THE CRYSTAL STRUCTURE OF FEIST'S ACID

Thesis by

Donald R. Petersen

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1955

ACKNOWLEDGEMENTS

The author is very grateful to Professor J. H. Sturdivant for generous and patient assistance throughout this study and for helpful criticism during the preparation of the thesis. Thanks are due to Professor J. C. Speakman for making known to the author unpublished experimental results and to Professor M. G. Ettlinger for supplying samples of the material studied.

Fellowship grants from the Allied Chemical and Dye Corporation and from E. I. du Pont de Nemours and Company are acknowledged with thanks.

ABSTRACT

The crystal structure of Feist's acid, 1-methylene-cyclopropane-trans-2,3-dicarboxylic acid, has been examined. The substance crystallizes in the triclinic system with space group $P\bar{1}$. Two enantiomorphous molecules of formula $C_6H_6O_4$ are in the unit cell; the direct-cell constants are $a = 4.84$ Å, $b = 9.63$ Å, $c = 7.60$ Å, $\alpha = 91.7^\circ$, $\beta = 102.1^\circ$, and $\gamma = 110.1^\circ$. There is good cleavage at the face (010), and this is also the twinning plane.

The intensity data from equi-inclination Weissenberg photographs about each crystal axis were utilized in selecting and then refining a trial structure. Punched-card computing techniques were used to carry out least-squares refinements of atomic positions; two Fourier summations aided in final refinement. All refining work was based on full three-dimensional data.

Hydrogen bonds bind individual molecules into chains which extend in the $\underset{\sim}{c}$ direction through the crystal. The methylene groups extended in the $\underset{\sim}{b}$ direction form cogs on the chains, and two chains related by centers of symmetry are intermeshed closely.

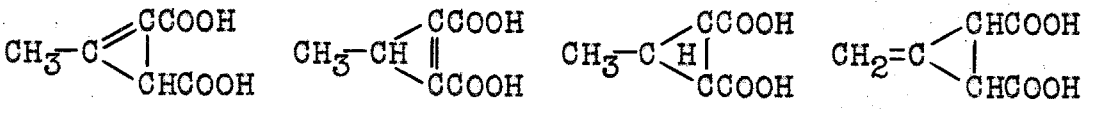
TABLE OF CONTENTS

INTRODUCTION

In 1893, Feist[1] found a previously unknown dibasic acid $C_6H_6O_4$. The method of preparation indicated it was a derivative of cyclopropene[1,2] (Figure 1a,b). Later investigators[3] proposed a structure with a central hydrogen atom (Figure 1c), which symbolized the unexpected stability of the acid. The most recent suggestion[4] (Figure 1d) was based on a convincing chemical proof. Each of these

Figure 1

Structures ascribed to Feist's acid



Asymmetric a | Symmetric b | Semi-aromatic c | Methylene d

structures has been challenged, however, and the evidence given by the principal investigators seems in part contradictory.

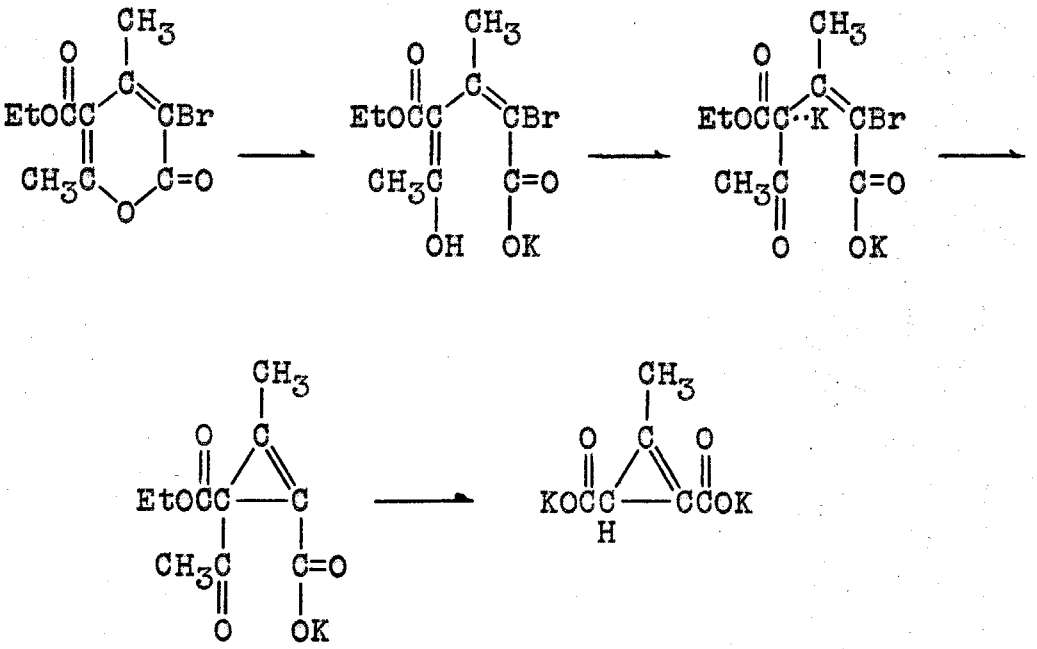
A full crystal structure determination was called for, not only to solve the puzzle of the configuration of Feist's acid, but to add to the information on small-ring compounds. Few complete structure determinations of compounds containing three-membered rings have been carried out. The

effect of substituent groups on the dimensions of small rings is not well known experimentally, and the bond lengths and bond angles in such small-ring compounds are of theoretical interest.

An investigation based on analyses of the complete diffraction data from crystalline Feist's acid was begun. The methods used in this investigation and the results obtained are described in the following sections.

CHEMICAL BACKGROUND

The acid $C_6H_6O_4$ was first prepared by Feist[1] when he treated 3-bromo-4,6-dimethyl-5-carbethoxy-2-pyrone with strong potassium hydroxide solution. He suggested that this pyrone retained the properties of a substituted acetoacetic ester as well as those of a δ-lactone and so proposed the steps below for the reaction with the base.



The resulting form of the molecule is the asymmetric, shown in Figure 1a; an alternate set of steps suggested by Feist leads to the symmetric form, shown in Figure 1b. Other preparations have been described; the diethyl ester of α,α'-dibromo-β-methylglutaric acid, when treated with base, forms the salt of Feist's acid[5], which is then easily changed

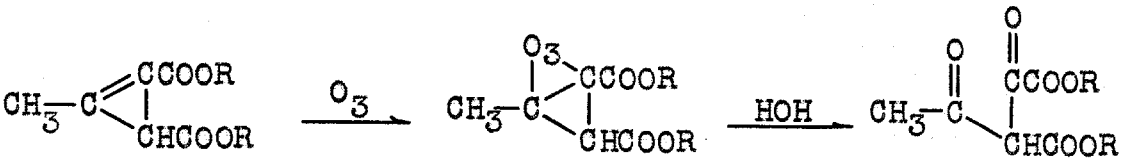
to the acid itself. It was also found[6] that the isomeric saturated acids analogous to Feist's acid, when brominated and then treated with sodium amalgam, each gave the acid melting at 200° described by Feist.

Feist[1] isolated two substances of formula $C_6H_6O_4$. Both forms were said to be unsaturated dibasic acids, but several striking differences were observed. He found that the solubilities of the two acids in ether were quite different, that one of the acids sublimed while the other did not, that the crystal forms of the calcium salts of the acids were entirely different, and that one of the acids melted at 200° but the other at 189°. No number of recrystallizations from water served to raise the latter melting point to 200°. Feist implied that the 189° form and the 200° form corresponded to the symmetric and the asymmetric structures. He later reported[7], however, that both of these forms could be resolved into optical isomers and eliminated the symmetric form of the molecule as a possible structure. Goss, Ingold, and Thorpe[3,8] then showed the 189° form to be an impure sample of the 200° form.

The novel <u>semi-aromatic</u> structure proposed for Feist's acid was the outgrowth of early investigations of glutaconic acid[9]. The unusual properties of glutaconic acid and its derivatives, now explained on the basis of tautomerism and isomerism[10,11], led to the use of unorthodox formulas to represent the structure of such compounds. To Feist's acid

were erroneously ascribed similar properties[3]; these were indicated by writing the structural formula as shown in Figure 1c. The hydrogen atom in the center of the ring apparently was meant to represent not only tautomeric behavior but also the unusual stability and relative inertness characteristic of aromatic systems. Feist[7], and later Kon and Nanji[12], showed that no such representation was necessary to account for the reactions of Feist's acid and that the acid had no semi-aromatic character as described above. The resolution of Feist's acid into two optical isomers[7,8] also eliminated the semi-aromatic structure as a possibility.

In an addendum to one of their papers, Goss, Ingold, and Thorpe[3] discussed the possibility that the diethyl ester of Feist's acid, and presumably the acid itself, might have the methylene structure, as in Figure 1d. They treated the diethyl ester with ozone; the decomposition of the resulting ozonide gave no formaldehyde, a product which they expected if the acid has the methylene structure. Actually, they found diethyl acetylglyoxaloacetate and deduced the asymmetric structure to be the correct one.



Kon and Nanji[12] performed this experiment and found as hydrolysis products acetic acid, oxalic acid, and diethyl acetylglyoxaloacetate. Speakman and his colleagues[13] carried out the ozonolysis and found no formaldehyde. On the basis of such evidence it is almost without doubt that ozonolysis breaks the three-membered ring of Feist's acid. Since ozone is such a specific and effective reagent for breaking double bonds[14], this was thought to be strong evidence for the asymmetric structure.

Recently a very convincing proof of the methylene structure was proposed[4]. When Feist's acid $C_6H_6O_4$ is brominated, one of the products is a bromo lactone monoacid $C_6H_5O_4Br$. Reduction of the bromo lactone by sodium amalgam gives a lactone acid $C_6H_6O_4$ quite different from the original Feist's acid. On oxidation this lactone acid gives trans-cyclopropane-1,2,3-tricarboxylic acid; the original Feist's acid is required to be a methylenecyclopropane derivative. Corroboration of the methylene structure came from an analysis which showed that Feist's acid contains no C-methyl group.

The methylene structure is established by the crystal structure determination to be described. The anomalous results of the ozonolysis experiment might be explained by the conjunction of the three-membered ring and the double bond, although such abnormalities are rare in the addition of ozone to compounds containing double bonds. The results

of the ozonolysis of the comparable substance methylene-cyclopropane are inconclusive, since formaldehyde was the only identified product; the yield was 2% of the theoretical[15]. A possible reaction path for the abnormal addition of ozone to Feist's acid has been suggested, but no experimental work has been done as yet to examine the suggestion[16].

EXPERIMENTAL PART

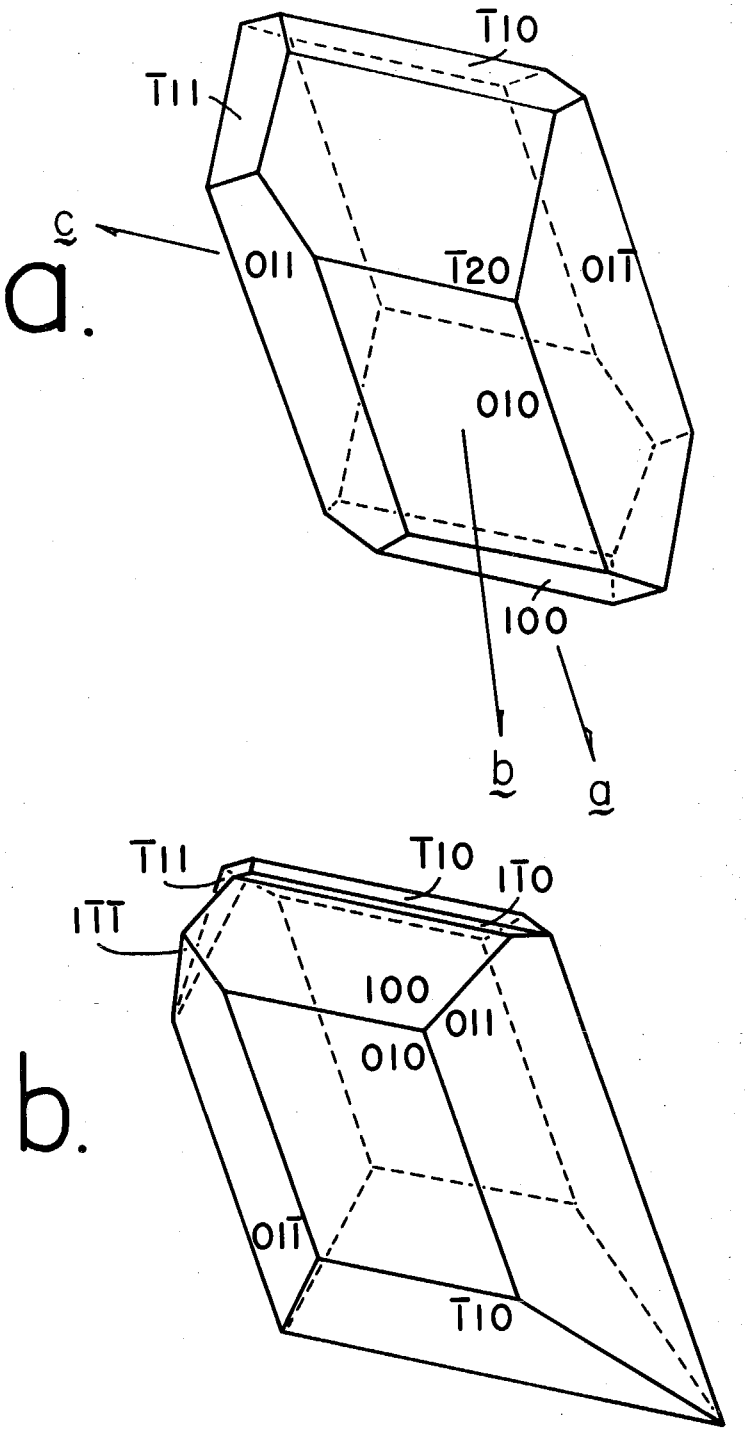
1. Crystal morphology

A sample of crystalline Feist's acid, melting at about 200°, was obtained through the kindness of Professor M. G. Ettlinger. The crystals are colorless and rather brittle and dissolve easily in water. Recrystallizations were carried out from water and from formic acid; both batches of crystals melted at 198-199°, and powder samples from each gave the same x-ray diffraction pattern. The crystals used in the subsequent x-ray analysis were grown from saturated water solutions allowed to evaporate slowly at room temperature.

Individual crystals, usually split from twins, were mounted in the customary way in order to examine the principal crystallographic zones. Neither the optical goniometer nor Laue photographs showed that any symmetry elements were present, other than perhaps a center, which indicates that Feist's acid crystallizes in the triclinic system. The most obvious crystallographic zone axis, shown as $\underset{\sim}{a}$ in Figure 2a, was found to have an identity distance of about 4.8 Å. This was chosen as one of the unit cell axes, and two others were selected in morphologically convenient directions.

The crystals grown from water were found to be almost

Figure 2



(a) Idealized single crystal of Feist's acid
(b) Typical twinned crystal

invariably twinned on the (010) plane, as shown in Figure 2b. This plane also is the principal cleavage plane, although minor cleavage is shown more or less parallel to (100), giving a fibrous type of cleavage when the crystal is carefully stressed in an arbitrary direction. The brittleness of the crystals tends to obscure this fibrous cleavage.

A saturated water solution of Feist's acid, when examined with a polarimeter, showed no significant optical rotation, for with a tube length of two decimeters, the specific rotation at 20° for sodium D light was found to be less than 0.4°. The solution must be racemic, since the acid can be resolved into two optically active forms, each with large specific rotation[7,8].

2. Accurate cell constants

In the triclinic system, the expression relating the reciprocal cell parameters to the observable ϑ is

$$4\lambda^{-2}\sin^2\vartheta = h^2a^{*2} + k^2b^{*2} + \ell^2c^{*2} + 2hka^*b^*\cos\gamma^* + 2h\ell a^*c^*\cos\beta^* + 2k\ell b^*\ c^*\cos\alpha^*$$

Here ϑ is the Bragg angle of reflection for x-rays; λ is the wavelength of the x-radiation; h, k, and ℓ are the reflection indices; and the starred symbols represent the six reciprocal-cell parameters. The six reciprocal-cell parameters were measured approximately from Weissenberg

photographs taken about the three principal crystal axes. The accuracy of these measurements was estimated at one to two percent. From these approximate reciprocal-cell parameters, a value of $\sin^2\Theta$ was calculated for each reflection hkℓ.

Single-crystal rotation photographs around each principal axis were made in a cylindrical camera of radius 50.0 mm and with very low eccentricity. Copper K radiation of wavelength 1.5418 Å was used. Precautions were taken to secure an accurate value of ϑ for each observed reflection, and for each identified reflection a value of $\sin^2\vartheta$ was then found. Many of the reflections were identified unambiguously by the comparison of the rotation photographs with corresponding Weissenberg photographs, and the observed and calculated values for $\sin^2\vartheta$ of these reflections were used to find accurate reciprocal-cell constants by a least-squares method. These reciprocal-cell constants and the direct-cell constants calculated from them are listed in Table 1.

Table 1

Reciprocal- and direct-cell constants for Feist's acid

$a^* = 0.2264$ Å^{-1}	$a = 4.839$ Å
$b^* = 0.1113$ Å^{-1}	$b = 9.630$ Å
$c^* = 0.1354$ Å^{-1}	$c = 7.599$ Å
$\alpha^* = 83^\circ 37'$	$\alpha = 91^\circ 42'$
$\beta^* = 76^\circ 27'$	$\beta = 102^\circ 6'$
$\gamma^* = 68^\circ 59'$	$\gamma = 110^\circ 8'$

The volume of the unit cell calculated from these constants is 323.0 $\mathring{A}^3$; the density of Feist's acid, calculated on the basis of two molecules of $C_6H_6O_4$ in the unit cell, is 1.461 g cm^{-3}. The observed density, found by flotation and by displacement, was 1.472 g cm^{-3} at room temperature.**

3. Intensity data

All photographs used to determine intensities were made on a Weissenberg camera of conventional design with unfiltered copper K radiation. Three films were superimposed in the camera. The film used was Kodak No-Screen Medical X-Ray Type, and it was developed and fixed in the manner described by the manufacturers.

