3.8	8.5
7	3	-9	-2.7	3.0
7	3	-8	-0.8	<1.3
7	3	-7	-3.2	3.7
7	3	-6	-4.0	4.4
7	3	-5	-6.0	6.6

h	k	l	F(calc)	F(meas)
7	3	-4	0.4	3.3
7	3	-3	-14.7	14.8
7	3	-2	6.9	6.7
7	3	-1	-8.1	9.3
7	3	0	-8.8	8.4
7	3	1	18.9	20.2
7	3	2	1.5	2.0
7	3	3	10.8	11.3
7	3	4	1.8	2.5
7	3	5	-14.4	15.2
7	3	6	-17.8	14.4
7	3	7	-16.6	15.2
7	3	8	-3.1	3.1
7	3	9	1.9	2.3
7	3	10	3.8	4.6
7	3	11	1.8	2.4
7	3	12	0.6	<1.0
7	3	13	-3.1	2.2
7	3	14	-1.8	<1.0
			.	.
9	3	-16	1.6	<1.0
9	3	-15	-2.1	6.4
9	3	-14	0.9	<1.0
9	3	-13	-2.6	2.0
9	3	-12	-0.8	2.2
9	3	-11	2.6	3.0
9	3	-10	-6.4	6.0
9	3	-9	-0.3	<1.3
9	3	-8	4.6	4.6
9	3	-7	-19.3	18.1
9	3	-6	14.2	11.3
9	3	-5	-22.2	19.3
9	3	-4	-4.9	4.8
9	3	-3	0.4	9.4
9	3	-2	2.1	2.0
9	3	-1	27.3	27.9
9	3	0	4.1	6.0
9	3	1	-10.8	9.7
9	3	2	-9.6	11.1
9	3	3	-14.8	15.5
9	3	4	-2.4	3.9
9	3	5	-5.2	5.7
9	3	6	-0.5	<1.3
9	3	7	-4.2	1.1
9	3	8	0.9	<1.3
9	3	9	-3.2	3.5
9	3	10	0.8	<1.3
9	3	11	-0.7	<1.0
9	3	12	-0.2	<1.0
9	3	13	-2.3	<1.0
			.	.
11	3	-14	-5.4	<1.0
11	3	-13	1.7	<1.0
11	3	-12	-0.9	<1.0
11	3	-11	-6.3	5.4
11	3	-10	10.7	8.8
11	3	-9	-12.0	9.5
11	3	-8	2.9	3.8
11	3	-7	-1.0	<1.3
11	3	-6	4.4	4.2

h	k	l	F(calc)	F(meas)
11	3	-5	6.6	6.2
11	3	-4	2.3	3.7
11	3	-3	-0.5	<1.3
11	3	-2	-4.7	4.5
11	3	-1	-0.7	<1.3
11	3	0	2.3	<1.3
11	3	1	-1.1	2.9
11	3	2	0.8	<1.3
11	3	3	-7.7	7.1
11	3	4	1.2	<1.3
11	3	5	-4.3	4.6
11	3	6	0.0	<1.3
11	3	7	1.2	<1.3
11	3	8	2.7	2.3
11	3	9	-2.5	<1.0
11	3	10	5.0	4.3
11	3	11	-0.6	<1.0
11	3	12	-1.5	<1.0
			.	.
13	3	-15	-0.3	<1.0
13	3	-14	2.3	<1.0
13	3	-13	0.0	<1.0
13	3	-12	1.5	<1.0
13	3	-11	5.4	4.7
13	3	-10	3.5	<1.3
13	3	-9	0.9	2.8
13	3	-8	1.4	<1.3
13	3	-7	-0.5	<1.3
13	3	-6	-1.7	<1.3
13	3	-5	5.7	5.1
13	3	-4	0.6	<1.3
13	3	-3	5.5	5.2
13	3	-2	-0.9	<1.3
13	3	-1	1.1	<1.3
13	3	0	1.1	2.4
13	3	1	2.3	<1.3
13	3	2	-2.8	<1.3
13	3	3	0.3	<1.0
13	3	4	3.5	3.8
13	3	5	-5.0	5.1
13	3	6	8.8	8.1
13	3	7	0.8	<1.3
13	3	8	-2.2	<1.3
13	3	9	9.9	6.7
			.	.
15	3	-14	-0.2	<1.0
15	3	-13	2.5	<1.0
15	3	-12	-1.1	<1.0
15	3	-11	2.8	<1.0
15	3	-10	-0.2	<1.3
15	3	-9	2.6	2.4
15	3	-8	0.1	<1.3
15	3	-7	2.5	<1.3
15	3	-6	-1.9	<1.3
15	3	-5	4.1	2.5
15	3	-4	-1.5	<1.3
15	3	-3	7.3	5.8
15	3	-2	-7.4	6.3
15	3	-1	2.8	2.4
15	3	0	1.9	<1.3

h	k	l	F(calc)	F(meas)
15	3	1	- 4.1	4.2
15	3	2	10.7	8.2
15	3	3	- 0.9	0.8
15	3	4	- 3.2	<1.9
15	3	5	7.4	7.4
15	3	6	- 1.7	<1.0
15	3	7	7.1	6.5
15	3	8	1.3	<1.0
15	3	9	0.7	<1.0
			.	.
17	3	- 11	1.0	<1.0
17	3	- 10	- 0.3	<1.3
17	3	- 9	2.6	3.0
17	3	- 8	0.3	<1.3
17	3	- 7	0.7	<1.3
17	3	- 5	- 0.9	<1.3
17	3	- 3	1.9	<1.3

h	k	l	F(calc)	F(meas)
17	3	- 1	1.4	<1.3
17	3	1	- 0.0	<1.0
17	3	2	- 1.8	<1.0
17	3	3	1.0	<1.0
17	3	4	- 2.1	<1.0
17	3	5	2.0	<1.0
17	3	6	- 1.9	<1.0
			.	.
19	3	- 4	0.7	<1.0
19	3	- 2	1.0	<1.0
19	3	0	- 1.3	<1.0
19	3	1	- 1.0	<1.0
19	3	2	- 2.0	<1.0
19	3	3	0.0	<1.0
19	3	4	- 0.2	<1.0
			.	.