Equi-inclination Weissenberg photographs were made about each of the selected crystal axes. Of the 1450 non-equivalent reflections calculated to lie within the sphere of reflection of copper K radiation, approximately 1300 were identified. A table listing the sets of films and the number of reflections indexed in each is given here. Relatively low overlapping of reflections among the sets is observed because of the low symmetry of the space group of Feist's acid.

** The similarity of the observed and the calculated density suggests that the crystals contain no water of hydration, as stated elsewhere[17]. The function of electron distribution to be described gave no maxima other than those associated with the molecule $C_6H_6O_4$.

Table 2

The number of reflections indexed on each set of equi-inclination photographs

Zone	Number	Zone	Number
0kℓ	146	h4ℓ	131
1kℓ	295	h5ℓ	125
2kℓ	262	hk0	97
h0ℓ	85	hk1	174
h1ℓ	139	hk2	167
h2ℓ	147	hk3	163
h3ℓ	132	hk4	141

A film factor was determined experimentally for x-ray film of the type used; the value found was 3.72 ± 0.10. This agreed well with the value previously used in these Laboratories[18]. Intensity strips based on a logarithmic relation were prepared[18], again with three superimposed films. The films were exposed to the reflection $0\bar{1}2$ from a crystal of Feist's acid for lengths of time proportional to 3.72^x, where x ranged from 2.0 to 5.0 in increments of 0.2 unit. On the second film each spot was reduced in intensity by a factor of 3.72, so that x for the series on this film ranged from 1.0 to 4.0. The third film showed x ranging from 0.0 to 3.0. The overlapping ranges gave spots on the film corresponding to relative intensities from unity ($x=0.0$) to over 700 ($x=5.0$). The principal value of the logarithmic scale based on the film factor is the integral change in value of a given intensity when observed on a different film in the set. The x-numbers are easily changed into relative intensities for a set of films when all visual estimating is

done.

The reflections of each set of films were used to find visually estimated intensities. The intensity $I(hk\ell)$ so determined for reflection $hk\ell$ from the $j^{\underline{th}}$ set of films is related to the square of the structure factor $|F_o(hk\ell)|^2$ as shown[19]:

$$|F_o(hk\ell)|^2 = k_j I(hk\ell) \cdot \left(\frac{\sin 2\theta}{1+\cos^2 2\theta}\right)\left(1-\frac{\sin^2\mu}{\sin^2\theta}\right)^{\frac{1}{2}}$$

Here k_j is the scale factor for the $j^{\underline{th}}$ set of films, θ is the Bragg angle, and μ is the equi-inclination angle. The multiplier terms other than k_j are the reciprocal Lorentz and polarization factors. The factor $\left(\frac{\sin 2\theta}{1+\cos^2 2\theta}\right)$ was calculated for each value of $\sin\theta$ between 0 and 1 at intervals of 0.002 unit, and the points were plotted. Similarly $\left(1-\frac{\sin^2\mu}{\sin^2\theta}\right)^{\frac{1}{2}}$ was calculated as a function of $\sin\theta$ for each of the eleven non-zero values of $\sin\mu$, and eleven graphs were made. Values of $\sin\theta$ were found for each value $hk\ell$, and the modifications to be made for each intensity were read from the proper graphs. Multiplication then gave for each intensity $I(hk\ell)$ the reduced intensity $I_r(hk\ell)$; this is directly proportional to $|F_o(hk\ell)|^2$.

The proportionality constants $k_1, k_2, \ldots k_j, \ldots$ relating $|F_o|^2$ and I_r differ for each set of films and are unknown. The best set of ratios of the type k_j/k_1 was selected by the examination of the reduced intensities of corresponding

reflections from various sets of films. Each reduced intensity I_r form the $j^{\underline{th}}$ film was then multiplied by the ratio k_j/k_1. In this way all values of I_r were related to the corresponding values of $|F_o|^2$ by the same proportionality constant.

This scale factor k_1, or simply K, was determined by Wilson's method[20]. If for any atom the scattering amplitude is

$$f = f_o \exp(-B\sin^2\theta/\lambda^2)$$

where f_o is the scattering for the atom at rest and the exponential factor is due to the thermal vibration of the atom, here assumed isotropic, then it is approximately true that in any small range of $\sin\theta$

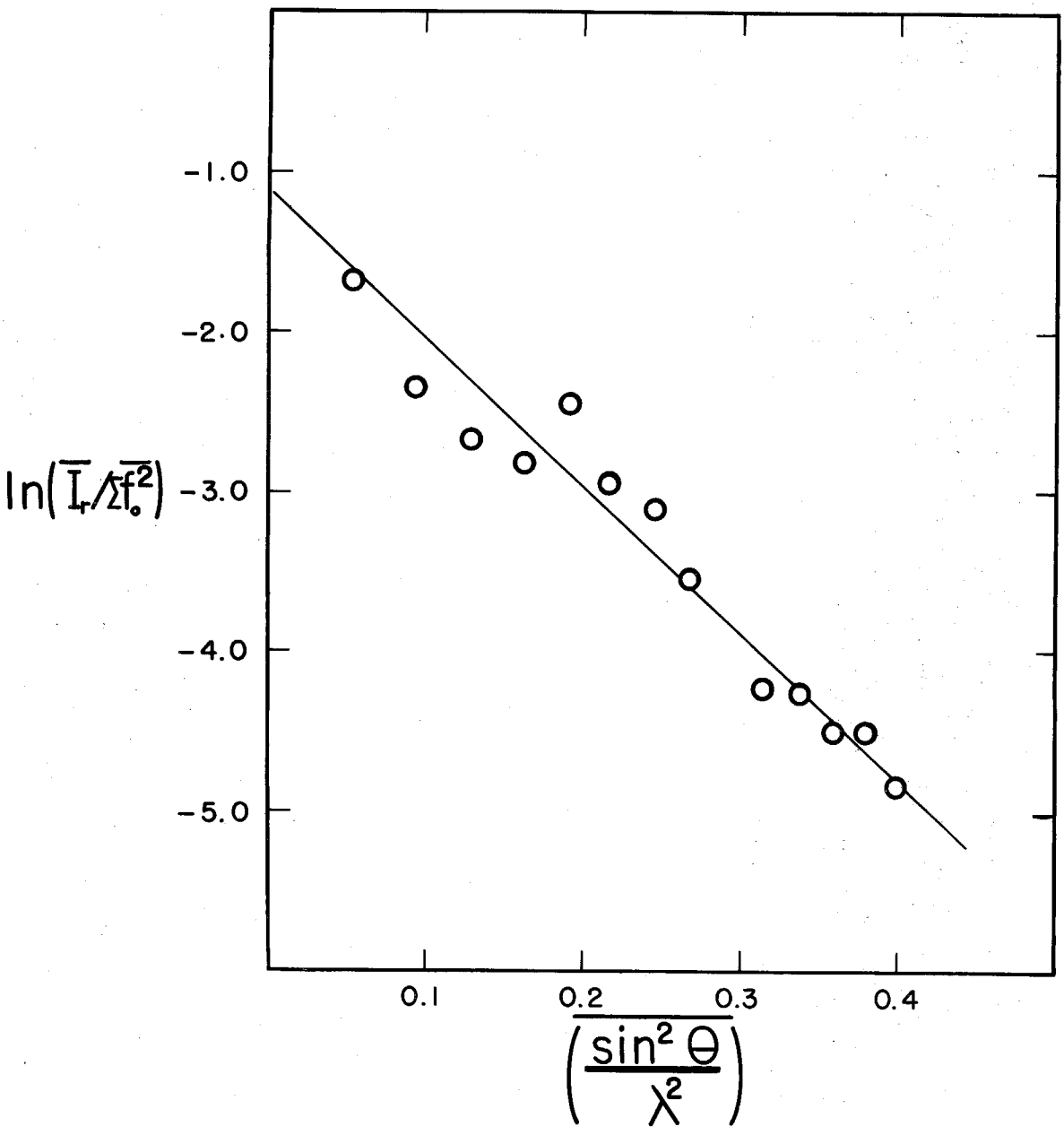
$$\overline{KI_r} = \overline{\sum f_o^2 \exp(-2B \sin^2\theta/\lambda^2)}$$

where the bars indicate the average is to be taken over the range; the summation is made over the unit cell. A further approximation gives

$$\ln(\overline{I_r}/\overline{\sum f_o^2}) = -\ln K - 2B\overline{(\sin^2\theta/\lambda^2)}$$

For Feist's acid, fourteen overlapping groups each of one hundred reflections gave these average values. A plot of $\ln(\overline{I_r}/\overline{\sum f_o^2})$ versus $\sin^2\theta/\lambda^2$ is shown in Figure 3. The slope of the best straight line through the points and its intercept on the ordinate axis gave values of 4.63 and 3.00

Figure 3



Determination of scale and temperature factors by the method of Wilson

for B and K, respectively. The scale factor K was then used to find the set of values $|F_o|^2$; the list of F_o values is given in Appendix B. Since these structure factors were determined indirectly from observed data, they are identified as observed structure factors F_o.

4. Space group

Only two space groups are allowed in the triclinic system, P1 and $P\bar{1}$. The former has no symmetry elements whatever, while the latter possesses a center. The external form of the observed crystals of Feist's acid was not useful in determining the presence or absence of a center of symmetry, for none of the crystals examined had fully developed faces; most were ill-formed or twinned.

The phenomenon of piezo-electricity is sometimes useful in determining the absence of a center. Large crystals of Feist's acid, examined in a modified Giebe-Scheibe[21] apparatus**, showed no piezo-electric effect, however, and so this experiment was inconclusive.

The distribution of reflected intensities is dependent on the presence or absence of a center of symmetry[22]. The fraction $\overline{N(z)}$ of reflections whose reduced intensities are less than or equal to a fraction z of the local average

---

** I am indebted to Dr. W. G. Sly for the use of this instrument.

reduced intensity is given by $N(z)=1-\exp(-z)$ for a noncentrosymmetric structure and by $N(z)=\mathrm{erf}(z/2)^{\frac{1}{2}}$ for a centrosymmetric structure. These two functions are usefully different in the range between $z=0$ and $z=1$. In practice, reduced intensities from each of the three principal zones of Feist's acid were separated into groups with a small range of $\sin\theta$, and local averages $\overline{I_r}$ were found for each group. The fraction $N(z)$ was evaluated in each group at a set of points 0.1 unit apart and ranging between zero and unity. For each value of z a value of $\overline{N(z)}$ was found by averaging over the groups, and these values are listed in Table 3 for the three principal zones; the average values of $\overline{N(z)}$ are plotted in Figure 4.

Table 3

Values of $\overline{N(z)}$ for the three principal zones of Feist's acid

Zone	z = 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0kℓ	.287	.345	.447	.515	.557	.595	.623	.654	.668	.702
hOℓ	.171	.288	.417	.597	.529	.570	.633	.668	.686	.696
hk0	.287	.365	.416	.486	.551	.569	.577	.598	.623	.675
Average	.248	.336	.427	.499	.546	.578	.611	.640	.659	.691

The results given in Table 3 indicate that each of the projections has a center of symmetry. In the triclinic system this could occur only with the space group $P\bar{1}$.

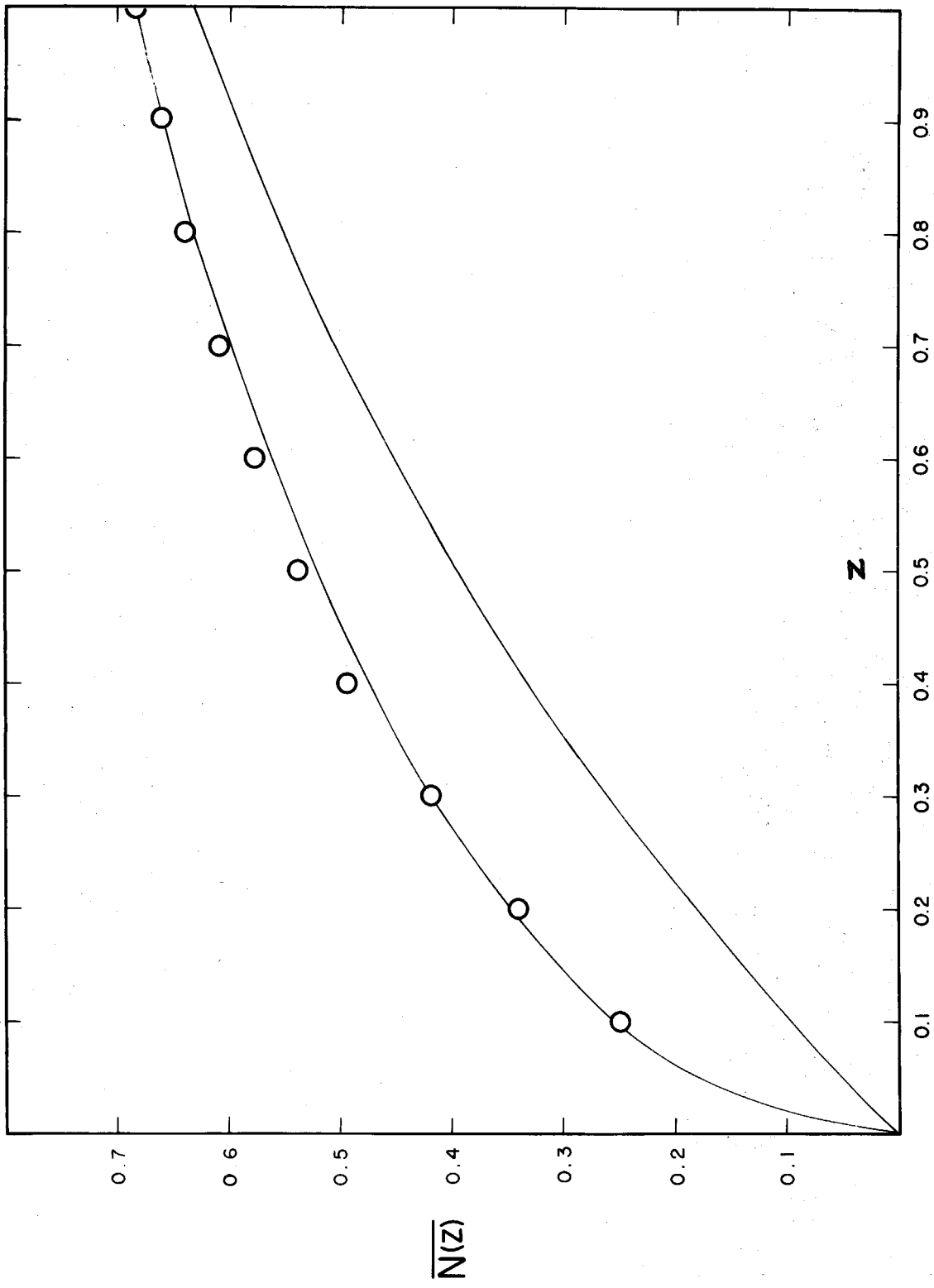


Figure 4

Determination of center of symmetry by a statistical method. Upper curve indicates center, lower curve no center.

THE TRIAL STRUCTURE

Three Patterson projections were made from the $0k\ell$, the $h0\ell$, and the $hk0$ reduced intensity data; of these, the first was most significant and most easily interpreted. It is shown in Figure 5a. From the definition of the projected Patterson function for this zone[23]

$$P(vw) = \frac{1}{A}\sum_{k=-\infty}^{\infty}\sum_{\ell=-\infty}^{\infty}|F(0k\ell)|^2\cos 2\pi(kv+\ell w)$$

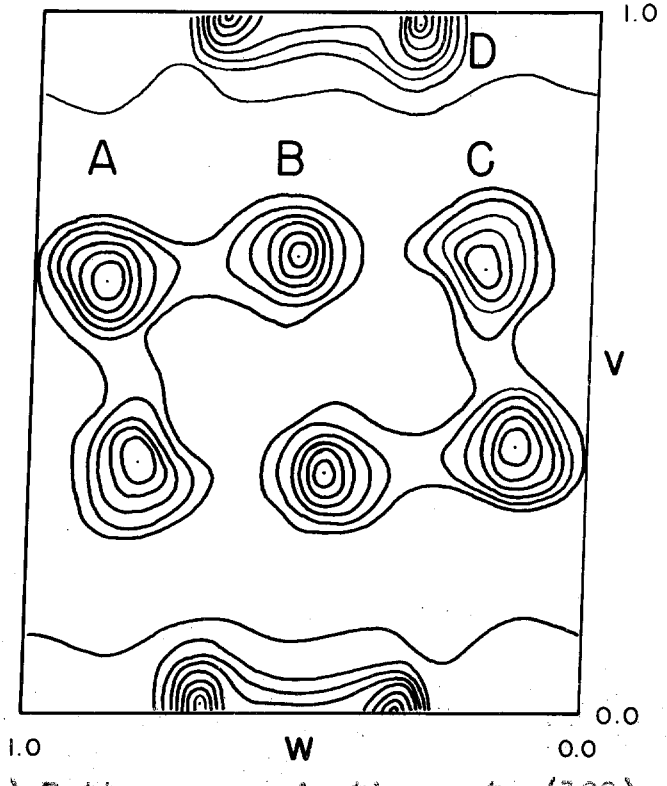
the following expression was derived for space group $P\bar{1}$; $P'(vw)$ contains multiplicative and additive constants of no significance in the location of function maxima.

$$\begin{aligned}P'(vw) = &\sum_{k=1}^{\infty}|F(0k0)|^2\cos 2\pi kv \\ &+\sum_{k=-\infty}^{\infty}\cos 2\pi kv\sum_{\ell=1}^{\infty}|F(0k\ell)|^2\cos 2\pi\ell w \\ &-\sum_{k=-\infty}^{\infty}\sin 2\pi kv\sum_{\ell=1}^{\infty}|F(0k\ell)|^2\sin 2\pi\ell w\end{aligned}$$

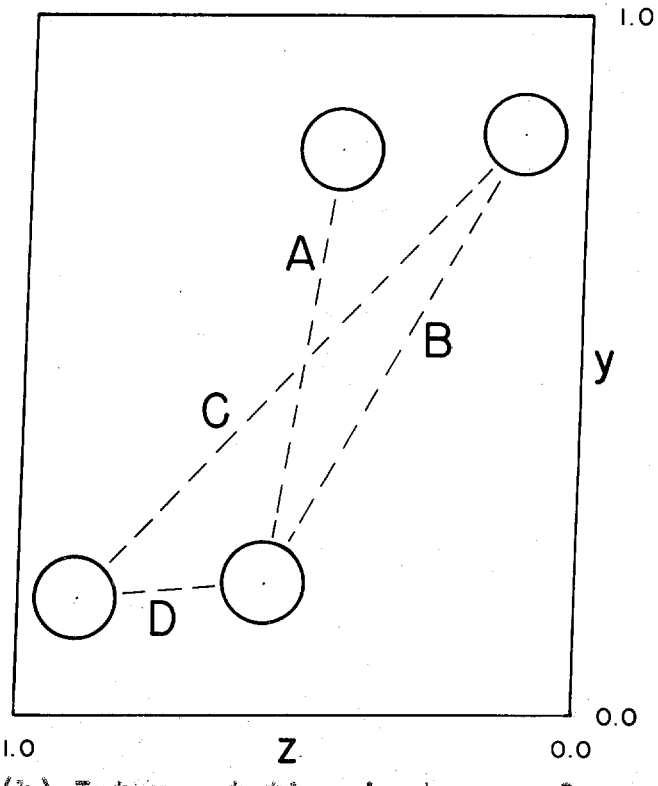
The peak at the origin was not removed, nor were the peaks sharpened. All summations were carried out with Beevers-Lipson strips. The function $P'(vw)$ was evaluated with w ranging in sixtieths from zero to one and, because of the center of symmetry, v going from zero to one-half in sixtieths. The values were then plotted, and contours were drawn at arbitrary, equal intervals.

The function maxima represent the ends of projected interatomic vectors rooted at the origin. Each corner of

Figure 5



(a) Patterson projection onto (100)



(b) Interpretation in terms of projected scattering centers

the parallelepiped shown in Figure 5a is such an origin. The four non-equivalent peaks lettered A through D were interpreted to arise from the vectors connecting the projected scattering centers shown in Figure 5b; the coordinates for these are given in Table 4.

Table 4

Coordinates of projected scattering centers

y	z
0.83	1.11
0.81	0.44
0.17	-0.11
0.19	0.56

The positions of the projected scattering centers at the points tabulated above are not difficult to explain if it is assumed that the observed Patterson peaks are due solely to oxygen-oxygen interactions. The approximate equivalence of peak heights in the Patterson projection does not contradict this assignment. Thus, to account for all oxygen atoms, each of the four scattering centers must contain two of the eight oxygens in the unit cell.

Hydrogen bonding across carboxyl groups is significant in Feist's acid; this is indicated by a comparison of its high melting point, almost 200°, with the melting points of the dimethyl and the diethyl esters of the acid, 38° and 30°, respectively[2]. In many straight-chain dicarboxylic acids, hydrogen bonds bind individual molecules into chains extending through the crystal[24]. This carboxyl-carboxyl

bonding of molecules into chains was assumed for Feist's acid. The orientation of the carboxyl groups relative to the crystal faces was determined from several pieces of evidence. The hydrogen bonds probably lie parallel to the principal cleavage face (010); the fibrous cleavage more or less parallel with the c axis made it reasonable to say that the hydrogen bonds and the assumed chains were aligned in this direction. Packing considerations implied that each of the projected scattering centers is due to one carboxyl group with the two oxygens superimposed. This means that the plane containing all four oxygens of a given molecule is approximately the cleavage plane (010).

These four oxygen atoms were then located in the unit cell. Wire models of molecules of 1-methylenecyclopropane-trans-2,3-dicarboxylic acid were prepared on a scale of one inch to the Ångstrom. Normal carbon-carbon and carbon-oxygen bond distances and bond angles were used. Shadows of these wire models were projected onto the walls of a model unit cell. The carboxyl groups were arranged so that their shadows fell on the projected scattering centers. It was found that this required the plane of the cyclopropane ring to be more or less normal to the plane of the carboxyl groups, so that the direction of the methylene double bond was very nearly parallel to the b axis.

Within these general limits imposed on the orientation and the configuration of the molecule, several different

molecular orientations were investigated. The shadow of the wire model was cast on the (100) plane and on the (010) plane. Atomic positions were noted and then transferred to square grids; Bragg-Lipson charts were used to eliminate a few of the orientations. The strong reflections which were used as tests are listed in Table 5.

Table 5

Strong reflections in the 0kℓ and the hOℓ classes used in testing possible trial structures by Bragg-Lipson charts

Class 0kℓ		Class hOℓ
010	012	100
020	021	$10\bar{3}$
030	$01\bar{2}$	$10\bar{4}$
$01\bar{3}$	$02\bar{2}$	$20\bar{2}$
$03\bar{2}$		$30\bar{5}$
		$20\bar{4}$

The projected atomic positions in the (100) plane were determined quite closely as a result of this procedure. Thus approximate y and z coordinates for the ten principal atoms in the asymmetric unit were found. The x coordinates could not be found without ambiguity, since it was not possible to decide the tilt of the plane of the three-membered ring relative to the (100) plane; the chosen molecular model, however, allowed only two sets of x coordinates corresponding to the established y and z coordinates. One of these sets was chosen at random; the

atomic coordinates for this trial structure are given in in Table 6. They were rounded off to the nearest 0.05 of a cell edge to indicate the degree of confidence placed in them.

Table 6

Atomic coordinates for the first trial structure

Atom	x	y	z
C_1	0.50	0.50	0.25
C_2	0.50	0.40	0.25
C_3	0.50	0.25	0.15
C_4	0.75	0.25	0.40
C_5	0.50	0.25	0.00
C_6	0.50	0.25	0.50
O_1	0.25	0.10	0.00
O_2	0.75	0.25	0.60
O_3	0.75	0.25	0.00
O_4	0.25	0.25	0.50

This trial structure compared favorably with that independently proposed by Speakman and his colleagues[25,26,27]. Although this work is described in Appendix A, the atomic coordinates found by Speakman are listed in Table 7 so that comparisons may be made. The transformation from his coordinate system to the one used in this paper has been made.

Table 7

Atomic coordinates for the structure proposed by Speakman and coworkers

Atom	x	y	z	Speakman's convention
C_1	0.42	0.48	0.23	C(4)
C_2	0.48	0.34	0.23	C(3)
C_3	0.46	0.20	0.16	C(5)
C_4	0.64	0.25	0.32	C(2)
C_5	0.49	0.17	0.99	C(6)
C_6	0.63	0.22	0.49	C(1)
O_1	0.29	0.09	0.85	O(4)
O_2	0.84	0.25	0.64	O(1)
O_3	0.75	0.22	0.96	O(3)
O_4	0.36	0.14	0.51	O(2)

REFINEMENT OF THE TRIAL STRUCTURE

1. Application of least-squares methods

In the structure refinements which will be described, the three-dimensional least-squares refining technique applied to atomic coordinates is the most significant. This method is now often used in the final stages of the refinement of a structure, since it has several important advantages over successive Fourier syntheses. The least-squares procedure does not require the plotting of peak contours, and the possibility of weighting the data used makes the method very satisfying, both theoretically and practically[28]. In applying the least-squares process to the initial stages of refinement, as well as to the final stages, a measure of its value as a means of refinement is shown. For the space group $P\bar{1}$, this expression may be written for each reflection hkℓ:

$$\omega^{1/2}\Delta F = \omega^{1/2}(F_o - F_c) = \omega^{1/2}\sum_{i=1}^{N/2}\left[\frac{\partial F}{\partial x_i}\Delta x_i + \frac{\partial F}{\partial y_i}\Delta y_i + \frac{\partial F}{\partial z_i}\Delta z_i + \delta_i\right]$$

where

$$F_c = 2\sum_{j=1}^{N/2} f_j \cos 2\pi (hx_j + ky_j + \ell z_j)$$

and $x_j y_j z_j$ are coordinates of $j^{\underline{th}}$ atom expressed in fractions of the cell edges a, b, and c, respectively. The total number of atoms in the unit cell is N, and in the

second equation f_j is the scattering factor for the $j^{\underline{th}}$ atom, with temperature effect included. The weight given each equation is $w^{\frac{1}{2}}$. The term δ_i consists of higher order terms and is considered to be vanishingly small. The sign found for F_c in the second equation is used for both F_o and F_c in the first equation. For each reflection hkl, the first equation shows a sum of 3N/2 terms equal to a residual ΔF. The best set of 3N/2 unknowns of the sort Δx_i is defined as the set minimizing the sum $\sum w \Delta F^2$, where this sum is made over all reflections. In the case of Feist's acid there are thirty unknowns. The equations of the first type above are reduced to thirty normal equations, the first of which is

$$\sum \omega \Delta F \frac{\partial F}{\partial x_1} = \sum \omega \left(\frac{\partial F}{\partial x_1}\right)^2 \Delta x_1 + \sum \omega \left(\frac{\partial F}{\partial x_1}\right)\left(\frac{\partial F}{\partial y_1}\right) \Delta y_1 + \sum \omega \left(\frac{\partial F}{\partial x_1}\right)\left(\frac{\partial F}{\partial z_1}\right) \Delta z_1$$

plus 27 other terms for which $i \neq 1$. In general, any cross terms such as

$$\sum \omega \left(\frac{\partial F}{\partial x_i}\right)\left(\frac{\partial F}{\partial x_j}\right)$$

were left out of the calculation. Terms such as

$$\sum \omega \left(\frac{\partial F}{\partial x_i}\right)\left(\frac{\partial F}{\partial y_i}\right)$$

applying to the same atom were found to be relatively important and were retained. In this way the 30 x 30 determinant required to solve the 30 equations in 30 unknowns was separated into ten 3 x 3 determinants. These sums of

products required for the solution of the normal equations were made by using straightforward techniques on IBM computing equipment.

Four least-squares refinements of the atomic coordinates were made. Each of these refinements took about thirty hours and required about ten thousand IBM cards. The essential material concerning these refinements is given in Table 8.

Table 8

Results of the four least-squares refinements of atomic coordinates

Refinement Number	Reflections Used	Average Coordinate Change	R	$\sum w\Delta F^2$
1	81	0.0106	0.387	3529
2	262	0.0043	0.314	2503
3	1000	0.0031	0.269	1277
4	1000	0.0011	0.265	1229

In each refinement, those reflections with the largest values of $|F_o|$ were used. The factor R is the customary reliability factor calculated from those reflections with $|F_o|$ larger than one, the average minimum observable. The last column is the sum of weighted values of ΔF^2 for all reflections. The final atomic position parameters are listed in Table 9.

Table 9

Final atomic coordinates

Atom	x	y	z
C_1	0.4525	0.4698	0.2314
C_2	0.5003	0.3432	0.2357
C_3	0.4044	0.1868	0.1522
C_4	0.6705	0.2500	0.3206
C_5	0.4816	0.1710	0.9758
C_6	0.6150	0.2043	0.4981
O_1	0.2722	0.0936	0.8461
O_2	0.8442	0.2448	0.6323
O_3	0.7488	0.2364	0.9600
O_4	0.3491	0.1330	0.5134

2. Fourier summations

The structure factors calculated from the final atomic coordinates were used, with the corresponding observed structure factors, to calculate a Fourier F_o synthesis and a ΔF synthesis, both in three dimensions. The full number of observed reflections was used to furnish data. As an example of the sums involved for space group $P\bar{1}$,

$$\rho(xyz) = \frac{V}{2}\Big\{\sum_h F(h00)C_h + \sum_k F(0k0)C_k + \sum_l F(00l)C_l$$
$$+ \sum_h\sum_k [F(hk0) + F(h\bar{k}0)]C_hC_k + \sum_h\sum_k [-F(hk0) + F(h\bar{k}0)]S_hS_k$$
$$+ \sum_h\sum_l [F(h0l) + F(h0\bar{l})]C_hC_l + \sum_h\sum_l [-F(h0l) + F(h0\bar{l})]S_hS_l$$
$$+ \sum_k\sum_l [F(0kl) + F(0k\bar{l})]C_kC_l + \sum_k\sum_l [-F(0kl) + F(0k\bar{l})]S_kS_l$$

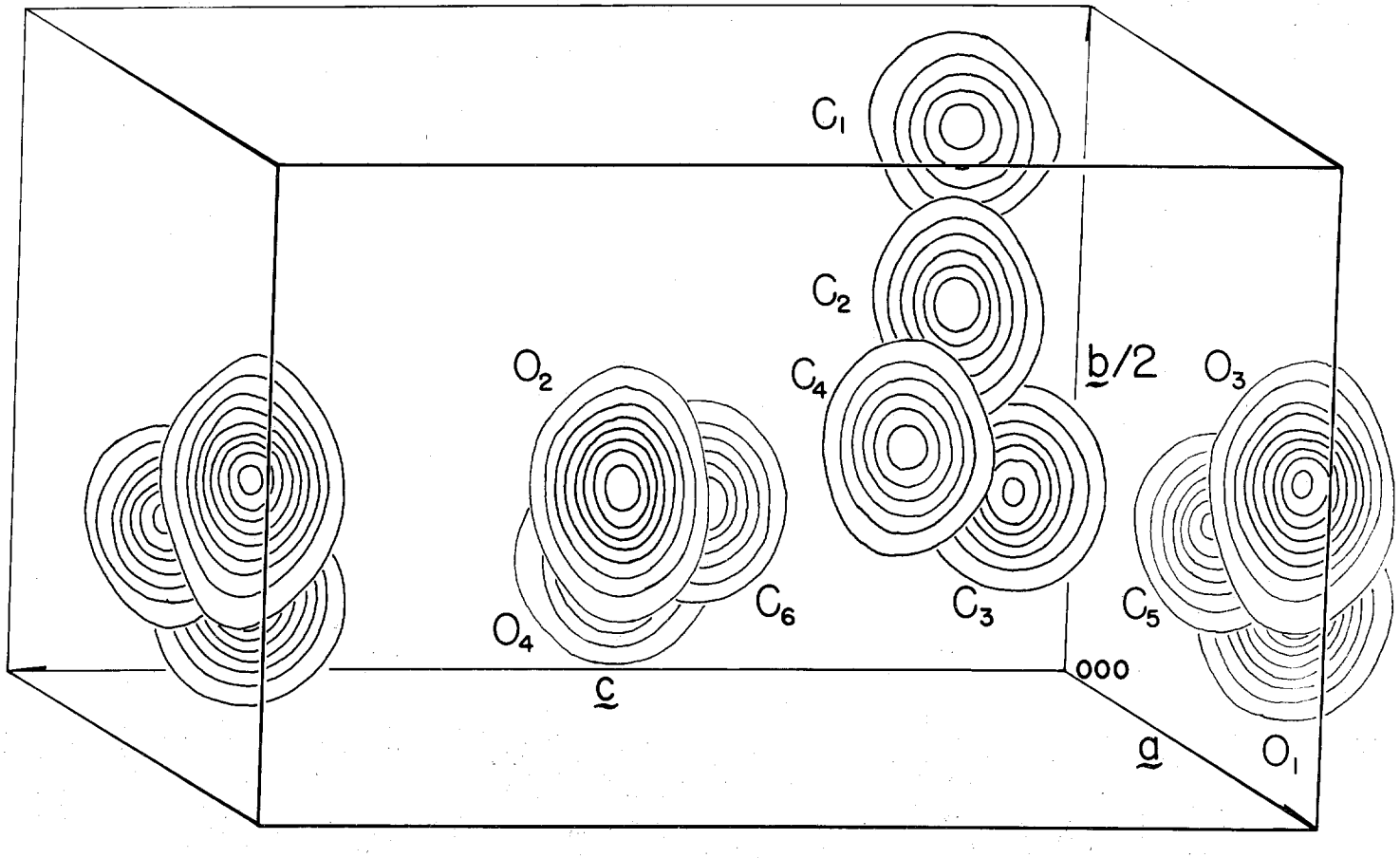
$$+\sum_h\sum_k\sum_l [F(hkl)+F(hk\bar{l})+F(h\bar{k}l)+F(\bar{h}kl)]C_hC_kC_l$$
$$+\sum_h\sum_k\sum_l [-F(hkl)-F(hk\bar{l})+F(h\bar{k}l)+F(\bar{h}kl)]S_hS_kC_l$$
$$+\sum_h\sum_k\sum_l [-F(hkl)+F(hk\bar{l})-F(h\bar{k}l)+F(\bar{h}kl)]S_hC_kS_l$$
$$+\sum_h\sum_k\sum_l [-F(hkl)+F(hk\bar{l})+F(h\bar{k}l)-F(\bar{h}kl)]C_hS_kS_l \}$$

The expression for $\Delta\rho$ is analogous. $C_h = \cos 2\pi hx$, etc.

All Fourier summations were accomplished by means of IBM punched card techniques using the M-card system devised by Professor V. Schomaker[29]. These summations were made with the intervals 1/30, 1/60, and 1/60 for the edges a, b, and c, respectively. About thirty-five thousand cards were used in each of the two syntheses, and roughly sixty hours of calculation time and thirty hours of plotting time were required for each.

The centers of the peaks in the Fourier F_o synthesis were found by a method[30] which involved the twenty-seven grid points nearest the apparent peak center and which assumed the scattering density ρ to be Gaussian near its maxima. Some difference was expected between the atomic positions from the Fourier F_o synthesis and those determined by least-squares refinements because of the difference in weighting in the two methods. Nevertheless, the two sets of coordinates agree to within 0.001 in most cases. Figure 6 shows a representation of the three-dimensional Fourier synthesis. The contours shown are those lying on planes parallel to (100) passing near the peak maxima.