h	k	l	F(calc)	F(meas)
21	3	- 5	- 0.5	<1.0
21	3	- 4	- 0.2	<1.0
21	3	- 3	- 0.9	<1.0
21	3	- 2	0.7	<1.0
			.	.
			.	.
0	4	2	- 1.2	<0.8
			.	.
2	4	- 2	2.8	<0.7
2	4	- 1	4.8	<0.7
2	4	0	1.6	<0.7
2	4	1	3.8	<0.7
2	4	2	0.6	<0.7
			.	.
4	4	- 2	1.5	<0.7
4	4	- 1	1.5	<0.7

h	k	l	F(calc)	F(meas)
4	4	0	2.1	<0.7
4	4	1	2.3	<0.7
4	4	2	- 1.0	0.0
			.	.
6	4	- 2	- 0.9	<0.8
6	4	- 1	- 0.2	<0.8
6	4	2	5.1	<0.7
			.	.
8	4	- 1	4.8	<0.7
8	4	0	0.8	<0.7
			.	.
1	5	0	- 1.1	<0.8
			.	.
3	5	0	0.2	<0.7
			.	.
5	5	0	- 0.8	<0.8

Appendix 1b

Structure Factors for Crotonic Acid

h	k	l	F(calc)	F(meas)
0	0	2	63.3	61.4
0	0	4	- 71.8	79.5
0	0	6	7.1	7.1
0	0	8	28.8	27.7
0	0	10	28.0	28.4
0	0	12	6.1	10.2
0	0	14	7.8	6.1
0	0	16	9.9	8.1
0	0	18	- 1.8	<2.6
2	0	- 20	4.1	<1.7
2	0	- 18	3.7	<2.8
2	0	- 16	0.0	<3.3
2	0	- 14	4.6	4.6
2	0	- 12	16.8	16.7
2	0	- 10	20.5	22.9
2	0	- 8	- 31.1	30.1
2	0	- 6	- 34.1	29.8
2	0	- 4	184.6	195.5
2	0	- 2	55.0	65.0
2	0	0	- 8.2	11.6
2	0	2	- 2.2	<1.4
2	0	4	- 48.1	50.1
2	0	6	- 14.5	12.7
2	0	8	- 5.3	4.9
2	0	10	15.1	14.7
2	0	12	15.9	14.3
2	0	14	- 12.5	11.4
2	0	16	- 11.5	11.7
2	0	18	2.1	<2.2
4	0	- 20	1.7	<3.4
4	0	- 18	- 1.9	<2.9
4	0	- 16	- 6.8	7.8
4	0	- 14	- 2.1	<3.4
4	0	- 12	- 9.4	11.0
4	0	- 10	- 19.3	16.1
4	0	- 8	- 9.2	12.8
4	0	- 6	- 51.3	54.7
4	0	- 4	- 27.4	29.5
4	0	- 2	4.2	5.5
4	0	0	- 61.2	60.0
4	0	2	- 61.8	57.8
4	0	4	- 93.0	86.3
4	0	6	- 10.8	9.1
4	0	8	34.9	33.2
4	0	10	- 12.2	12.3
4	0	12	- 23.2	24.4
4	0	14	- 6.8	6.1
4	0	16	- 1.0	<2.7
6	0	- 20	- 5.3	<3.7
6	0	- 18	- 8.1	5.6
6	0	- 16	- 6.4	7.2
6	0	- 14	- 2.4	<3.4
6	0	- 12	1.2	<3.2
6	0	- 10	- 20.7	19.6
6	0	- 8	- 20.6	19.9
6	0	- 6	- 20.5	22.2
6	0	- 4	- 30.0	37.1
6	0	- 2	11.2	11.7
6	0	0	- 54.7	62.4
6	0	2	- 37.1	38.9
6	0	4	30.5	29.9
6	0	6	5.8	<3.7
6	0	8	- 1.7	<3.1
6	0	10	- 4.8	4.9
6	0	12	- 9.3	6.5
6	0	14	0.4	<3.0
6	0	16	1.5	<2.1
8	0	- 20	0.5	<1.9
8	0	- 18	0.4	<2.8
8	0	- 16	- 1.3	<4.5
8	0	- 14	5.6	6.3
8	0	- 12	22.2	20.7
8	0	- 10	1.1	<3.0
8	0	- 8	- 35.0	31.9
8	0	- 6	19.6	17.8
8	0	- 4	43.6	42.9
8	0	- 2	27.2	25.2
8	0	0	15.9	17.4
8	0	2	0.3	<2.7
8	0	4	27.9	28.2
8	0	6	18.2	17.4
8	0	8	- 5.4	<3.4
8	0	10	3.2	4.9
8	0	12	2.2	<3.1
8	0	14	3.3	<2.4
10	0	- 18	0.8	<2.6
10	0	- 16	20.4	18.6
10	0	- 14	16.9	13.6
10	0	- 12	- 11.9	10.4
10	0	- 10	- 3.6	5.7
10	0	- 8	16.3	17.2
10	0	- 6	32.5	28.2
10	0	- 4	27.3	25.1
10	0	- 2	4.8	4.7
10	0	0	20.6	20.1
10	0	2	3.0	<3.1
10	0	4	- 7.1	6.3
10	0	6	14.0	11.5
10	0	8	2.9	<3.4
10	0	10	- 2.0	<3.1
10	0	12	3.9	<2.5
12	0	- 18	6.1	<2.5
12	0	- 16	- 3.4	<2.9
12	0	- 14	- 3.7	<3.3
12	0	- 12	- 3.3	<3.4
12	0	- 10	- 4.3	5.3
12	0	- 8	- 0.6	4.5
12	0	- 6	6.1	7.8
12	0	- 4	20.3	19.2
12	0	0	- 39.2	35.6
12	0	2	1.3	<3.4
12	0	4	6.5	7.8
12	0	6	- 1.6	<3.3
12	0	8	- 1.3	<3.0
12	0	10	- 4.1	<2.4
14	0	- 16	- 0.7	<2.5
14	0	- 14	- 6.6	4.7
14	0	- 12	- 15.0	10.3
14	0	- 10	- 8.0	6.2
14	0	- 8	14.6	13.2
14	0	- 6	- 1.7	<3.5
14	0	- 4	- 29.3	27.0
14	0	- 2	- 15.8	15.0
14	0	0	- 5.3	<3.4
14	0	2	2.5	<3.3
14	0	4	3.6	8.5
14	0	6	- 4.7	<2.8
14	0	8	- 0.2	<2.2
16	0	- 14	- 4.3	<2.4
16	0	- 12	3.0	<2.8
16	0	- 10	3.0	<3.0
16	0	- 8	- 2.0	<3.2
16	0	- 6	- 1.8	<3.2
16	0	- 4	- 8.3	5.4
16	0	- 2	- 1.9	<3.2
16	0	0	6.9	4.3
16	0	2	4.2	3.9
16	0	4	6.6	6.1
18	0	- 12	2.6	<1.9
18	0	- 10	5.9	<2.3
18	0	- 8	1.2	<2.4
18	0	- 6	0.8	<2.5
18	0	- 4	2.4	<2.5
18	0	- 2	2.6	<2.3
18	0	0	10.6	8.1
1	1	- 19	1.7	<1.3
1	1	- 18	6.4	<1.7
1	1	- 17	- 1.5	<1.9
1	1	- 16	4.9	3.7
1	1	- 15	- 2.9	<2.3
1	1	- 14	2.2	<2.3
1	1	- 13	3.8	<2.3
1	1	- 12	8.1	9.7
1	1	- 11	1.8	2.1
1	1	- 10	14.8	19.5
1	1	- 9	- 12.5	16.3
1	1	- 8	12.5	15.5
1	1	- 7	- 34.3	33.2
1	1	- 6	- 17.8	17.5
1	1	- 5	39.7	38.4
1	1	- 4	36.7	28.3
1	1	- 3	119.8	124.5
1	1	- 2	137.0	164.0
1	1	- 1	- 25.2	21.2
1	1	0	43.4	35.3
1	1	1	- 64.5	47.2
1	1	2	- 17.2	27.7
1	1	3	6.9	7.1
1	1	4	6.6	6.8
1	1	5	15.8	15.4
1	1	6	16.4	11.6
1	1	7	30.5	27.5
1	1	8	12.2	13.5
1	1	9	12.5	13.0
1	1	10	1.5	<2.8
1	1	11	7.6	4.8
1	1	12	7.6	7.5
1	1	13	1.6	<2.3
1	1	14	10.1	8.9
1	1	15	- 6.1	4.7
1	1	16	- 1.3	<2.0
1	1	17	2.1	<1.8
1	1	18	- 3.5	<1.5
3	1	- 19	- 1.1	<1.5
3	1	- 18	1.4	<1.8
3	1	- 17	- 0.8	<2.1
3	1	- 16	0.9	<2.2
3	1	- 15	6.0	4.8
3	1	- 14	- 8.9	<2.3
3	1	- 13	10.0	7.7
3	1	- 12	- 3.5	<2.2
3	1	- 11	- 9.6	9.3
3	1	- 10	- 14.3	14.7
3	1	- 9	- 4.3	2.9
3	1	- 8	- 4.3	5.8
3	1	- 7	39.9	37.2
3	1	- 6	26.0	24.4
3	1	- 5	31.4	29.6
3	1	- 4	- 20.0	21.3
3	1	- 3	21.1	18.4
3	1	- 2	- 21.3	22.9
3	1	- 1	- 0.7	<2.4
3	1	0	- 6.6	5.3
3	1	1	- 27.0	25.0
3	1	2	- 36.1	34.7
3	1	3	10.0	9.9
3	1	4	- 28.0	25.0
3	1	5	16.9	16.1
3	1	6	- 24.5	26.7
3	1	7	30.3	30.4
3	1	8	0.8	<1.9
3	1	9	10.5	10.3
3	1	10	10.0	10.4
3	1	11	- 19.9	19.2
3	1	12	- 10.9	11.3
3	1	13	- 6.3	7.9
3	1	14	- 11.8	11.8
3	1	15	5.6	4.5
3	1	16	- 0.9	<1.8
3	1	17	2.0	<1.5
5	1	- 19	- 1.2	<1.6
5	1	- 18	- 4.1	3.9
5	1	- 17	4.9	3.0
5	1	- 16	- 9.9	7.5
5	1	- 15	3.0	3.7
5	1	- 14	- 11.9	10.0
5	1	- 13	1.6	3.0