Figure 6



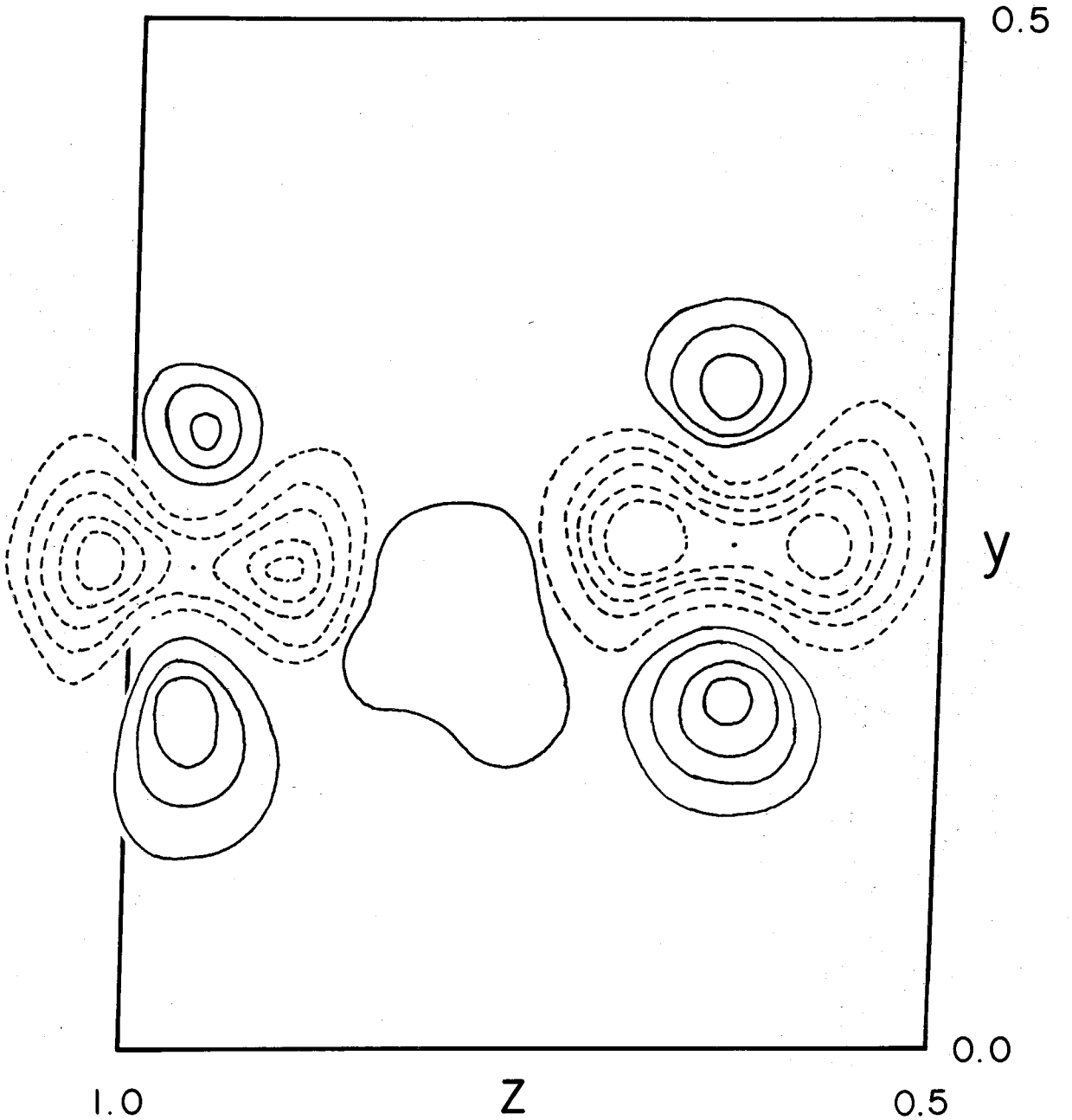
Representation of the three-dimensional Fourier F_o synthesis. The lowest contour is 1 electron per cubic Angstrom and the interval is 1 electron per cubic Angstrom.

The ΔF synthesis resulted in an interesting distribution of $\Delta\rho$. This distribution near the two oxygens of one of the hydrogen bonds is shown in Figure 7. The negative regions indicate a smaller vibration in the $\underset{\sim}{c}$ direction than allowed for by the isotropic temperature factor. To a somewhat lesser extent, this decrease in vibration in the $\underset{\sim}{c}$ direction is shown by all the atoms of the structure. The positive regions, which indicate a greater vibration than allowed for in a direction approximately parallel to $\underset{\sim}{b}$, are shown only by oxygen atoms. The hydrogen atom of the hydrogen bond appears as a smear of low density between the positions occupied by the oxygens. All of the hydrogens appear in the distribution of $\Delta\rho$ at a smaller electron density than might be expected at this stage of refinement.

3. Correction for anisotropic scattering

One of the assumptions made in the determination of the scale and the temperature factors by the method of Wilson is that this temperature factor is a constant and represents equal root mean square thermal vibrations in all directions for all atoms. That the scattering density, and so the root mean square thermal vibration, is dependent on direction is shown in Figures 6 and 7. As mentioned above, this anisotropy is most pronounced in the $\underset{\sim}{c}$ direction. The correction for this was made by superimposing upon the

Figure 7



Section in the three-dimensional Fourier ΔF synthesis near the centers of atoms $O_3 \ldots H_6\text{-}O_2$. The lowest contour is 0.2 electron per cubic Ångstrom and the interval is 0.2 electron per cubic Ångstrom.

constant isotropic thermal vibration a linear vibration parallel to $\underset{\sim}{c}$. This correction reduced to $\exp(q\ell^2)$, where q is a constant and ℓ is the index number for the $\underset{\sim}{c}$ direction. The constant q was found empirically.

Values of $|F_o|$ and $|F_c|$ were used to find the relation between the ℓ index and the deviation of $\sum|F_c|$ from the corresponding $\sum|F_o|$ for each zone of constant ℓ.

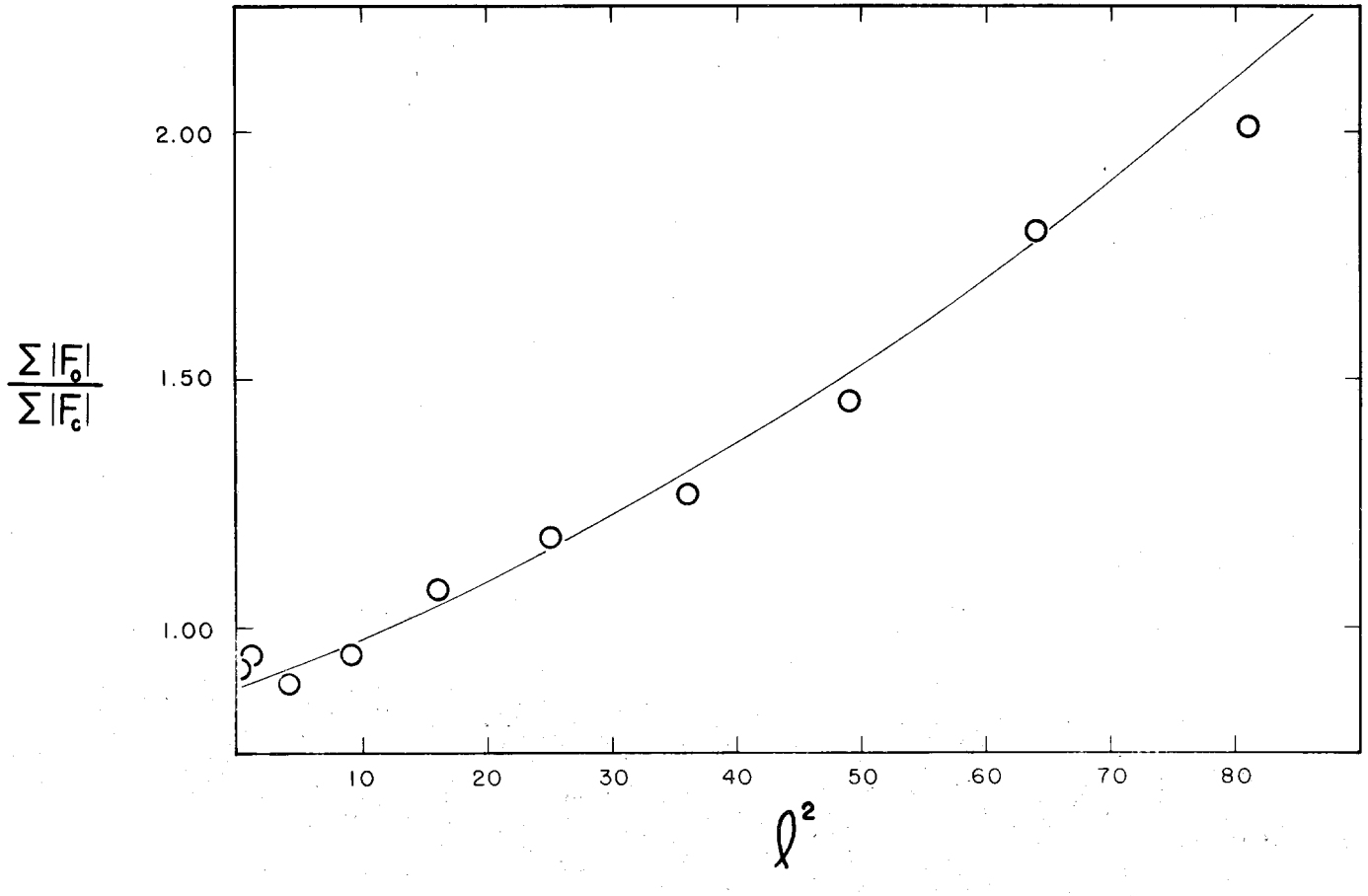
Table 10

Relation of sum of $|F_o|$ and $|F_c|$ for zones of constant ℓ

Zone	$\sum\|F_o\|$	$\sum\|F_c\|$	$\sum\|F_o\|/\sum\|F_c\|$
hk0	541	591	0.92
1	720	762	0.94
2	759	855	0.89
3	783	825	0.95
4	443	410	1.08
5	447	378	1.18
6	341	270	1.26
7	153	105	1.46
8	121	68	1.78
9	54	27	2.00

A graph of $\sum|F_o|/\sum|F_c|$ as a function of ℓ^2 must be fitted by an exponential function of the type $\exp(q\ell^2)$. By trial, a value of $q = -0.01$ was chosen, giving the curve shown in Figure 8. A slight change in scale factor was also called for. These changes were made to give the values in Table 11.

Figure 8



The effect of anisotropic scattering in zones of constant ℓ

Table 11

Relation of sums of $|F_o|$ and $|F_c|$ for zones of constant ℓ after anisotropy correction

Zone	$\sum\|F_o\|$	$\sum\|F_c\|$	$\sum\|F_o\| / \sum\|F_c\|$
hk0	540	544	0.99
1	818	779	1.05
2	863	901	0.96
3	880	902	0.98
4	497	482	1.03
5	502	485	1.04
6	383	388	0.99
7	172	172	1.00
8	136	128	1.06
9	60	60	1.00

The anisotropy correction reduced R and $\sum w\Delta F^2$ to 0.181 and 1070, respectively.

4. Correction for scattering by hydrogens

Approximate positions for the six hydrogen atoms in the asymmetric unit were calculated on the basis of geometrical considerations and previous determinations of structures having carbon-hydrogen bonds. The hydrogen bonds were assumed to be symmetric. These considerations gave the hydrogen positions listed in Table 12.

Table 12

Approximate atomic coordinates for the hydrogen atoms

	Atom	x	y	z
(C_1)	H_1	0.279	0.493	0.134
(C_1)	H_2	0.582	0.565	0.325
(C_3)	H_3	0.180	0.130	0.130
(C_4)	H_4	0.900	0.250	0.320
(O_1)	H_5	0.311	0.114	0.680
(O_2)	H_6	0.797	0.241	0.796

The corrections to the calculated structure factors due to scattering by hydrogens were found. The isotropic temperature factor B= 4.63 was assumed for the hydrogen atoms. It was not necessary to calculate corrections for those reflections with $\sin\theta > 0.5$, for scattering here is reduced to 0.1 for each hydrogen. The final values of R and $\sum w\Delta F^2$ were found to be 0.172 and 962, respectively. The resulting sets of $|F_o|$ and F_c are listed in Appendix B; the corrections to values of F_c due to scattering by hydrogens are listed as F(H).

RESULTS AND DISCUSSION

1. Configuration of the molecule

All bond lengths and bond angles described below were calculated using the final set of atomic position parameters listed in Table 9 and the direct-cell constants listed in Table 1.

For the unit cell defined in Table 1, the square of the bond length is

$$r_{ij} = 23.413(x_i-x_j)^2 + 92.731(y_i-y_j)^2 + 57.743(z_i-z_j)^2 - 32.089(x_i-x_j)(y_i-y_j) - 15.418(x_i-x_j)(z_i-z_j) - 4.355(y_i-y_j)(z_i-z_j)$$

where $x_i y_i z_i$ are the coordinates of the $i^{\underline{th}}$ atom. The values found for the bond lengths are listed in Table 13. The bond angles are also listed in Table 13. Figure 9 gives the identification scheme used in this table.

The standard deviations σ of bond lengths were found by the method of Cruikshank[31]. The standard deviations of the bond angles were derived from these. It is assumed conventionally that discrepancies of $\pm 3\sigma$ may be expected. The average standard deviation for bond lengths is near 0.01 Å and for bond angles near 2°.

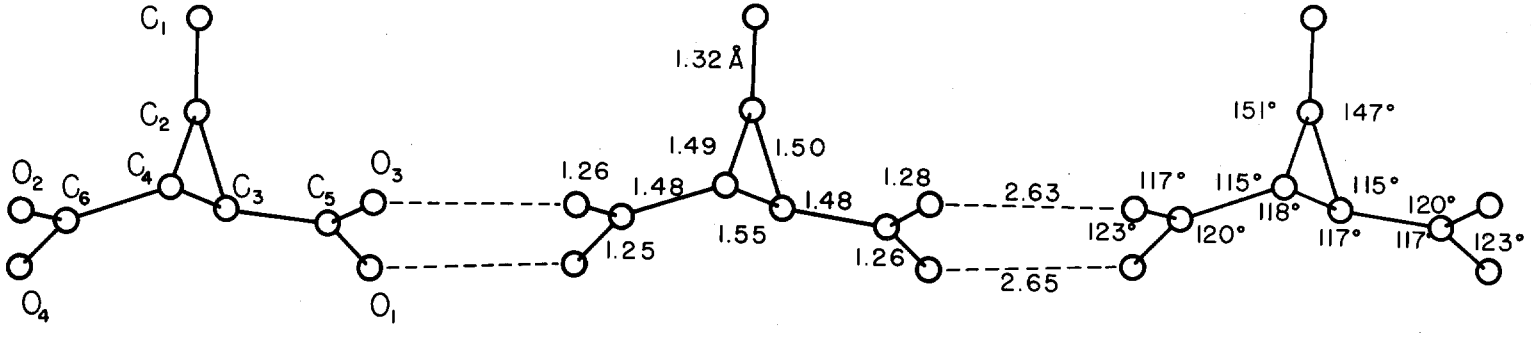
Table 13

Bond lengths and bond angles for the Feist's acid molecule

C_1-C_2	1.317 Å	C_5-O_1	1.253 Å
C_2-C_3	1.497 Å	C_5-O_3	1.261 Å
C_2-C_4	1.490 Å	C_6-O_2	1.275 Å
C_3-C_4	1.545 Å	C_6-O_4	1.263 Å
C_3-C_5	1.482 Å	$O_1\ldots O_4$	2.652 Å
C_4-C_6	1.480 Å	$O_2\ldots O_3$	2.625 Å

$C_1-C_2-C_3$	146°35'
$C_1-C_2-C_4$	150°40'
$C_2-C_3-C_5$	114°51'
$C_2-C_4-C_6$	115° 3'
$C_3-C_4-C_6$	117°44'
$C_4-C_3-C_5$	117°12'
$C_3-C_2-C_4$	62°45'
$C_2-C_3-C_4$	58°48'
$C_2-C_4-C_3$	58°27'
$C_3-C_5-O_1$	116°56'
$C_4-C_6-O_2$	116°49'
$C_3-C_5-O_3$	120°27'
$C_4-C_6-O_4$	120°18'
$O_1-C_5-O_3$	122°37'
$O_2-C_6-O_4$	122°53'

Figure 9



Bond lengths and bond angles in the molecule of Feist's acid

The carbon atoms of the cyclopropane molecule form an equilateral triangle with sides of 1.52 Å[32]. The bond lengths between atoms in the three-membered ring of Feist's acid suggest that this triangle is not equilateral, even though the differences from 1.52 Å are within the $\pm 3\sigma$ limit. The general agreement between equivalent parts of the molecule unrelated by symmetry elements of the space group is remarkably good, and for this reason high confidence is placed in the measured bond lengths and bond angles. The slight shortening of the carbon-carbon bonds in the ring adjacent to the methylene group might be caused by double bond character, but convincing resonance structures are not easily found; however, structures involving separation of charge may be written.

The carbon-carbon bonds from carboxyl groups are considerably shortened from the normal single-bond distance of 1.54 Å. The distance 1.48 Å represents about 15% double bond character (on the Pauling scale[33]) for these bonds. This decrease in bond length has been noticed in other carboxylic acids[34,35] and is probably not unusual.