h	k	l	F(calc)	F(meas)
5	1	-12	-5,3	5,0
5	1	-11	0,0	<2,1
5	1	-10	-1,7	<1,9
5	1	-9	-7,5	5,9
5	1	-8	-20,0	20,0
5	1	-7	6,9	11,2
5	1	-6	-23,6	23,4
5	1	-5	18,6	16,3
5	1	-4	-18,7	17,7
5	1	-3	-0,6	<2,3
5	1	-2	-41,6	44,1
5	1	-1	-10,7	6,0
5	1	0	-40,7	41,9
5	1	1	-46,7	47,3
5	1	2	-47,4	49,0
5	1	3	11,3	14,3
5	1	4	-0,0	9,0
5	1	5	30,7	30,2
5	1	6	15,6	16,9
5	1	7	-16,3	16,9
5	1	8	-9,3	10,2
5	1	9	-17,6	18,1
5	1	10	-15,6	14,3
5	1	11	-5,6	<3,1
5	1	12	-4,9	<3,6
5	1	13	0,0	<2,2
5	1	14	-2,0	<2,0
5	1	15	0,1	<1,0
5	1	16	-0,6	<1,5
			.	.
7	1	-19	0,7	<1,5
7	1	-18	-0,4	<1,8
7	1	-17	0,0	<1,0
7	1	-16	-0,4	<2,0
7	1	-15	1,3	<2,3
7	1	-14	-1,7	<2,3
7	1	-13	-4,0	<2,3
7	1	-12	-1,7	<2,2
7	1	-11	-9,1	4,0
7	1	-10	9,0	9,1
7	1	-9	-17,3	16,3
7	1	-8	-1,6	<3,0
7	1	-7	-0,0	3,0
7	1	-6	-23,3	20,2
7	1	-5	21,3	21,2
7	1	-4	-3,3	6,1
7	1	-3	-20,1	24,0
7	1	-2	-1,0	2,0
7	1	-1	-33,0	30,9
7	1	0	10,0	10,1
7	1	1	4,4	5,6
7	1	2	20,1	23,5
7	1	3	-1,3	0,0
7	1	4	0,0	<1,9
7	1	5	0,4	<2,0
7	1	6	5,0	6,7
7	1	7	-11,0	9,1
7	1	8	0,3	4,3
7	1	9	-10,3	6,7
7	1	10	-3,0	3,1
7	1	11	2,6	<2,2
7	1	12	1,1	<2,1
7	1	13	1,0	<3,2
7	1	14	3,1	<1,7
7	1	15	1,4	<1,4
			.	.
9	1	-19	-2,3	<1,4
9	1	-18	-1,9	<1,7
9	1	-17	0,7	3,6
9	1	-16	1,0	<2,1
9	1	-15	3,6	<2,2
9	1	-14	10,2	13,7
9	1	-13	-13,2	14,1
9	1	-12	14,0	12,9
9	1	-11	-21,1	20,1
9	1	-10	-7,1	9,1
9	1	-9	10,2	10,6
9	1	-8	2,7	<2,0
9	1	-7	14,3	17,2
9	1	-6	17,6	19,7
9	1	-5	-3,5	5,6
9	1	-4	27,9	29,6
9	1	-3	-10,3	10,5
9	1	-2	21,4	24,0
9	1	-1	-16,5	18,5
9	1	0	9,0	6,1
9	1	1	9,7	10,9
9	1	2	20,1	21,9
9	1	3	6,6	<2,1
9	1	4	11,9	10,0
9	1	5	-2,5	<2,2
9	1	6	-5,2	<2,3
9	1	7	5,7	7,6
9	1	8	3,0	<2,3
9	1	9	-2,9	5,5
9	1	10	4,3	<2,1
9	1	11	1,3	4,5
9	1	12	3,3	4,4
9	1	13	4,3	<1,5
			.	.
11	1	-18	7,3	<2,4
11	1	-17	0,0	3,3
11	1	-16	6,9	3,0
11	1	-15	-9,2	3,7
11	1	-14	-2,2	<2,2
11	1	-13	-2,1	<2,3
11	1	-12	-0,7	3,1
11	1	-11	5,0	4,0
11	1	-10	3,0	<2,3
11	1	-9	11,2	11,6
11	1	-8	5,7	4,6
11	1	-7	10,9	10,1
11	1	-6	0,4	7,3
11	1	-5	0,5	<2,1
11	1	-4	0,9	6,0
11	1	-3	2,1	<2,1
11	1	-2	16,0	19,5
11	1	-1	-0,0	6,0
11	1	0	-1,1	<2,2
11	1	1	0,0	<2,2
11	1	2	-16,3	15,0
11	1	3	21,9	24,0
11	1	4	0,4	<2,3
11	1	5	0,0	<2,3
11	1	6	2,7	4,2
11	1	7	-3,0	<2,2
11	1	8	0,1	<2,1
11	1	9	2,6	<1,9
11	1	10	2,1	<1,7
11	1	11	1,0	<1,5
11	1	12	-0,4	<1,1
			.	.
13	1	-18	-4,9	<1,1
13	1	-17	0,7	<1,3
13	1	-16	-2,6	<1,7
13	1	-15	1,3	<1,9
13	1	-14	-0,7	<2,0
13	1	-13	0,7	<2,1
13	1	-12	-4,9	3,0
13	1	-11	4,0	3,0
13	1	-10	-11,2	7,0
13	1	-9	11,6	10,4
13	1	-8	-4,7	3,3
13	1	-7	11,9	9,5
13	1	-6	9,4	10,5
13	1	-5	-12,5	13,2
13	1	-4	-7,9	8,0
13	1	-3	-14,0	13,3
13	1	-2	-20,6	20,0
13	1	-1	13,0	15,3
13	1	0	-9,0	7,6
13	1	1	10,4	11,0
13	1	2	-2,4	2,3
13	1	3	1,3	<2,2
13	1	4	-1,0	<2,2
13	1	5	-2,1	<2,1
13	1	6	-0,3	<2,0
13	1	7	-3,7	<1,8
13	1	8	-3,1	<1,6
13	1	9	1,1	<1,4
			.	.
15	1	-16	-2,6	<1,3
15	1	-15	-3,2	<1,3
15	1	-14	-3,3	3,4
15	1	-13	1,1	<1,9
15	1	-12	-3,7	<1,9
15	1	-11	9,0	7,3
15	1	-10	3,0	<2,1
15	1	-9	-0,7	<2,2
15	1	-8	-3,1	<2,2
15	1	-7	-12,0	11,0
15	1	-6	-9,9	11,0
15	1	-5	-4,9	7,2
15	1	-4	-0,0	<2,2
15	1	-3	-0,3	3,9
15	1	-2	-4,6	<2,2
15	1	-1	3,3	<2,0
15	1	0	-1,3	<2,1
15	1	1	0,0	<2,1
15	1	2	2,3	<2,0
15	1	3	-4,6	<1,9
15	1	4	-0,4	<1,8
15	1	5	-2,0	<1,6
15	1	6	1,9	4,3
			.	.
17	1	-12	-0,1	<1,5
17	1	-11	-1,5	<1,6
17	1	-10	-0,0	<1,7
17	1	-9	-3,0	<1,8
17	1	-8	2,9	<1,8
17	1	-7	-6,4	<1,8
17	1	-6	0,1	3,3
17	1	-5	-1,1	3,5
17	1	-4	1,2	<1,8
17	1	-3	2,5	<1,9
17	1	-2	3,7	<1,8
17	1	-1	1,0	<1,7
17	1	0	3,5	3,2
17	1	1	1,7	4,4
17	1	2	5,9	4,1
			.	.
19	1	-3	4,7	1,4
			.	.
			.	.
0	2	1	-50,0	45,2
0	2	2	16,1	13,6
0	2	3	-39,4	33,2
0	2	4	25,0	23,3
0	2	5	25,0	23,5
0	2	6	16,4	14,2
0	2	7	17,3	17,1
0	2	8	8,5	9,9
0	2	9	5,2	7,9
0	2	10	2,2	<3,0
0	2	11	2,6	<3,1
0	2	12	2,1	<3,2
0	2	13	9,2	5,0
0	2	14	4,0	4,6
0	2	15	5,7	4,9
0	2	16	6,4	4,5
0	2	17	-3,0	<3,1
0	2	18	3,5	<1,5
			.	.
2	2	-18	0,0	<1,9
2	2	-17	-2,5	<2,4
2	2	-16	2,5	<2,7
2	2	-15	-0,0	<3,0
2	2	-14	4,7	5,5
2	2	-13	4,9	<3,2
2	2	-12	-3,1	4,0
2	2	-11	5,2	4,0
2	2	-10	-13,9	12,0
2	2	-9	-8,9	10,3
2	2	-8	4,4	6,7
2	2	-7	23,5	24,4
2	2	-6	33,2	30,9
2	2	-5	33,0	36,6
2	2	-4	10,3	11,1
2	2	-3	0,3	<2,3
2	2	-2	-25,0	23,5

h	k	l	F(calc)	F(obs)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

h	k	l	F(calc)	F(obs)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

h	k	l	F(calc)	F(obs)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

h	k	l	F(calc)	F(obs)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

h	k	l	F(calc)	F(meas)
1	3	4	6.8	5.4
1	3	5	6.6	7.0
1	3	6	6.2	5.2
1	3	7	6.4	6.3
1	3	8	0.2	5.6
1	3	9	6.7	6.0
1	3	10	3.3	<1.1
1	3	11	10.5	9.1
1	3	12	2.5	6.6
1	3	13	7.8	4.9
1	3	14	1.4	<3.8
1	3	15	- 1.4	<6.6
			.	.
3	3	- 14	0.5	6.6
3	3	- 13	- 1.4	6.7
3	3	- 12	- 13.5	14.3
3	3	- 11	9.4	9.3
3	3	- 10	- 4.6	<0.9
3	3	- 9	25.8	27.8
3	3	- 8	10.3	10.4
3	3	- 7	16.7	17.1
3	3	- 6	- 5.5	8.3
3	3	- 5	- 8.6	9.4
3	3	- 4	- 11.7	9.7
3	3	- 3	1.7	<2.9
3	3	- 2	- 6.7	4.0
3	3	- 1	12.3	11.5
3	3	0	0.6	<0.9
3	3	1	6.9	6.4
3	3	2	7.4	6.5
3	3	3	13.1	9.3
3	3	4	- 4.5	4.6
3	3	5	10.7	10.3
3	3	6	1.9	<3.7
3	3	7	4.8	5.4
3	3	8	0.2	6.3
3	3	9	3.7	5.5
3	3	10	- 6.3	6.9
3	3	11	- 4.4	6.4
3	3	12	3.6	<0.7
3	3	13	- 0.2	<0.6
3	3	14	3.2	6.5
			.	.
5	3	- 16	- 4.1	<0.9
5	3	- 15	0.5	6.2
5	3	- 14	- 2.6	<1.0
5	3	- 13	11.6	10.9
5	3	- 12	3.0	5.1
5	3	- 11	9.3	8.8
5	3	- 10	- 4.8	4.9
5	3	- 9	- 3.7	<1.0
5	3	- 8	- 7.4	7.1
5	3	- 7	- 1.5	3.5
5	3	- 6	0.0	3.9
5	3	- 5	- 8.0	9.2
5	3	- 4	5.2	7.8
5	3	- 3	- 15.1	12.4
5	3	- 2	- 2.7	2.8
5	3	- 1	1.9	2.8
5	3	0	- 17.8	14.5
5	3	1	11.2	9.5
5	3	2	4.8	7.5
5	3	3	7.5	8.3
5	3	4	9.8	10.1
5	3	5	- 6.9	7.2
5	3	6	- 13.3	13.9
5	3	7	- 17.5	15.8
5	3	8	- 7.0	6.3
5	3	9	- 4.1	<0.3
5	3	10	1.8	<0.8
5	3	11	0.4	6.2
5	3	12	1.9	6.6
5	3	13	- 2.5	6.5
			.	.
7	3	- 16	6.0	3.9
7	3	- 15	- 3.1	6.5
7	3	- 14	1.9	<0.6
7	3	- 13	- 2.6	<0.8
7	3	- 12	- 4.3	5.8
7	3	- 11	2.3	6.4
7	3	- 10	- 1.1	6.5
7	3	- 9	- 10.9	12.2
7	3	- 8	13.6	14.3
7	3	- 7	- 26.5	25.6
7	3	- 6	10.7	12.0
7	3	- 5	- 13.5	13.6
7	3	- 4	- 13.2	15.5
7	3	- 3	3.7	5.5
7	3	- 2	- 0.2	<3.2
7	3	- 1	9.8	11.1
7	3	0	16.4	10.9
7	3	1	- 5.6	5.2
7	3	2	- 1.2	<3.2
7	3	3	- 19.9	15.4
7	3	4	- 6.8	5.2
7	3	5	- 8.2	6.8
7	3	6	- 4.2	5.2
7	3	7	- 5.5	6.2
7	3	8	3.5	6.0
7	3	9	- 4.8	5.4
7	3	10	3.2	<1.0
7	3	11	2.7	5.4
7	3	12	- 3.0	<2.1
			.	.
9	3	- 15	2.8	<1.0
9	3	- 14	- 3.8	<2.3
9	3	- 13	- 2.1	<0.6
9	3	- 12	1.8	6.7
9	3	- 11	- 12.0	14.5
9	3	- 10	10.8	14.1
9	3	- 9	- 9.6	8.0
9	3	- 8	1.2	<3.0
9	3	- 7	- 0.6	<3.3
9	3	- 6	0.5	<3.9
9	3	- 5	8.2	8.7
9	3	- 4	6.8	10.7
9	3	- 3	4.2	<3.2
9	3	- 2	- 0.3	<3.1
9	3	- 1	- 2.9	<3.1
9	3	0	- 0.2	<3.1
9	3	1	0.7	<3.2
9	3	2	- 2.0	<2.9
9	3	3	- 8.4	<3.8
9	3	4	4.0	6.2
9	3	5	- 7.7	<3.0
9	3	6	4.5	6.1
9	3	7	7.0	<3.3
9	3	8	- 3.5	5.2
9	3	9	7.6	<1.0
9	3	10	2.2	6.5
			.	.
11	3	- 14	- 2.2	<2.5
11	3	- 13	3.4	<0.6
11	3	- 12	- 1.1	6.7
11	3	- 11	4.0	6.5
11	3	- 10	1.1	<1.0
11	3	- 9	4.4	<1.6
11	3	- 8	1.9	6.2
11	3	- 7	4.9	<2.9
11	3	- 6	- 3.7	9.5
11	3	- 5	8.2	9.7
11	3	- 4	- 4.2	<3.5
11	3	- 3	11.3	7.8
11	3	- 2	- 4.7	<1.5
11	3	- 1	- 3.0	<3.3
11	3	0	3.9	<2.4
11	3	1	- 7.1	6.0
11	3	2	5.5	<3.8
11	3	3	6.3	<3.8
11	3	4	- 6.4	5.9
11	3	5	8.2	7.3
11	3	6	- 0.1	<1.1
11	3	7	6.0	6.3
			.	.
13	3	- 12	- 1.9	6.6
13	3	- 11	1.8	<1.1
13	3	- 10	0.6	<0.3
13	3	- 9	4.3	6.5
13	3	- 8	- 0.1	5.8
13	3	- 7	7.0	<2.3
13	2	- 6	- 6.1	<3.5
13	3	- 5	- 1.3	<3.9
13	3	- 4	- 4.5	<3.9
13	3	- 3	- 3.1	<3.7
13	3	- 2	5.0	<3.5
13	3	- 1	2.8	<3.5
13	3	0	- 1.7	<3.7
13	3	1	2.0	<3.9
13	3	2	- 1.5	<3.8
13	3	3	3.7	<3.3
13	3	4	- 0.2	<1.8
			.	.
15	3	- 7	- 2.8	<4.3
15	3	- 6	0.5	<2.8
15	3	- 5	1.0	<3.5
15	3	- 4	1.9	<3.8
15	3	- 3	- 2.3	<3.9
15	3	- 2	3.1	<3.9