The carbon-oxygen bond lengths in the carboxyl groups are puzzling. All of the bonds are very nearly the same length, 1.26 Å, which is about the length expected if each of the carbon-oxygen bonds had 50% double bond character. It was suggested[36] that this might be indicative of a random arrangement of pairs of carboxyl groups in the crystal, the

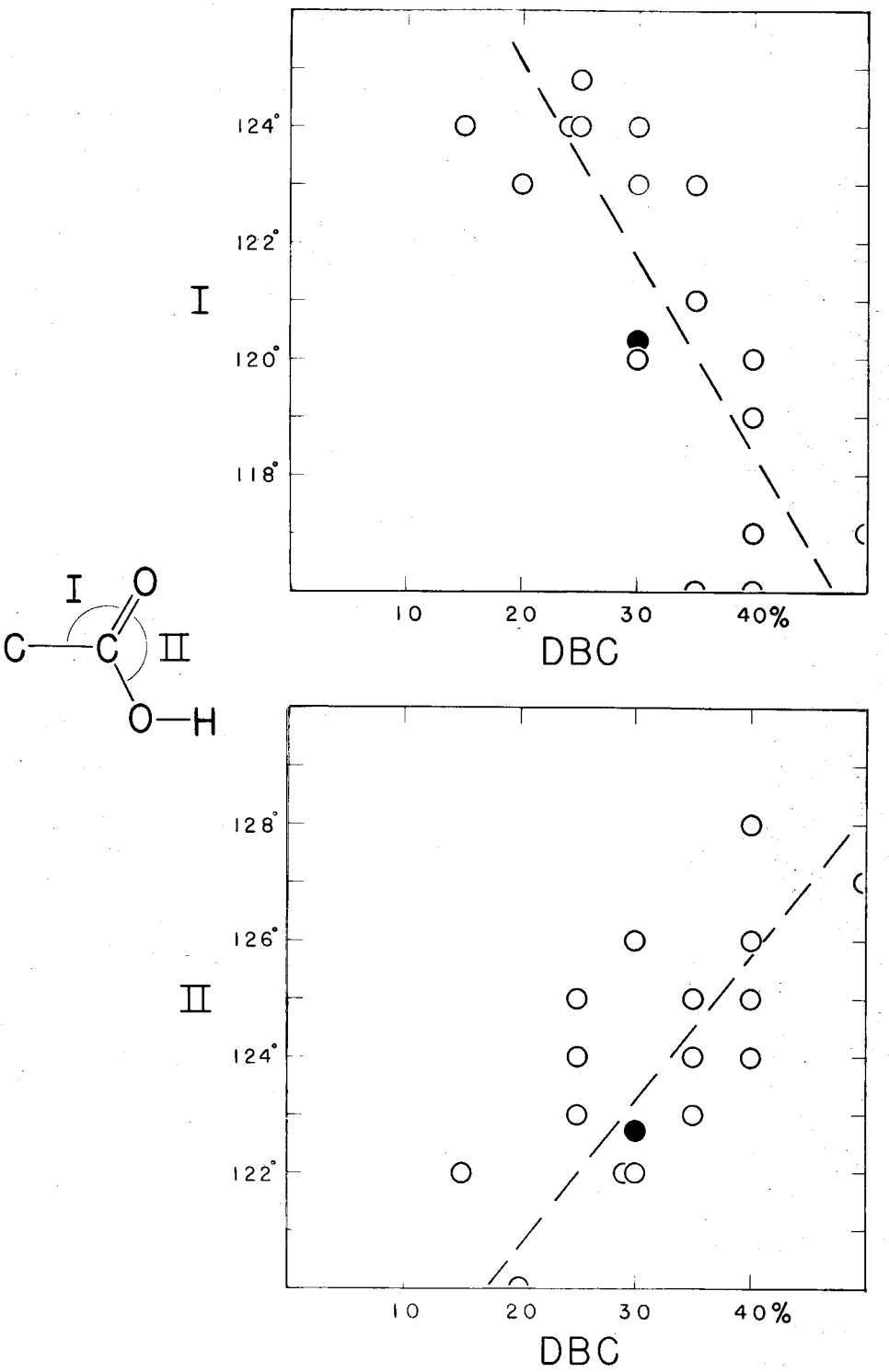
randomness being confined to the flipping of the groups through a half-circle. The bond angles in each of the carboxyl groups suggest this is not the case. An empirical relation between the bond angles and the double bond character of the carbon-oxygen single bond in a carboxyl group indicates about 30% double bond character for these bonds in Feist's acid. This is shown in Figure 10; the plotted points were calculated from a dozen recent structure determinations of carboxylic acids[24,37], and the darkened points were determined for Feist's acid.

The double bond is clearly outside of the ring, for the bond length 1.32 Å for the C_1-C_2 bond is very close to the conventional double bond length 1.33 Å. The trans position of the carboxyl groups above and below the plane of the cyclopropane ring (Figure 11) also shows that the methylene structure is the correct one.

2. Intermolecular contacts

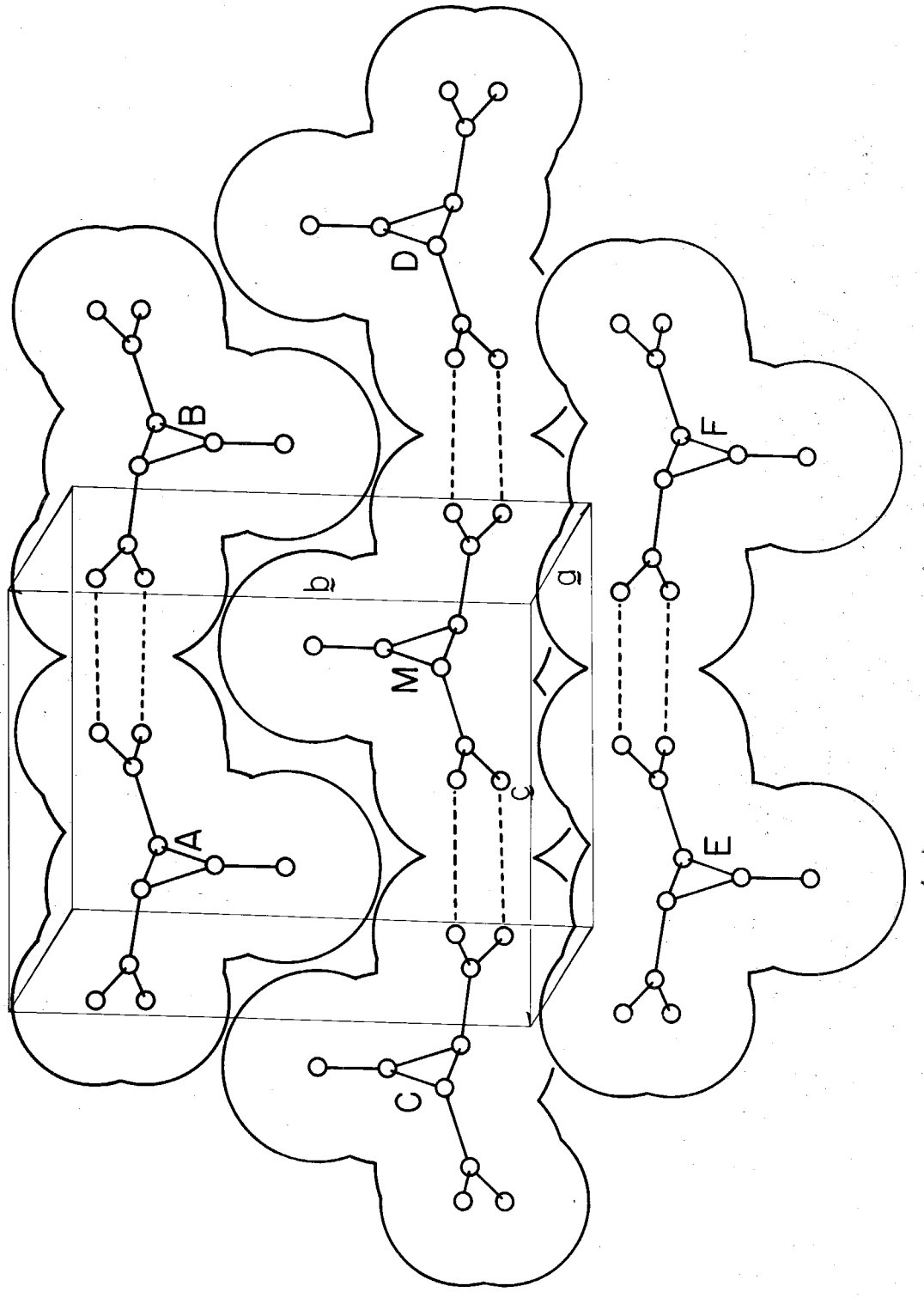
The contact distances between neighboring molecules are of interest. Only those intermolecular contacts on the order of 4 Å or less in length are given. Figure 11 shows the method of identifying molecules, and the lengths of the significant intermolecular contacts are listed in Table 14. The primed molecules are those in the layer directly below the unprimed molecules; thus M' is located at the end of the vector $-\underset{\sim}{a}$ rooted at the molecule M. The double primed

Figure 10



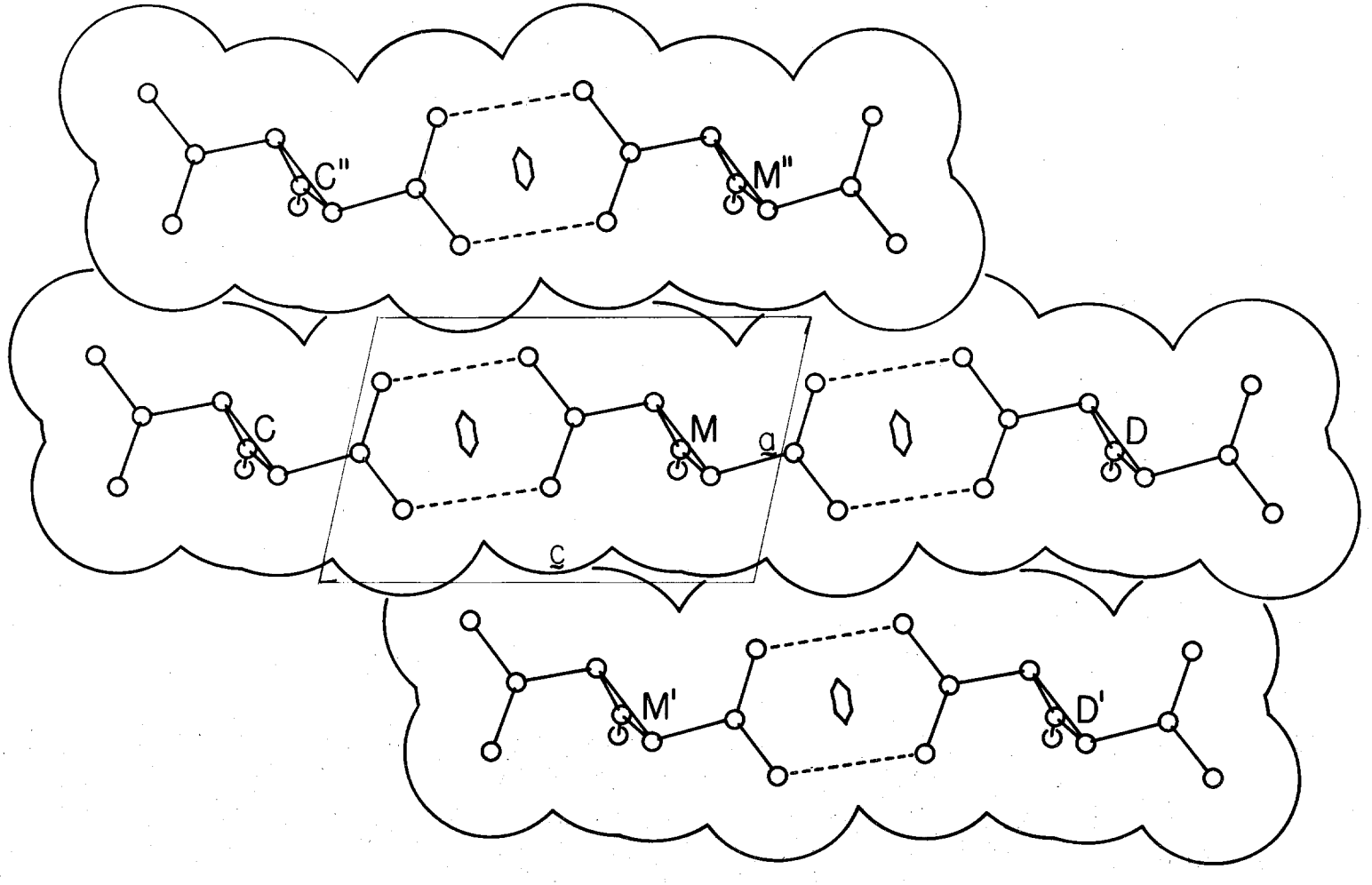
Empirical relation between bond angles in the carboxyl group and double bond character in the carbon-oxygen single bond. Darkened circles are for Feist's acid.

Figure 11



(a) Packing in the (100) plane

Figure 11



(b) Packing in the (010) plane

Table 14

Distances of intermolecular contacts between the molecule M and its neighbors

M to A		M to B	
C_1--C_1	4.01 Å	C_1--C_1	3.68 Å
C_1--C_6	3.85 Å	C_1--C_5	3.78 Å
C_1--O_2	3.73 Å	C_1--O_1	4.05 Å
C_1--O_4	3.94 Å	C_1--O_3	3.55 Å
M to E		**M to F**	
C_6--C_6	3.71 Å	C_5--C_5	3.39 Å
C_4--O_4	3.83 Å	C_3--O_3	3.92 Å
O_2--O_4	3.50 Å	O_3--O_1	3.52 Å
M to M'		**M to D'**	
C_2--O_3	3.57 Å	O_1--O_2	3.16 Å
C_3--O_3	3.40 Å		
C_5--O_3	3.79 Å		
O_4--C_4	3.85 Å	**M to E'**	
O_4--C_6	3.82 Å	O_4--O_4	3.43 Å
O_1--O_3	3.54 Å		
O_4--O_2	3.26 Å		

molecules are in the layer above the unprimed molecules.

Individual molecules of Feist's acid are bound into chains by hydrogen bonding across the carboxyl groups; these chains extend in the $\underset{\sim}{c}$ direction. Each chain is built up of only one enantiomorph and is related to a nearby chain made up of units of the other enantiomorph by a center of symmetry. The double bond of the methylene group is extended in the $\underset{\sim}{b}$ direction, and the resulting shape of the molecule is such that each chain appears to have teeth or cogs if looked down upon in the $\underset{\sim}{a}$ direction (Figure 10). The cogs of two chains interlock to give tight packing. It is interesting to note that each methylene carbon C_1 is nestled in the center of the ring formed by two carboxyl groups in the opposite chain. The van der Waals contact distances of the oxygen atoms are longer than might be expected; the pronounced anisotropy of the oxygens is probably related to this. Also of interest is the root mean square thermal vibration of the atoms; in the $\underset{\sim}{c}$ direction, $\overline{(u_s^2)}^{\frac{1}{2}} = 0.172$ Å, and in the plane normal to $\underset{\sim}{c}$, $\overline{(u_s^2)}^{\frac{1}{2}} = 0.243$ Å. Other directions have values intermediate to these.

3. Significance of the results

The dimensions of the three-membered ring, the position of the double bond, and the trans configuration of the carboxyl groups show that the methylene structure is correct. The results of the ozonolysis experiment must have been

interpreted incorrectly. It is suggested that a thorough investigation of the addition of ozone to Feist's acid and to related compounds[15] might throw light on the general problem of the mechanism of the ozonolysis reaction.

APPENDIX A

Trial structure proposed by Speakman

During the course of this investigation of the crystal structure of Feist's acid, it was learned[25] that a similar investigation was being carried on by Professor J. C. Speakman of the University at Glasgow. Preliminary Fourier projections were shown by him, and a trial structure was based on these projections. The following direct unit cell was given.

Table 15

Direct-cell constants for Feist's acid

$a' = 4.83$ Å	$\alpha' = 95^\circ$
$b' = 7.6$ Å	$\beta' = 96^\circ$
$c' = 9.15$ Å	$\gamma' = 78^\circ$

with two molecules of formula $C_6H_6O_4$ in the unit cell and with space group $P\bar{1}$. Table 16 lists the coordinates of atoms in the trial structure proposed by Speakman.

Table 16

Trial structure proposed by Speakman

Nomenclature of this paper	x'	y'	z'	Nomenclature of Speakman
C_1	-0.16	0.27	0.02	C(4)
C_2	0.14	0.27	0.16	C(3)
C_3	0.26	0.34	0.30	C(5)
C_4	0.39	0.18	0.25	C(2)
C_5	0.32	0.51	0.33	C(6)
C_6	0.41	0.01	0.28	C(1)
O_1	0.20	0.65	0.41	O(4)
O_2	0.59	-0.14	0.25	O(1)
O_3	0.53	0.54	0.28	O(3)
O_4	0.22	-0.01	0.36	O(2)

The unit cell described by Speakman is related to that used in this investigation (Table 1) by the vector equations

$$\underset{\sim}{a} = -\underset{\sim}{a}'$$
$$\underset{\sim}{b} = \underset{\sim}{a}' + \underset{\sim}{c}'$$
$$\underset{\sim}{c} = \underset{\sim}{b}'$$

Similarly the reciprocal cells are related by

$$\underset{\sim}{a}^* = -\underset{\sim}{a}'^* + \underset{\sim}{c}'^*$$
$$\underset{\sim}{b}^* = \underset{\sim}{c}'^*$$
$$\underset{\sim}{c}^* = \underset{\sim}{b}'^*$$

The atomic coordinates in direct space will transform in the

same way reciprocal axes do; the transformation of Speakman's atomic coordinates to the system used in this paper was carried out. It was necessary to add $\frac{1}{2}$ to each coordinate value so found and to invert each resulting atomic position through a center of symmetry before comparable values were obtained. The trial structure proposed by Speakman is given in Table 7 on Page 26 and should be compared with the trial structure found independently (Table 6) and with the final atomic parameters (Table 9).

APPENDIX B

Values of the observed and the calculated structure factors

The number representing the observed structure factor $|F_o|$ for the reflection hkℓ was found from the intensity of the reflected x-ray beam from a small crystal of Feist's acid as described on Page 12. The calculated structure factor F_c is a function of the positions of the atoms in the unit cell and the scattering capabilities of these atoms. Ideally $|F_o|$ and $|F_c|$ should be equal for each given reflection, but the limits of experimental accuracy prevent this; some function of the differences F_o-F_c for all reflections is usually used as a measure of the quality of a structure determination.

The third column lists values of a function F(H); this function is the contribution of the scattering by hydrogen atoms to the calculated structure factor. The terms F_c in the second column already contain this contribution. Where no value is listed for F(H), it is negligibly small. No values of F(H) were calculated for reflections with $\sin\theta > 0.5$.

The value of $|F_o|$ corresponding to the lowest observed intensity averaged somewhat less than unity. Any reflection with an unobservably small intensity was given one-half the minimum observable intensity; the resulting values of $|F_o|$ are all less than unity in Table 17.