APPENDIX II

SOME PROGRAMMES WRITTEN FOR THE DEUCE COMPUTER

APPENDIX II

Some Programmes Written for the Deuce Computer

Deuce is a binary digital electronic computer containing both fast access and slow access information stores. The fast stores consist of 21 mercury delay lines capable of holding 1, 2, 4 or 32 32-digit binary numbers, having an access time of 32 to 1024 microseconds. The slow store comprises a magnetic drum holding 8192 32-digit binary numbers, having access time of 13 to 48 milliseconds.

Input and output can be in the form of punched cards or punched tape.

Programmes may be written in basic machine language or may utilize a simplified coding scheme such as STAC or Alphacode. STAC (Storage Allocation and Coding) translates decimally punched instructions to basic machine language. The STAC control also includes instructions which facilitate the testing and development of a programme.

Programme I

This programme, using the STAC control system calculates the variance (V) of modified intensities (F_o^2) and also computes values for the N(z) test.

Input

The input, on punched cards, consists of:

1. The values of R_{ij} for the cell
2. The limits of the desired ranges of $\sin^2\theta$ into which the F_o^2 data should be divided - four ranges are allowed
3. The modified intensities
4. A "last card"

Output

1. The values of V for each range
2. The number of reflections included in each range
3. The values of N(z) for z = 0(.1)1.0 for each range