Table 17

Comparison of observed and calculated structure factors

	$\|F_o\|$	F_c	F(H)
00ℓ			
1	2.05	2.28	.56
2	6.76	6.29	-3.58
3	8.16	- 8.14	.46
4	7.75	9.32	- .94
5	1.43	- .29	- .50
6	13.54	12.55	
7	3.89	- 4.70	
8	5.44	6.07	
9	3.59	- 2.74	
01ℓ			
0	31.03	19.50	- .72
1	4.92	- 3.24	.54
2	19.25	20.12	- .24
3	10.80	10.68	- .74
4	.90	.76	- .16
5	.64	- 1.43	.16
6	17.71	17.71	
7	5.31	6.36	
8	4.24	3.34	
9	1.24	.13	
02ℓ			
0	47.49	-46.64	- .36
1	23.84	22.38	.14
2	10.79	-10.99	- .10
3	14.20	-16.14	- .52
4	3.87	- 3.28	- .30
5	6.39	6.37	
6	5.51	- 5.22	
7	5.25	4.28	
8	1.60	- 1.25	
9	4.37	5.08	
03ℓ			
0	45.35	-35.10	-2.82
1	3.44	2.26	.08
2	9.92	- 9.61	-1.68
3	6.29	4.30	.08
4	9.45	-10.47	1.34
5	5.66	- 4.96	
6	16.48	-16.79	
7	3.06	3.59	
8	1.50	- 1.63	

	$\|F_o\|$	F_c	F(H)
04ℓ			
0	5.30	7.80	.58
1	5.29	6.26	- .18
2	5.91	4.65	- .06
3	14.36	15.37	- .10
4	9.12	- 9.81	
5	6.15	- 4.42	
6	4.60	- 4.38	
7	2.11	- 2.77	
8	.63	- .49	
05ℓ			
0	.89	.28	- .68
1	4.00	5.45	.02
2	9.20	9.18	.44
3	5.37	8.21	
4	1.52	1.15	
5	1.94	- 1.72	
6	3.75	4.96	
7	2.72	- 2.02	
8	1.07	1.52	
06ℓ			
0	1.97	- 5.04	- .48
1	.63	.12	.24
2	.65	- 1.21	
3	4.11	- 5.69	
4	7.26	9.13	
5	2.45	2.65	
6	.65	.97	
7	.65	- .75	
07ℓ			
0	3.96	- 5.12	
1	7.26	- 9.51	
2	1.74	- .67	
3	2.52	- .28	
4	3.90	3.43	
5		- .41	
6		- 1.23	
08ℓ			
0	1.07	3.50	
1	1.56	- 2.20	
2	1.96	- .54	
3	.65	.09	
4	.63	- .61	
5		1.95	
6		.77	

	$\lvert F_o \rvert$	F_c	F(H)
09ℓ			
0	1.75	2.68	
1	3.01	- 2.22	
2	1.40	- 1.04	
3	.65	1.51	
4	.63	.73	
5		- .56	
0.10.ℓ			
0	.89	- 1.76	
1	.63	1.37	
2	.65	.40	
3	1.55	- 2.28	
0.11.ℓ			
0	1.25	.48	
1	1.43	1.13	
2		- 1.31	
10ℓ			
0	47.24	-48.40	.10
1	3.50	- 3.41	- .04
2	1.20	- .76	-3.28
3	4.72	5.69	- .90
4	18.57	-19.93	.92
5	1.70	- 2.21	
6	11.86	-11.61	
7	2.68	3.26	
8	3.09	- 3.57	
9		- 1.66	
11ℓ			
0	13.55	13.96	1.24
1	23.91	23.22	- .78
2	6.85	- 7.68	.04
3	19.54	18.47	- .08
4	4.80	- 3.87	- .18
5	3.44	- 1.34	
6	6.53	- 5.93	
7	6.68	- 6.23	
8	1.19	- 1.56	

	$\|F_o\|$	F_c	F(H)
12ℓ			
0	13.52	-12.34	-2.82
1	2.28	2.48	.14
2	10.79	9.73	.28
3	17.80	18.49	- .76
4	6.01	5.49	
5	8.12	- 7.94	
6	1.57	1.63	
7	1.38	.39	
8	2.40	2.24	
13ℓ			
0	18.44	-19.46	-1.92
1	.64	- .34	- .12
2	10.56	10.25	1.32
3	7.74	- 9.06	.26
4	4.33	3.92	
5	2.71	3.00	
6	1.52	1.38	
7	.66	0.00	
8	1.22	.95	
14ℓ			
0	1.43	1.56	.46
1	9.33	-11.31	- .46
2	5.03	- 3.44	- .38
3	3.95	- 4.64	
4	5.37	3.52	
5	4.50	3.29	
6	1.38	- 1.69	
7	.66	- .59	
15ℓ			
0	7.92	11.22	.42
1	8.28	- 6.75	
2	6.00	- 5.70	
3	3.76	3.33	
4	4.53	3.40	
5	1.91	1.31	
6	1.90	1.78	
7	1.79	- 2.19	
16ℓ			
0	1.22	- .40	
1	6.49	- 4.73	
2	1.27	.71	
3	.66	1.84	
4	1.05	1.62	
5		- 1.28	
6		2.72	

	$\lvert F_o \rvert$	F_c	F(H)
17ℓ			
0	1.09	- 2.00	
1	1.58	1.25	
2	.66	.27	
3	4.87	- 6.13	
4	1.32	- .49	
5		.98	
18ℓ			
0	2.33	.96	
1	1.61	.26	
2	2.42	- 1.73	
3	.66	- .77	
4	1.64	- 2.02	
5		- .64	
19ℓ			
0	1.29	1.82	
1	4.84	4.14	
2	.66	- .56	
3	.66	1.20	
1.10.ℓ			
0	.93	1.14	
1	.64	1.29	
2		- .54	
20ℓ			
0	9.44	- 9.42	-1.48
1	5.73	- 6.69	-1.40
2	5.91	4.26	.20
3	4.50	- 5.03	.48
4	3.85	3.62	
5	3.89	4.13	
6	5.04	- 4.21	
7	1.28	- 2.25	
8	3.36	2.96	
21ℓ			
0	2.09	- .60	.60
1	11.12	-12.74	- .70
2	1.15	1.18	- .46
3	2.25	2.45	
4	1.62	- 1.53	
5	1.52	- .13	
6	1.44	- .77	
7	1.63	1.01	

	$\|F_o\|$	F_c	F(H)
22ℓ			
0	12.66	13.58	- .28
1	2.48	3.30	- .68
2	6.99	- 6.33	.56
3	1.40	- 1.62	
4	5.01	4.70	
5	3.55	3.13	
6	6.35	5.16	
7	1.36	- 2.28	
23ℓ			
0	5.37	4.18	.32
1	10.93	- 9.76	.50
2	4.83	- 3.75	
3	1.70	- .55	
4	7.29	7.37	
5	.64	- .90	
6	3.18	2.55	
7		- .26	
24ℓ			
0	4.45	- 5.10	
1	7.93	- 7.64	
2	2.43	2.60	
3	5.86	- 6.39	
4	2.10	- 1.74	
5	.64	.41	
6	.65	- .40	
25ℓ			
0	1.46	.68	
1	4.59	2.30	
2	1.27	- .85	
3	2.57	- 1.77	
4	4.80	- 4.70	
5	.64	0.00	
6	.65	- 2.21	
26ℓ			
0	4.75	5.04	
1	8.40	9.31	
2	3.29	- 2.98	
3	1.56	2.38	
4	2.11	- 2.16	
5	.64	.51	

	$\|F_o\|$	F_c	F(H)
27ℓ			
0	1.28	.28	
1	1.99	2.67	
2	.66	.17	
3	2.22	2.84	
4	.80	.26	
28ℓ			
0	1.75	- 2.24	
1	.63	- .71	
2	2.09	2.12	
3	.74	- 1.77	
29ℓ			
0		- .12	
1	1.99	- 2.67	
30ℓ			
0	.63	- .46	- .12
1	9.40	-10.71	
2	1.26	1.29	
3	3.53	- 3.28	
4	4.27	4.13	
5	1.06	- 1.21	
6	4.66	4.61	
7		1.53	
31ℓ			
0	1.76	2.40	
1	11.47	-10.26	
2	1.37	- 1.15	
3	8.38	- 9.32	
4	1.43	- 1.29	
5	3.03	2.93	
6	.63	.20	
32ℓ			
0	1.24	1.10	
1	1.36	- 2.18	
2	2.91	- 2.60	
3	.64	1.42	
4	3.84	- 3.50	
5	1.35	- 1.41	
6	2.73	- 2.95	

	$\|F_o\|$	F_c	F(H)
33ℓ			
0	1.08	.64	
1	14.05	14.16	
2	.64	- .44	
3	2.98	2.76	
4	3.08	- 2.84	
5	.62	.03	
34ℓ			
0	3.29	1.66	
1	6.27	6.36	
2	.64	0.00	
3	1.70	2.12	
4	.62	.47	
5	.62	.62	
35ℓ			
0	.63	- .90	
1	3.25	- 2.67	
2	1.70	1.87	
3	1.15	- 1.16	
4	.62	- .56	
36ℓ			
0	2.11	- 1.22	
1	2.86	- 3.62	
2	1.47	.67	
3		- .98	
37ℓ			
0	.73	- .24	
1	.61	.57	
2		- .04	
40ℓ			
0	.61	.86	
1	11.59	11.47	
2	1.59	- 1.69	
3	2.02	1.49	
4	1.43	.56	
5	.60	.98	
41ℓ			
0	1.44	- 1.04	
1	5.48	4.00	
2	2.32	2.02	
3	4.09	3.89	
4	.60	- .35	
5	.60	- .44	

	$\lvert F_o \rvert$	F_c	F(H)
42ℓ			
0	1.02	.24	
1	1.14	- .10	
2	2.26	2.02	
3	1.67	- 1.51	
4	2.71	- 2.35	
43ℓ			
0	.61	.68	
1	3.42	- 3.23	
2	1.04	- .96	
3	1.78	- .96	
44ℓ			
0	2.38	- 1.88	
1	.59	.04	
2	.62	.50	
45ℓ			
0	.95	- .54	
1	.59	- .10	
50ℓ			
0	.94	- .94	
1	1.23	- 1.33	
2	.78	.62	
3	.62	- .37	
51ℓ			
0	1.32	- .88	
1	1.29	1.21	
2	.62	.25	
52ℓ			
0	.61	- .26	
1	1.70	- 1.78	
$01\bar{\ell}$			
1	6.59	4.65	- .88
2	24.70	25.20	.40
3	33.16	-35.53	.90
4	8.96	- 9.53	.54
5	9.09	- 8.16	- .10
6	.65	2.55	
7	.65	- .59	
8	2.74	- 2.62	
9	7.47	- 8.14	

	$\lvert F_o \rvert$	F_c	F(H)
$02\bar{\ell}$			
1	14.66	-14.33	.92
2	27.02	-24.27	1.98
3	15.94	-16.58	.42
4	1.88	3.00	- .66
5	5.45	- 4.71	- .42
6	9.25	-10.03	
7	1.97	1.18	
8	1.96	- .83	
9	1.33	- 1.21	
$03\bar{\ell}$			
1	5.11	- 3.54	-1.78
2	21.53	-24.13	3.48
3	14.11	14.56	.60
4	.64	.41	- .60
5	10.91	11.27	
6	2.51	3.38	
7	4.29	- 3.26	
8	3.25	- 3.64	
9	5.40	4.68	
$04\bar{\ell}$			
1	5.55	- 5.46	.58
2	10.84	-11.75	- .84
3	16.55	21.71	- .48
4	3.58	3.10	.24
5	9.32	11.27	
6	4.31	3.50	
7	1.91	- 2.77	
8	2.72	- 2.62	
9	.65	1.17	
$05\bar{\ell}$			
1	2.21	- 3.53	- .66
2	5.69	5.97	- .44
3	2.31	1.43	.12
4	3.17	1.34	
5	1.85	1.90	
6	1.98	- 3.12	
7	2.75	2.25	
8	.63	- 1.75	
9		- 3.01	

	$\lvert F_o \rvert$	F_c	F(H)
06$\bar{\ell}$			
1	1.64	1.31	.36
2	2.56	1.94	- .12
3	2.59	- 5.19	
4	4.56	4.81	
5	.64	- 2.31	
6	4.59	- 7.14	
7	.65	1.27	
8	2.23	2.43	
07$\bar{\ell}$			
1	4.08	4.34	
2	6.46	6.64	
3	2.36	2.23	
4	3.61	- 3.48	
5	1.89	- 2.41	
6	.65	2.38	
7	1.65	- 1.21	
8	.63	- .34	
08$\bar{\ell}$			
1	3.64	- 3.78	
2	.65	2.06	
3	5.29	7.18	
4	.63	.38	
5	3.47	- 4.78	
6	1.63	- .57	
7	.65	- .91	
09$\bar{\ell}$			
1	.63	.40	
2	1.40	.60	
3	3.89	- 4.81	
4	1.09	.63	
5	.64	- .23	
6		- .75	
0.10.$\bar{\ell}$			
1	.63	- .28	
2	1.06	.52	
3	1.87	- 3.59	
4	.80	- .73	
5		- .95	

	$\lvert F_o \rvert$	F_c	F(H)
0.11.$\bar{\ell}$			
1	1.13	1.47	
2	.65	- 1.27	
3		.18	
4	.63	- .75	
10$\bar{\ell}$			
1	6.67	- 4.42	1.36
2	3.00	.09	4.44
3	27.05	23.69	.08
4	12.09	-12.98	-1.36
5	9.05	8.00	.04
6	7.36	7.34	
7	1.91	- 1.86	
8	1.82	- 2.24	
9	2.97	1.35	
11$\bar{\ell}$			
1	25.76	-29.22	.88
2	16.34	-16.51	-2.06
3	37.18	33.78	- .24
4	9.40	10.85	.80
5	13.85	13.36	.06
6	6.36	- 6.36	
7	4.82	- 5.58	
8	.64	.80	
9	1.18	1.08	
12$\bar{\ell}$			
1	3.55	2.93	.04
2	1.91	2.88	1.90
3	5.90	- 5.73	.18
4	6.75	6.51	.66
5	7.65	7.27	.18
6	4.97	- 4.38	
7	1.38	- .72	
8	6.88	- 7.21	
9	.66	- .54	

	$\lvert F_o \rvert$	F_c	F(H)
13$\bar{\ell}$			
1	3.48	3.34	- .20
2	1.29	- 3.01	- .22
3	1.00	- 1.67	- .38
4	4.68	6.18	.52
5	4.87	- 5.03	
6	3.63	- 4.38	
7	4.80	5.71	
8	.64	- .34	
9	.93	1.53	
14$\bar{\ell}$			
1	5.92	6.12	- .08
2	9.03	7.33	- .02
3	9.37	9.12	.28
4	4.10	- 4.46	- .28
5	2.27	- 1.41	
6	.66	1.26	
7	.66	.03	
8	4.22	3.68	
9	3.57	4.23	
15$\bar{\ell}$			
1	1.07	- 1.38	.20
2	8.47	10.06	-1.02
3	4.89	6.15	
4	2.44	- 3.17	
5	5.24	- 3.85	
6	2.67	- 1.72	
7	4.22	- 3.82	
8	1.52	3.19	
9		.90	
16$\bar{\ell}$			
1	2.17	- 1.68	
2	4.99	7.27	
3	6.83	- 7.33	
4	1.54	- .82	
5	7.01	- 7.32	
6	.66	- .77	
7	1.18	- 1.47	
8		- 1.10	

	$\lvert F_o \rvert$	F_c	F(H)
17$\bar{\ell}$			
1	3.08	- 2.22	
2	3.45	- 4.12	
3	4.51	- 5.82	
4	3.58	3.90	
5	2.05	- 3.95	
6	.66	- .52	
7		1.34	
8	.64	2.31	
18$\bar{\ell}$			
1	4.72	4.36	
2	1.31	- 2.52	
3	2.41	- 1.51	
4	1.75	- 2.32	
5	4.36	5.29	
6	3.61	4.90	
7	.87	.59	
19$\bar{\ell}$			
1	1.82	1.27	
2	.66	- .02	
3	3.30	4.86	
4	2.55	- 3.01	
5	.65	2.34	
6	.88	1.35	
1.10.$\bar{\ell}$			
1	1.25	1.37	
2	1.50	- 1.21	
3		- .24	
4		.16	
20$\bar{\ell}$			
1	5.20	5.41	
2	24.16	-23.59	.58
3	5.97	6.44	.84
4	13.79	15.16	.32
5	1.86	1.46	
6	5.07	- 6.39	
7	1.46	1.70	
8	.63	.57	
9	4.53	5.26	

	$\lvert F_o \rvert$	F_c	F(H)
$21\bar{\ell}$			
1	13.01	13.24	.64
2	14.17	15.73	- .16
3	8.50	7.79	- .06
4	10.33	-11.96	- .06
5	8.48	8.24	
6	5.85	5.22	
7	.65	.85	
8	4.15	1.10	
9	1.72	2.47	
$22\bar{\ell}$			
1	6.62	- 6.77	.16
2	18.26	18.38	-1.50
3	8.74	7.58	- .06
4	4.70	- 4.33	1.16
5	9.51	- 7.68	
6	5.00	- 5.13	
7	.65	.36	
8	4.05	4.93	
9	1.63	- 1.89	
$23\bar{\ell}$			
1	1.03	1.18	- .54
2	6.22	6.59	- .22
3	14.56	-14.91	.10
4	1.39	1.08	
5	13.17	-13.61	
6	3.80	- 2.61	
7	4.82	- 3.75	
8	.63	- .34	
9	.65	- 1.08	
$24\bar{\ell}$			
1	1.77	- 1.09	
2	3.23	- 3.52	
3	9.24	- 8.14	
4	2.73	3.03	
5	6.89	- 8.63	
6	3.93	3.04	
7	.65	- .03	
8	1.93	2.12	
9	.65	- .85	