Time

Thirty reflections per minute

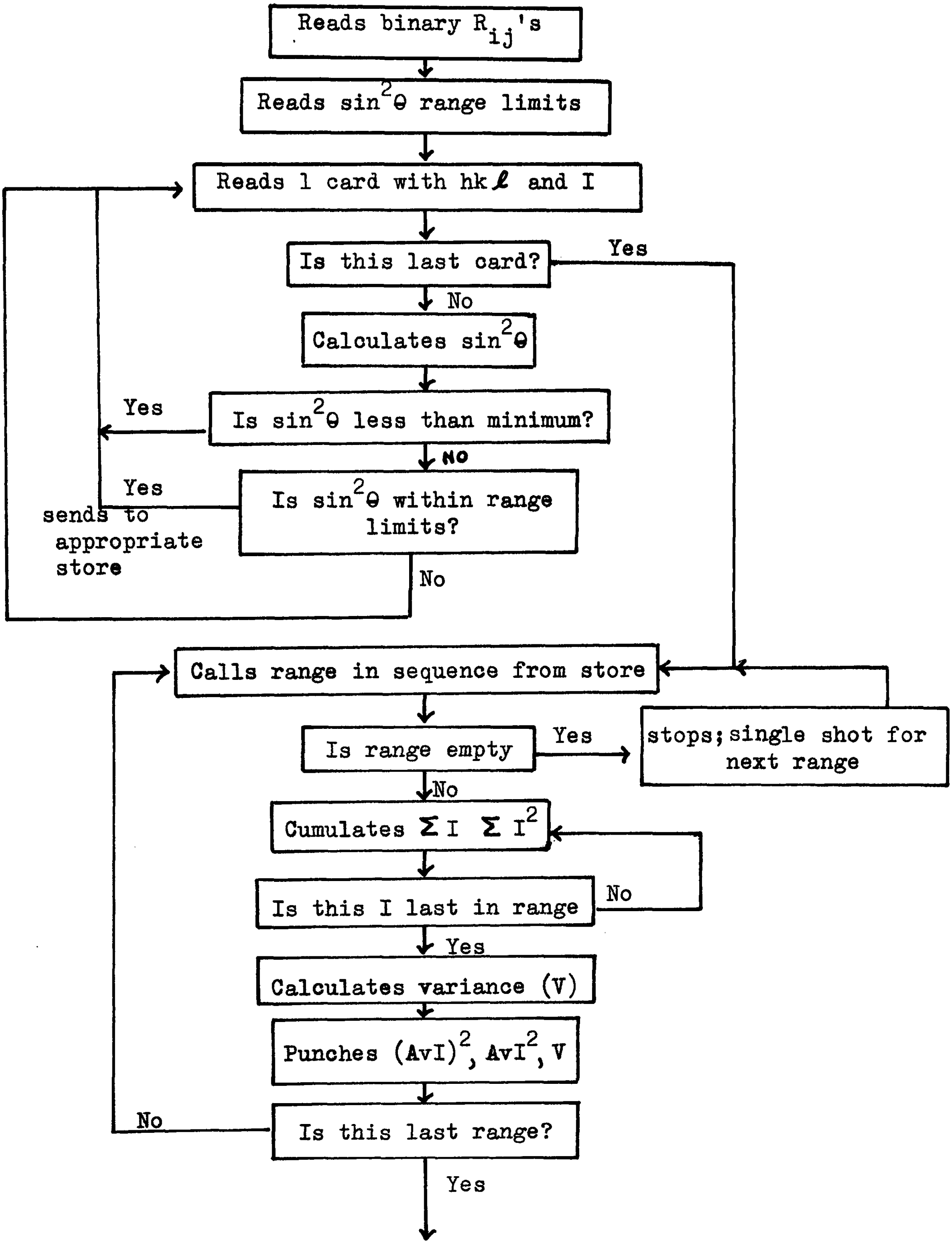
Method

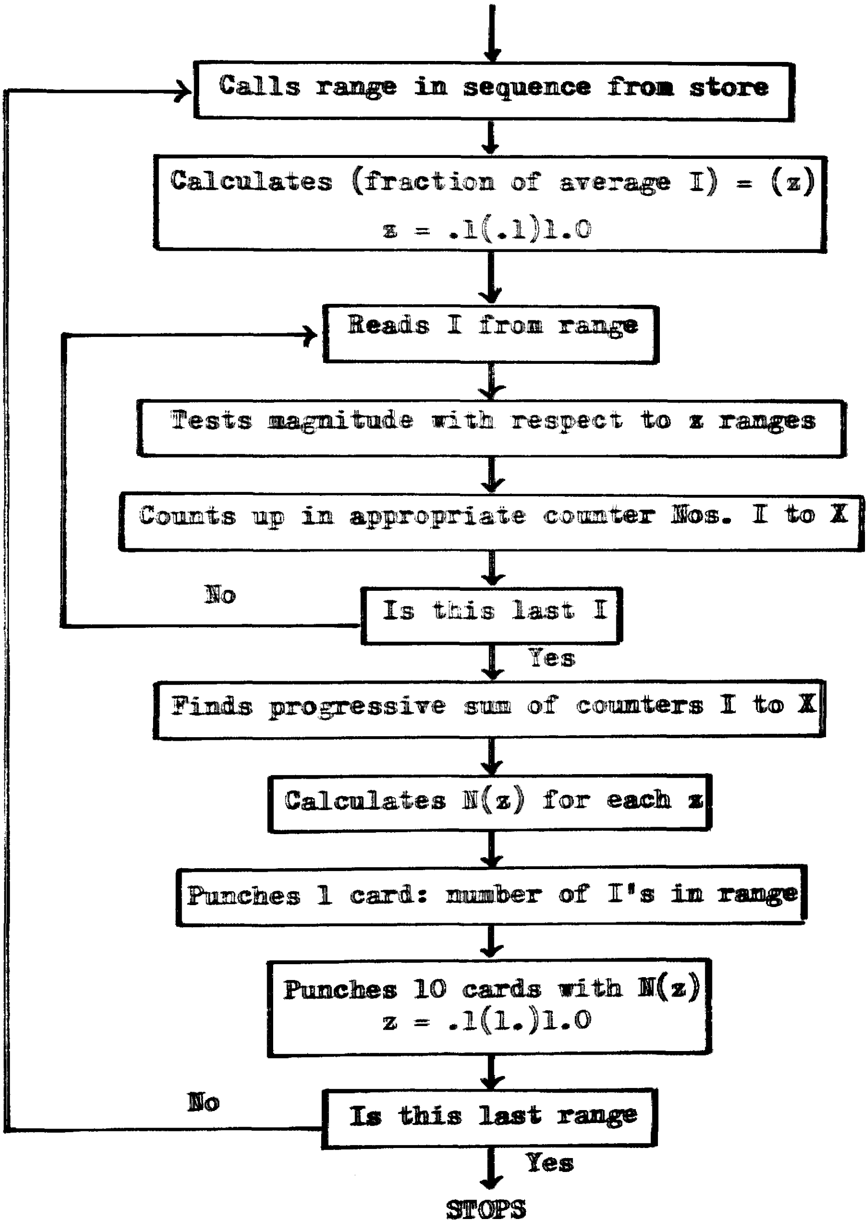
The programme calculates $\sin^2\theta$ for each reflection as it is read, and assigns the F_o^2 to the appropriate storage. When all the intensities have been read, one range at a time is recalled to the fast store, and $\sum I$ and $\sum I^2$ are accumulated. For the variance, the function computed is

$$V = \frac{\mathrm{AvI}^2}{(\mathrm{AvI})^2} - 1$$

The second part of the programme, which may be omitted, computes the proportion of intensities N(z) in each range less than a given fraction of the average intensity for that range. Unobserved terms must be included.

Flow diagram for Programme I




Calls range in sequence from store
Calculates (fraction of average I) = (z)
z = .1(.1)1.0
Reads I from range
Tests magnitude with respect to z ranges
Counts up in appropriate counter Nos. I to X
No
Is this last I
Yes
Finds progressive sum of counters I to X
Calculates N(z) for each z
Punches 1 card: number of I's in range
Punches 10 cards with N(z)
z = .1(1.)1.0
No
Is this last range
Yes
STOPS

Programmes II and III

These programmes, written in basic DEUCE language, were designed as supplements to the least squares refinement programme. Input and output are on punched cards.

Programme II calculates the standard deviation of positional and thermal parameters.

Input

1. The number of degrees of freedom, (n-s); $\sum w\Delta^2$ and cell dimensions
2. Optional output (b) from least squares programme containing the appropriate derivatives (see section II.1).

Output

Four cards per atom

1. $\sigma\, ^{x}/a$ $\quad\sigma\, ^{y}/b$ $\quad\sigma\, ^{z}/c$
2. $\sigma\, x$ $\quad\sigma\, y$ $\quad\sigma\, z$
3. $\sigma\beta_{11}$ $\quad\sigma\beta_{22}$ $\quad\sigma\beta_{33}$
4. $\sigma\beta_{23}$ $\quad\sigma\beta_{13}$ $\quad\sigma\beta_{12}$

Time

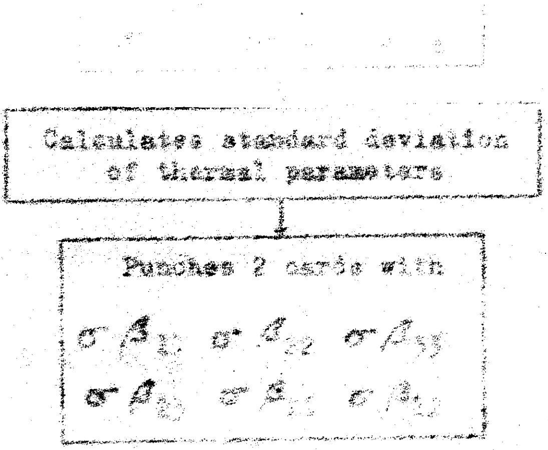
Approximately 10 seconds per atom.

Method

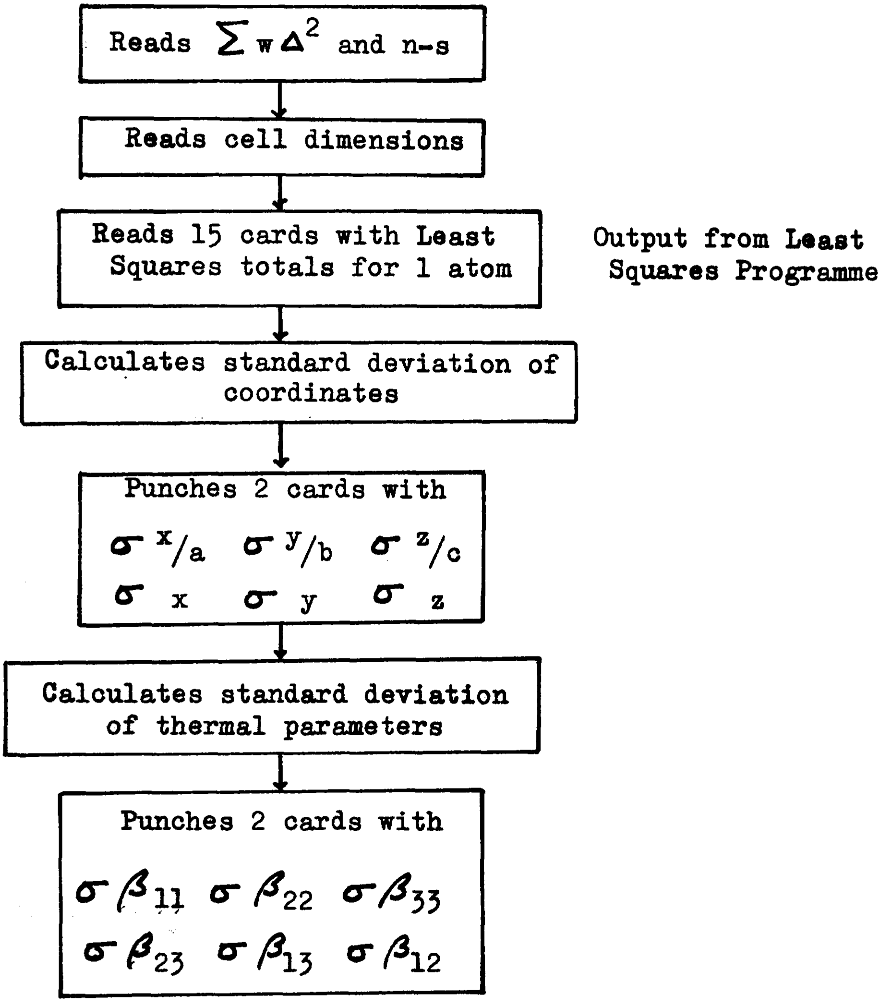
The programme calculates the expression

$$\sigma\xi = \left[\frac{\Sigma w\Delta^2}{(n-s)\,(\partial F/\partial\xi)^2}\right]^{\frac{1}{2}}$$

for each parameter, then computes σx, σy and σz by multiplying by the appropriate cell parameter (no correction is made for nonoblique axes).



Flow Diagram for Programme II



Programme III calculates the standard deviation of electron density.

Input

1. Complete structure factor output from structure factor programme (including unobserved terms)
2. The appropriate volume or area (for projections)

Output

$\sigma(\rho)$

Time

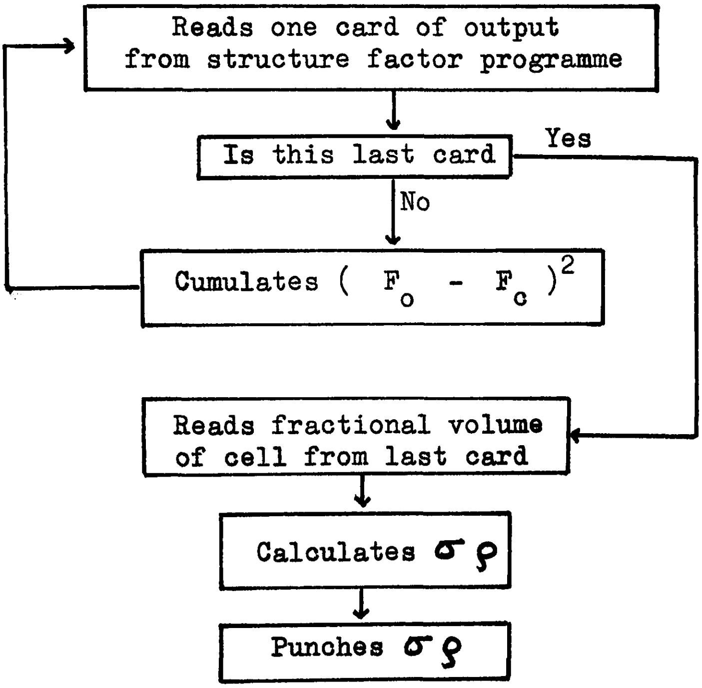
200 reflections per minute. (This is the limit of card reading time for DEUCE).

Method

Forms progressive sum of $(F_o - F_c)^2$ then calculates

$$\sigma \rho = \frac{1}{V} \left(\Sigma (F_o - F_c)^2 \right)^{\frac{1}{2}}$$

Flow Diagram for Programme III



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