	$\lvert F_o \rvert$	F_c	F(H)
25$\bar{\ell}$			
1	1.81	1.25	
2	2.09	- 2.35	
3	1.56	1.99	
4	1.71	- 1.81	
5	6.81	7.04	
6	5.00	5.90	
7	2.51	1.86	
8	2.19	2.62	
26$\bar{\ell}$			
1	3.91	2.57	
2	3.31	- 1.96	
3	3.50	4.66	
4	2.14	- 2.25	
5	6.54	8.11	
6	.65	.49	
7	2.50	3.10	
8	.79	- .27	
27$\bar{\ell}$			
1	3.84	4.34	
2	1.65	- 1.48	
3	1.50	- 1.77	
4	3.05	- 2.49	
5	1.37	1.49	
6	.65	- .83	
7	1.16	1.31	
28$\bar{\ell}$			
1	2.31	- 2.06	
2	1.09	- 1.96	
3	.66	- .61	
4	.64	.87	
5	2.00	- 3.88	
6	.93	- 1.89	
29$\bar{\ell}$			
1	1.56	- 2.12	
2	.66	- .37	
3	1.06	- 1.16	
4	1.00	1.50	

	$\|F_o\|$	F_c	F(H)
30$\bar{\ell}$			
1	3.05	.68	- .92
2	8.94	9.37	
3	11.72	-12.72	.32
4	6.76	- 6.76	
5	17.94	-18.80	
6	3.39	3.67	
7	2.06	- 1.08	
8	1.86	- 2.35	
9	1.77	- 2.07	
31$\bar{\ell}$			
1	6.00	- 5.43	- .12
2	7.02	- 6.62	
3	4.57	- 3.74	
4	5.98	4.98	
5	13.73	-13.38	
6		1.12	
7		- .16	
8		6.98	
9		- .09	
32$\bar{\ell}$			
1	4.41	4.08	
2	1.53	1.81	
3	2.24	- 1.53	
4	.62	- .89	
5	10.74	11.15	
6	5.63	5.39	
7		- .42	
8		3.34	
9		.85	
33$\bar{\ell}$			
1	3.34	1.56	
2	1.28	1.35	
3	6.48	5.89	
4	3.82	- 2.21	
5	9.39	9.07	
6	2.46	.75	
7		4.90	
8		- 2.05	
34$\bar{\ell}$			
1	3.80	4.28	
2	7.50	- 6.95	
3	.64	- 1.09	
4	2.45	- 1.17	
5	1.78	1.67	
6	1.31	- 1.15	
7		1.50	
8		- 5.84	

	$\lvert F_o \rvert$	F_c	F(H)
$35\bar{\ell}$			
1	1.41	- .44	
2	3.99	- 5.00	
3	3.14	- 2.14	
4	.62	- .66	
5	2.26	- 3.00	
6	1.23	- .60	
7		- .65	
$36\bar{\ell}$			
1	2.80	- 3.15	
2	2.16	1.79	
3	1.34	- .83	
4	.62	.16	
5		.44	
6		.29	
7		- 2.06	
$37\bar{\ell}$			
1	3.00	- 3.15	
2	1.22	2.48	
3	1.88	1.95	
4		2.28	
5		.49	
$38\bar{\ell}$			
1	.61	.91	
2	.64	.06	
3	.64	- .04	
$40\bar{\ell}$			
1	3.78	3.03	
2	.62	- 1.10	
3	3.81	3.06	
4	3.19	3.48	
5	7.47	7.86	
6	3.06	- 2.89	
7	1.66	1.99	
8	.84	- .49	
$41\bar{\ell}$			
1	3.91	4.67	
2	5.88	- 5.89	
3	1.35	- .92	
4	4.62	- 3.59	
5	3.95	3.13	
6		2.55	
7		- .78	
8		- 7.82	

	$\lvert F_o \rvert$	F_c	F(H)
$42\bar{\ell}$			
1	3.19	- 3.84	
2	6.49	- 6.66	
3	.62	1.14	
4	2.06	- 1.29	
5	3.57	- 3.11	
6	.61	.03	
7		.95	
8		- 1.14	
$43\bar{\ell}$			
1	2.23	- 1.70	
2	.62	.58	
3	3.59	- 3.02	
4	1.95	1.15	
5	1.40	2.49	
6	1.75	- 1.12	
7		- 1.73	
$44\bar{\ell}$			
1	1.56	- 1.68	
2	4.13	4.58	
3	.62	.85	
4	1.15	1.31	
5	.60	.08	
6	.61	- .95	
$45\bar{\ell}$			
1	1.54	- .20	
2	.62	.19	
3	2.44	1.71	
4	1.36	1.67	
5	1.17	- 1.39	
$46\bar{\ell}$			
1		- .06	
2		- 1.02	
3	.62	.92	
4		.77	
$50\bar{\ell}$			
1	.59	- .95	
2	1.40	1.42	
3	3.05	- 2.56	
4	.60	- .12	
5	.97	1.77	
6	.97	.43	
7		.75	

	$\lvert F_o \rvert$	F_c	F(H)
$51\bar{\ell}$			
1	.59	- 1.09	
2	2.32	1.83	
3	.62	.70	
4	1.74	2.25	
5		- 1.16	
6		- 2.38	
$52\bar{\ell}$			
1	.59	.93	
2	.62	.35	
3	1.32	.63	
4	.60	.16	
5	.60	- .54	
6	.61	.03	
$53\bar{\ell}$			
1	1.49	- 1.35	
2	.62	.54	
3	2.00	2.19	
4		.07	
$11\bar{\ell}$			
0	21.75	-17.58	1.42
1	6.12	- 3.58	2.34
2	12.14	-12.56	- .44
3	16.09	-15.59	.40
4	1.17	- 1.20	.02
5	4.82	4.98	
6	6.66	- 7.68	
7	6.53	5.61	
8	1.97	2.50	
9		2.56	
$12\bar{\ell}$			
0	29.06	26.48	- .88
1	21.57	20.78	1.00
2	16.09	17.45	.94
3	9.60	- 9.91	- .92
4	2.71	2.08	- .46
5	1.24	- .33	
6	15.61	16.91	
7	3.85	4.50	
8	2.42	2.20	
0		2.29	

	$\lvert F_o \rvert$	F_c	F(H)
$13\bar{\ell}$			
0	61.61	68.22	3.84
1	9.17	9.95	1.02
2	15.39	15.61	.10
3	4.53	2.73	.96
4	4.74	5.41	- .48
5	9.03	- 8.27	
6	15.74	13.04	
7	.66	- .85	
8	3.10	3.79	
9		- 2.83	
$14\bar{\ell}$			
0	14.01	16.20	.48
1	5.79	- 8.99	-1.80
2	6.17	5.86	- .34
3	10.17	-10.37	.66
4	1.76	- 2.23	.16
5	4.48	- 4.70	
6	5.54	- 3.18	
7	3.07	- 2.97	
8	1.03	.80	
9		- 5.89	
$15\bar{\ell}$			
0	21.01	-22.16	- .92
1	7.48	- 8.81	.26
2	13.04	-14.07	.42
3	10.41	-12.96	.36
4	2.17	- .94	
5	5.31	5.57	
6	7.67	- 7.85	
7	2.98	- 2.90	
8	2.96	- 2.28	
$16\bar{\ell}$			
0	19.14	-21.68	- .84
1	4.12	- 2.70	- .78
2	8.96	-11.03	.48
3	4.85	5.56	
4	3.72	- 2.61	
5	4.42	5.11	
6	3.17	4.24	
7	.66	1.80	
8	3.65	- 5.12	

	$\lvert F_o \rvert$	F_c	F(H)
$1\bar{7}\ell$			
0	5.73	6.84	
1	2.09	- .53	
2	8.13	- 9.45	
3	7.31	11.09	
4	4.93	5.52	
5	1.54	2.98	
6	1.66	1.15	
7	1.57	.88	
8		.30	
$1\bar{8}\ell$			
0	3.00	3.46	
1	4.65	3.62	
2	4.35	5.33	
3	2.40	- 1.49	
4	1.27	- .38	
5	2.17	2.62	
6		- .43	
7	.66	- 1.11	
$1\bar{9}\ell$			
0	2.28	- 3.58	
1	1.83	- 3.19	
2	5.28	5.52	
3	2.07	- .02	
4	.64	.16	
5	1.81	- 2.72	
6		- 3.41	
$1.\bar{10}.\ell$			
0	.65	- 1.52	
1	.64	- .02	
2	.66	.46	
3	1.23	.57	
4	.64	.87	
5	.65	- 1.31	
6		- .54	
$1.\bar{11}.\ell$			
0	.83	.54	
1	.64	.08	
2	1.05	- .33	
3	.66	1.47	
4	.64	.19	

	$\|F_o\|$	F_c	F(H)
$2\bar{1}\ell$			
0	31.40	-27.58	-1.66
1	7.99	8.09	1.30
2	13.46	12.52	.22
3	10.77	10.37	-1.18
4	4.39	2.56	
5	4.94	- 4.44	
6		1.60	
7		- .07	
8		- 1.40	
$2\bar{2}\ell$			
0	2.46	- 2.04	.38
1	8.34	10.83	.12
2	10.38	- 9.14	.04
3	17.50	17.95	- .30
4	2.91	2.49	
5	6.79	- 4.65	
6		- 4.44	
7		- 1.57	
8		- 1.93	
$2\bar{3}\ell$			
0	4.90	- 4.54	1.50
1	1.77	2.70	.60
2	9.96	- 6.86	- .66
3	3.14	.35	- .50
4	10.38	-11.11	
5	4.50	1.98	
6	7.84	- 7.28	
7		.03	
8		- .99	
$2\bar{4}\ell$			
0	3.51	- 2.60	.30
1	1.87	- 1.44	.54
2	3.23	3.24	- .42
3	11.58	-11.90	.70
4	8.89	- 8.59	
5	5.18	4.29	
6	.65	- 1.40	
7		2.90	
8		1.59	

	$\|F_o\|$	F_c	F(H)
$25\bar{\ell}$			
0	7.00	7.48	- .26
1	3.59	3.37	.36
2	10.62	12.64	.50
3	1.27	- 2.34	
4	2.60	1.90	
5	4.88	- 5.26	
6	7.17	8.40	
7	4.36	5.55	
8		2.35	
$26\bar{\ell}$			
0	19.67	23.16	- .06
1	6.39	7.47	
2	2.87	1.52	
3	1.53	- .22	
4	8.32	9.58	
5	4.56	- 4.11	
6	3.33	4.33	
7	1.60	- 1.73	
8		2.73	
$27\bar{\ell}$			
0	1.34	1.50	
1	.63	- .14	
2	3.31	3.04	
3	3.75	- 3.96	
4	2.68	- 3.43	
5	.64	.13	
6	.65	.80	
7		- 3.39	
$28\bar{\ell}$			
0	5.83	- 6.40	
1	7.76	- 8.87	
2	6.65	- 7.04	
3	.66	- 1.66	
4	2.32	- 2.18	
5	1.44	2.23	
6	2.97	- 4.24	
7		- .46	
$29\bar{\ell}$			
0	2.25	- 4.78	
1	.63	.95	
2	5.17	- 6.27	
3	1.59	- .83	
4	1.44	- .66	
5	2.32	3.70	
6		.89	

	$\lvert F_o \rvert$	F_c	F(H)
2.$\bar{1}$0.ℓ			
0	.65	.28	
1	1.45	2.00	
2	1.31	- 1.10	
3	1.41	3.37	
4	.64	1.48	
5	.64	.13	
2.$\bar{1}$1.ℓ			
0	1.09	1.54	
1	1.01	.42	
2	2.06	2.42	
3	.66	1.12	
4		.82	
2.$\bar{1}$2.ℓ			
0	.65	- .24	
1	.63	- 1.56	
2	.66	1.71	
3$\bar{1}\ell$			
0	11.15	11.06	- .22
1	5.89	4.41	- .64
2	6.97	- 6.70	
3	1.80	- .37	
4	7.34	7.72	
5	.62	.51	
6		2.32	
7		.16	
3$\bar{2}\ell$			
0	1.22	- .08	.16
1	4.60	1.78	- .22
2	1.60	1.17	
3	2.19	1.97	
4	3.44	- 2.07	
5	2.78	1.54	
6		- .49	
7		- 1.50	
3$\bar{3}\ell$			
0	8.38	- 9.62	.12
1	8.81	- 8.60	- .68
2	6.87	4.98	
3	3.21	2.60	
4	3.01	- 2.25	
5		1.64	
6		- 2.61	
7		- 2.02	

	$\|F_o\|$	F_c	F(H)
$3\bar{4}\ell$			
0	8.59	-12.16	- .38
1	4.35	- 2.94	.74
2	1.65	1.89	
3		6.61	
4	5.23	4.11	
5		- 2.44	
6		- 1.81	
7		.62	
$3\bar{5}\ell$			
0	.63	- 1.14	
1	6.63	9.86	
2	6.10	- 5.70	
3	.64	2.06	
4	3.41	3.45	
5		.08	
6		- 1.81	
7		- .95	
$3\bar{6}\ell$			
0	3.87	- 3.14	
1	2.14	2.53	
2	1.19	1.19	
3		1.01	
4	6.50	- 7.84	
5		- .82	
6		- .72	
7		1.11	
$3\bar{7}\ell$			
0	3.57	4.94	
1	2.69	- 3.37	
2	.64	.40	
3		- 2.17	
4	2.70	- 3.22	
5		.36	
6		- 1.86	
$3\bar{8}\ell$			
0	2.62	2.32	
1	3.34	2.61	
2	4.89	5.73	
3		- 2.91	
4	1.15	.70	
5		- .92	
6		3.41	

	$\lvert F_o \rvert$	F_c	F(H)
$3\bar{9}\ell$			
0	2.42	3.42	
1	.61	1.27	
2	2.40	1.62	
3		.66	
4	3.16	4.27	
5		- 2.44	
$3.\bar{10}.\ell$			
0	.63	1.46	
1	.61	- .10	
2	1.37	- 1.48	
3		- 1.16	
4		- .12	
5		.64	
$3.\bar{11}.\ell$			
0	.95	- 1.22	
1	1.26	- 2.00	
2	2.25	- 2.69	
3		- .98	
$4\bar{1}\ell$			
0	1.76	- .76	
1	.59	- .28	
2	1.40	- 1.23	
3	1.32	- .57	
4	3.12	- 3.31	
5		- .39	
$4\bar{2}\ell$			
0	3.41	4.38	
1	13.08	-11.19	
2	2.32	- 2.17	
3	3.83	- 4.73	
4	2.18	- 1.71	
5		.23	
$4\bar{3}\ell$			
0	3.75	4.12	
1	5.34	- 5.90	
2	1.20	- .50	
3	4.71	- 4.07	
4	3.18	3.26	
5		- .10	
6		2.15	

	$\lvert F_o \rvert$	F_c	F(H)
$4\bar{4}\ell$			
0	.61	1.22	
1	7.54	6.63	
2	1.42	.37	
3	.62	- 1.62	
4	2.78	3.76	
5		1.00	
6		1.55	
$4\bar{5}\ell$			
0	2.76	- 3.58	
1	2.42	.36	
2	1.82	1.25	
3	5.26	5.05	
4	1.30	- .68	
5		- .67	
6		- .63	
$4\bar{6}\ell$			
0	1.01	- .52	
1	3.37	- 3.74	
2	1.52	- 2.04	
3		2.17	
4	.60	- .05	
5		1.72	
$4\bar{7}\ell$			
0	3.07	- 5.30	
1		- 1.60	
2		1.54	
3		.72	
4	.60	- .19	
5		- .10	
$4\bar{8}\ell$			
0	.61	- .70	
1	.59	1.78	
2		- 1.52	
3		.39	
4		1.88	
5		- .95	
$4\bar{9}\ell$			
0	.61	.38	
1		2.85	
2	.62	.31	
3		- .53	
4		- 2.28	

	$\lvert F_o \rvert$	F_c	F(H)
4.$\bar{1}$0.ℓ			
0	.61	1.16	
1	.59	- .79	
2		1.21	
3		.24	
4.$\bar{1}$1.ℓ			
0		.74	
1		- .53	
2		1.48	
5$\bar{1}\ell$			
0	2.61	1.40	
1	1.66	- .36	
2	.90	.17	
3	.62	.66	
5$\bar{2}\ell$			
0	1.32	- .56	
1	4.19	3.19	
2	1.32	1.17	
3	1.95	2.01	
5$\bar{3}\ell$			
0	3.14	- 1.74	
1	5.18	5.33	
2	1.15	.58	
3		.61	
4		.12	
5$\bar{4}\ell$			
0	1.13	1.00	
1	1.76	- 1.31	
2	2.14	- 1.83	
3		- .39	
4		- .87	
5$\bar{5}\ell$			
0	4.03	4.42	
1	4.96	- 3.58	
2	1.99	- 2.17	
3		- 3.68	
4		- 1.13	
5$\bar{6}\ell$			
0	.61	.34	
1	2.09	- 2.97	
2	1.36	1.52	
3		- 1.27	

	$\lvert F_o \rvert$	F_c	F(H)
$5\bar{7}\ell$			
0	.61	.24	
1		1.74	
2		.10	
3		.11	
$5\bar{8}\ell$			
0	1.50	- 2.18	
1		1.58	
2		.48	
3		1.55	
$5\bar{9}\ell$			
0		- .54	
1		- 1.82	
2		- 1.21	
$5.\bar{1}0.\ell$			
0		- .44	
$\bar{1}1\ell$			
1	14.26	15.13	-2.06
2	33.12	-36.38	1.22
3	29.71	-31.66	.26
4	4.30	4.63	-1.50
5	2.20	- 1.61	- .12
6	3.21	- 3.50	
7	.66	- 1.66	
8	1.47	- .76	
9	.99	1.35	
$\bar{1}2\ell$			
1	12.07	-12.73	.68
2	4.10	3.94	.46
3	31.24	-29.66	- .14
4	2.78	1.80	.20
5	12.96	-13.74	- .18
6	2.35	1.89	
7	4.08	3.79	
8	1.81	- 1.63	
9	6.50	- 8.18	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{1}3\ell$			
1	9.99	-10.87	-1.84
2	18.26	19.48	-3.42
3	9.11	- 9.24	.06
4	1.25	.87	.12
5	3.39	3.83	
6	12.89	12.09	
7	2.92	- 3.23	
8	1.39	1.44	
9	5.15	- 4.14	
$\bar{1}4\ell$			
1	3.32	5.20	.68
2	9.66	9.23	- .70
3	6.54	7.75	.18
4	2.50	1.32	.24
5	7.14	6.42	
6	7.99	8.77	
7	.66	.55	
8	3.74	3.72	
9	.66	1.84	
$\bar{1}5\ell$			
1	9.83	11.52	- .56
2	9.34	-11.05	.32
3	2.78	1.50	- .08
4	.94	- .14	
5	.65	- .72	
6	6.42	- 6.02	
7	4.45	4.73	
8	1.55	.95	
$\bar{1}6\ell$			
1	5.64	6.14	.48
2	1.33	- 1.03	.12
3	3.49	1.40	
4	9.61	-10.54	
5	6.17	- 6.65	
6	5.95	- 7.65	
7	3.12	4.54	
8		- 2.73	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{1}7\ell$			
1	4.37	4.02	
2	1.36	1.69	
3	1.52	.61	
4	4.36	- 4.88	
5	.65	.59	
6	1.23	- 2.72	
7	2.20	- 3.23	
$\bar{1}8\ell$			
1	4.27	- 3.49	
2	3.50	3.77	
3	3.12	5.45	
4	2.43	2.54	
5	1.01	- .87	
6	1.02	1.86	
$\bar{1}9\ell$			
1	1.34	.77	
2	1.93	1.10	
3	1.37	- 1.62	
4	2.44	4.06	
5	1.39	1.21	
6		2.32	
$\bar{1}.10.\ell$			
1	1.40	- 2.67	
2	1.67	- 1.77	
3	1.19	- .42	
4	2.13	2.86	
$\bar{1}.11.\ell$			
1	1.15	- 1.88	
2	.66	.31	
3	.78	.50	
$\bar{2}1\ell$			
1	9.76	- 8.65	.90
2	.85	1.67	2.38
3	10.34	8.49	- .72
4	7.32	6.20	- .26
5	6.17	- 4.88	
6	5.37	- 4.33	
7	1.92	2.15	
8	7.91	- 7.44	
9	.65	- .40	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{2}2\ell$			
1	7.72	- 9.13	.10
2	6.15	5.11	- .68
3	11.53	10.56	- .10
4	1.03	1.80	.44
5	11.79	11.68	
6	5.33	- 5.02	
7	6.64	- 7.08	
8	2.17	- 1.25	
9	1.86	1.48	
$\bar{2}3\ell$			
1	1.38	- 2.46	1.32
2	4.62	- 4.55	.24
3	7.89	8.09	- .92
4	6.01	- 4.79	- .68
5	8.39	7.52	
6	.65	.86	
7	1.80	- 2.12	
8	3.89	3.11	
9	.65	- .36	
$\bar{2}4\ell$			
1	2.12	- .73	-1.72
2	17.44	-20.06	.24
3	9.74	-10.68	.46
4	.64	1.31	- .64
5	4.83	- 4.39	
6	2.64	3.04	
7	2.94	1.80	
8	1.24	- .57	
9	2.66	- 1.62	
$\bar{2}5\ell$			
1	1.61	- 2.67	- .14
2	.99	- .75	- .04
3	14.78	-17.68	- .04
4	1.06	.92	
5	4.77	- 5.75	
6	6.12	5.99	
7	.65	.78	
8	3.87	- 4.40	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{2}6\ell$			
1	4.47	- 5.93	- .60
2	5.80	6.83	- .52
3	4.29	- 5.49	
4	6.44	5.14	
5	4.00	3.85	
6	2.67	2.06	
7	2.65	- 3.13	
8	1.49	1.71	
$\bar{2}7\ell$			
1	2.64	- .79	
2		8.97	
3	5.26	7.50	
4	.64	- 1.85	
5	.64	1.41	
6	1.44	2.35	
7	1.98	2.38	
$\bar{2}8\ell$			
1	5.62	9.96	
2	2.91	- 4.37	
3	1.59	- .11	
4	3.04	- 3.05	
5	1.44	.74	
6	1.25	- 1.35	
7	1.08	1.86	
$\bar{2}9\ell$			
1	1.45	1.78	
2	3.53	- 4.58	
3	1.59	.79	
4	2.27	- 2.96	
5	2.40	- 3.80	
6	2.05	- 3.87	
$\bar{2}.10.\ell$			
1	.63	- .32	
2	1.29	2.10	
3	.66	- .35	
4	1.62	- 2.35	
5	.64	- .26	
$\bar{2}.11.\ell$			
1	1.18	- 1.11	
2	1.41	2.19	
3	.66	.85	
4		1.60	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{3}1\ell$			
1	4.42	3.17	.40
2	12.48	11.94	- .30
3	5.88	- 4.84	.30
4	2.59	- 2.47	
5	2.26	.41	
6	5.66	- 5.42	
7	3.01	- 1.86	
8	1.81	1.67	
9	.63	- .22	
$\bar{3}2\ell$			
1	2.74	2.44	.78
2	5.58	7.75	- .22
3	11.91	11.10	- .52
4	.62	- 2.58	
5	9.09	8.60	
6	2.94	- 2.12	
7	3.94	3.43	
8	2.53	2.09	
9	.63	- .04	
$\bar{3}3\ell$			
1	2.51	2.20	.52
2	9.32	- 9.51	.36
3	11.50	12.26	.38
4	4.29	4.79	
5	2.61	1.80	
6	.63	- 1.20	
7	1.87	1.14	
8	2.02	- 1.21	
9	3.51	4.23	
$\bar{3}4\ell$			
1	.61	.32	
2	2.25	- 3.72	.44
3	2.02	3.54	
4	3.06	3.48	
5	2.85	- 3.39	
6	1.44	- 1.98	
7	2.68	- 2.19	
8	2.43	- 4.06	
9	.63	3.24	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{3}5\ell$			
1	4.46	- 5.45	
2	2.90	2.06	
3	1.52	2.03	
4	1.56	2.68	
5	1.52	1.64	
6	4.56	- 5.30	
7	1.56	- 2.51	
8	1.69	1.21	
$\bar{3}6\ell$			
1	.61	- 1.72	
2	2.91	3.50	
3	1.43	- .02	
4	4.32	- 4.74	
5		3.77	
6		2.41	
7		.65	
8		.42	
$\bar{3}7\ell$			
1	2.85	1.01	
2	9.36	-10.68	
3	5.55	- 5.73	
4	1.03	2.32	
5		1.90	
6		2.41	
7		- 1.47	
$\bar{3}8\ell$			
1	4.65	- 4.52	
2	1.50	- 2.17	
3	.64	- 1.90	
4	1.58	2.04	
5		- 4.34	
6		2.32	
7		.69	
$\bar{3}9\ell$			
1	.61	.08	
2	4.76	5.39	
3	.64	- 2.69	
4	.92	.52	
5		1.26	
6		1.23	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{3}.10.\ell$			
1		1.35	
2	1.94	2.75	
3	.64	1.36	
4	.62	- .28	
5		1.34	
$\bar{3}.11.\ell$			
1		2.44	
2	.64	- 1.94	
3	.64	1.12	
4		- 1.69	
$\bar{4}1\ell$			
1	.59	.91	
2	5.75	6.41	
3	2.68	.72	
4	1.83	- .26	
5	1.83	3.88	
6	2.05	2.78	
7	3.76	3.49	
8	4.84	4.10	
$\bar{4}2\ell$			
1	2.69	- 1.98	
2	1.42	- 1.33	
3	5.55	- 5.34	
4	.60	- 1.22	
5	7.94	- 7.76	
6	4.61	4.36	
7	1.25	- 1.04	
8	4.60	4.93	
$\bar{4}3\ell$			
1	3.01	- .48	
2	1.62	- .31	
3	8.77	- 8.10	
4	3.34	- 3.50	
5	10.32	-10.94	
6	2.07	2.46	
7	3.55	- 2.48	
8	.59	- .27	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{4}4\ell$			
1	.59	.20	
2	4.16	5.08	
3	1.44	- 1.01	
4	1.35	- .42	
5	.60	- 1.21	
6	3.55	- 3.87	
7	.61	.62	
8	1.80	- .72	
$\bar{4}5\ell$			
1	4.41	4.10	
2	3.77	6.08	
3	4.12	4.62	
4	1.40	- .92	
5	6.75	7.19	
6	1.95	- 1.92	
7	1.75	1.86	
8		- 1.10	
$\bar{4}6\ell$			
1		.04	
2		- 5.35	
3	5.38	7.61	
4		3.83	
5		1.95	
6		- 2.81	
7		- .23	
$\bar{4}7\ell$			
1		- 1.94	
2		- .21	
3	2.56	3.81	
4		- 1.24	
5		- 4.49	
6		.89	
7		.03	
$\bar{4}8\ell$			
1		.73	
2		.54	
3	4.06	- 3.68	
4		.35	
5		1.28	
6		- .80	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{4}9\ell$			
1		- 1.66	
2		- .40	
3	1.29	- .96	
4		.70	
5		1.62	
$\bar{4}.10.\ell$			
1		- 1.05	
2		- 2.31	
3	.62	- .37	
4		.31	
$\bar{4}.11.\ell$			
1		- .77	
2		- .46	
3	.62	- .39	
$\bar{5}1\ell$			
1	1.29	- 2.71	
2	2.81	- 5.56	
3	1.39	- .07	
4	.60	- .42	
5	.60	1.34	
6	.61	.14	
7		- 1.31	
$\bar{5}2\ell$			
1	.59	.53	
2	4.04	- 4.58	
3	3.48	2.30	
4	1.79	- 1.60	
5	.60	1.21	
6	.61	.54	
7	1.69	- 1.24	
$\bar{5}3\ell$			
1	3.90	3.31	
2	3.34	1.37	
3	2.69	1.75	
4	1.30	1.06	
5	3.51	2.44	
6	.61	- .80	
7		1.86	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{5}4\ell$			
1	2.88	3.03	
2	3.42	3.58	
3	1.50	- 2.71	
4	1.98	.77	
5	1.71	2.23	
6	.61	1.46	
7	2.02	2.15	
$\bar{5}5\ell$			
1	3.84	- 3.66	
2	1.67	- 1.25	
3	1.71	- 2.10	
4	.60	- .19	
5	3.82	- 4.16	
6	1.95	1.86	
7		.33	
$\bar{5}6\ell$			
1		- 1.47	
2		.75	
3	2.85	- 2.98	
4		- 3.97	
5		- 4.49	
6		2.95	
$\bar{5}7\ell$			
1		1.88	
2		0.00	
3	1.38	- 1.14	
4		1.27	
5		.77	
6		- 2.78	
$\bar{5}8\ell$			
1		1.27	
2		2.27	
3	2.75	3.74	
4		.87	
5		1.41	
$\bar{5}9\ell$			
1		.61	
2		- .04	
3	1.34	2.67	
4		- .16	

	$\lvert F_o \rvert$	F_c	F(H)
$\bar{6}1\ell$			
2		.60	
3		1.05	
$\bar{6}2\ell$			
1	.60	.53	
2	.63	.40	
3	1.53	- .57	
4		.61	
$\bar{6}3\ell$			
1		- .34	
2		- .73	
3	1.57	- 1.55	
4		1.62	
$\bar{6}4\ell$			
1	2.55	- 2.81	
2	1.35	- 1.92	
3	1.29	1.40	
4	.76	- .09	
$\bar{6}5\ell$			
1	.60	.83	
2	.63	- .83	
3	1.04	.70	
4		- 2.00	
$\bar{6}6\ell$			
1		2.06	
2		- .60	
3	.89	.39	
4		1.27	

REFERENCES

1. F. Feist, Ber. 26, 747 (1893)
2. D. T. Jones, J. Chem. Soc. 87, 1062 (1905)
3. F. R. Goss, C. K. Ingold, and J. F. Thorpe, J. Chem. Soc. 123, 327 (1923)
4. M. G. Ettlinger, J. Am. Chem. Soc. 74, 5805 (1952)
5. C. K. Ingold, J. Chem. Soc. 121, 2676 (1922)
6. F. R. Goss, C. K. Ingold, and J. F. Thorpe, J. Chem. Soc. 123, 3342 (1923)
7. F. Feist, Ann. 436, 125 (1924)
8. F. R. Goss, C. K. Ingold, and J. F. Thorpe, J. Chem. Soc. 127, 460 (1925)
9. F. B. Thole and J. F. Thorpe, J. Chem. Soc. 99, 2187 (1911) and later papers
10. F. C. Whitmore, Organic Chemistry, Van Nostrand (1937) p. 473
11. J. W. Baker, Tautomerism, Routledge & Sons (1934) p. 164
12. G. A. R. Kon and H. R. Nanji, J. Chem. Soc. 2557 (1932)
13. D. Lloyd, T. C. Downie, and J. C. Speakman, Chem.& Ind. Feb. 20, 1954, p. 222
14. L. Long, Chem. Rev. 27, 437 (1940)
15. J. T. Gragson and others, J. Am. Chem. Soc. 75, 3344 (1953)
16. Professor J. D. Roberts, private communication
17. I. Heilbron, Dictionary of Organic Compounds, Oxford, 3, 361 (1953)
18. D. P. Shoemaker, Thesis, CIT (1947)
19. Chia-si Lu, Rev. Sci. Instrum. 14, 331 (1943)
20. A. J. C. Wilson, Nature 150, 152 (1942)

21. W. A. Wooster, Textbook on Crystal Physics, Cambridge (1938) p. 207

22. E. R. Howells, D. C. Phillips, and D. Rogers, Acta Cryst. 3, 210 (1950)

23. A. L. Patterson, Zeit. f. Krist. 90, 517 (1935)

24. J. D. Morrison and J. M. Robertson, J. Chem. Soc. 980, 987, 993, 1001 (1949)

25. J. C. Speakman, private communication

26. D. Lloyd, T. C. Downie, and J. C. Speakman, Chem. & Ind. April 24, 1954

27. T. C. Downie and J. C. Speakman, Acta Cryst. 7, 649 (1954)

28. E. W. Hughes, J. Am. Chem. Soc. 63, 1737 (1941)

29. V. Schomaker and R. A. Pasternak, unpublished description

30. D. P. Shoemaker and others, J. Am. Chem. Soc. 72, 2378 (1950)

31. D. W. J. Cruikshank, Acta Cryst. 2, 65 (1949)

32. H. G. Pfeiffer, Thesis, CIT (1949)

33. L. Pauling, Nature of the Chemical Bond, Cornell University (1948) p. 171

34. T. H. Goodwin and C. M. Thomson, Acta Cryst. 7, 166 (1954)

35. J. Trommel and J. M. Bijvoet, Acta Cryst. 7, 703 (1954)

36. Professor V. Schomaker, private communication

37. P. Vaughan and J. Donohue, Acta Cryst. 5, 530 (1950)

PROPOSITIONS

1. The structure suggested by Jones* for the tribasic acid $C_9H_8O_8$ is probably incorrect. A more satisfactory structure is proposed.

   *D. T. Jones, J. Chem. Soc. 87, 1062 (1905)

2. Molten sulfur becomes viscous and darkens in color as its temperature is raised to about 230°.* It is proposed that a similar behavior may be observed at a lower temperature if the molten sulfur is bombarded with high energy electrons.

   *L. Pauling, General Chemistry, Freeman & Co. (1953) p. 356

3. It is proposed that an interesting substance for structural analysis is the "two-dimensional" network of silicon atoms recently described.* A procedure is suggested.

   *H. Kautsky and L. Haase, Zeit. f. Nat. 8b, 45 (1953) as reported in Curr. Transl. 2, No. 2-3 (1954) p. 1

4. Concerning the separation of Co(II) from Ni(II) by paper chromatography with a ketone-hydrochloric acid solvent,* it is proposed that:

   (a) the separation is of the molecular species $NiCl_2 \cdot 6HOH$ and H_2CoCl_4; and

   (b) the use of NH_3 is an aid in locating and

identifying ion concentrations.

*T. V. Arden and others, Nature 162, 691 (1948)

5. A recent structure investigation* includes results which indicate that the thiocyanate ion is non-linear. It is proposed that this ion is shown linear by other experimental and theoretical considerations.

*H. Scouloudi, Acta Cryst. 6, 651 (1953)

6. If a crystal shows anisotropic scattering in the direction $\underset{\sim}{a}_i$, the correction for anisotropy to be superimposed on the isotropic temperature effect reduces to $\exp(qh_i^2)$, where q is a constant and h_i is the index associated with $\underset{\sim}{a}_i$.*

*This thesis, p. 33

7. The mechanism for the addition of ozone to carbon-carbon double bonds is not yet clear. It is proposed that:
   (a) an examination of the structures of crystalline ozonides* would give useful evidence; and
   (b) the anomalous ozonolysis of Feist's acid** may aid in the interpretation of the ozone reaction.

*R. Criegee and G. Lohaus, Chem. Ber. 86, 1 (1953)

**This thesis, p. 47

8. The abnormal reaction of ozone with Feist's acid suggests that:
   (a) a careful re-examination of the products of the hydrolysis of the ozonide of methylenecyclopropane* might show the presence of some acetyl-

acetaldehyde or related compounds; and

(b) the establishment of the structures of cyclopropene derivatives** by ozonolysis is not reliable.

*J. T. Gragson and others, J. Am. Chem. Soc. 75, 3344 (1953)

**J. R. Nunn, J. Chem. Soc. 313 (1952)

9. A traveller at point P on the surface of the earth moves 100.00 km due south, then 100.00 km due east, and then 100.00 km due north to find himself again at point P. It is proposed that there is more than one such point from which the traveller might begin.

The following proposition replaces number six on Page 97, which is unsatisfactory:

It is proposed that the experimental evidence* for the stability of $I_2 \cdot M$ compounds is related to the evidence for the effectiveness of M as a third body in the recombination of iodine atoms** and that some of the former evidence may be predicted qualitatively from the latter.

*H. Benesi and J. Hildebrand, J. Am. Chem. Soc. 71, 2703 (1949)

**Russell and Simons, Proc. Roy. Soc. A 217, 271 (1953)