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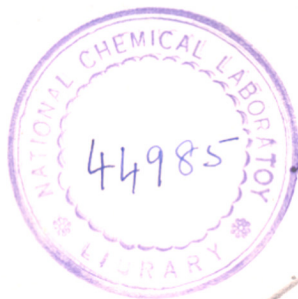
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THE CRYSTAL AND MOLECULAR STRUCTURE
STUDIES OF SODIUM SALTS OF SOME α - KETO ACIDS
BY
X-RAY DIFFRACTION

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S. S. TAVALE
M. Sc.

THE CRYSTAL AND MOLECULAR STRUCTURE STUDIES
OF SODIUM SALTS OF SOME α -KETO ACIDS
BY
X-RAY DIFFRACTION

A THESIS
SUBMITTED TO
THE UNIVERSITY OF POONA
FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

by
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National Chemical Laboratory
POONA 8.
APRIL - 1964

A C K N O W L E D G E M E N T S

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C H A P T E R - 1

INTRODUCTION

The history of crystallography is divisible into two parts: (1) before 1912 and (2) after 1912. Prior to 1912, crystals were studied by optical methods almost exclusively. Haüy, (1784) the founder of modern crystallography enunciated the laws which govern crystal symmetry and paved the way for his later discovery of the law of rational indices in 1801. Further progress was possible after the invention of the reflecting goniometer by Wollaston in 1809. By means of optical goniometers and microscopes thousands of crystals, particularly minerals and some organic compounds, had been investigated. From the great quantity of data thus obtained, a number of laws were deduced in the field of crystallography. Hessel in 1830, showed 32 classes of symmetry in crystals. Bravais in 1848, showed that there are seven crystal systems and 14 Bravais space lattices. Fedorov, Schoenflies and Barlow in 1890-94, had independantly shown, from theoretical considerations, that there are 230 different ways of arranging symmetry elements in a crystal.

The big turning point in crystallography came in 1912. Sommerfeld and Koch believed that X-rays were wave-like radiations, and their discussion of Walter and Pohl's experiments (1908) on passing these rays through various slits led them

to the view that X-rays probably had wavelengths of the order of 10^{-8} cm. With this environment of ideas, Laue thought, it would be interesting to see how X-rays would interact with a crystal. Friedrich and Knipping, in 1912, performed the experiment suggested by Laue, and obtained the remarkable result that X-rays were indeed diffracted by crystals of copper sulphate. In one stroke, then, crystals were shown to be triperiodic arrangements of matter with the periods on a molecular scale, and X-rays were proved to be wave-like radiations similar to visible light.

The year following the discovery of X-ray diffraction saw the publication of the first crystal analysis, that of sodium chloride by W.L. Bragg (1913). In 1914, W.H. Bragg evolved a method of defining and measuring the intensity of reflections satisfactorily. In 1915, he gave the elementary theory of the Fourier analysis of X-ray measurements in Bakerian Lecture of the Royal Society. In the first few years, however, the interest lay principally on the physical side, in the development of the technique of structure analysis and in the experimental verification of the conclusions of diffraction theory. It was not until after the invention of X-ray spectrometer (W.H. Bragg and W.L. Bragg, 1913) and the development of the powder (Debye and Scherrer, 1916; Hull, 1917) and rotation-photograph (Seeman, 1919; Polayni, 1921; Schiebold, 1923) methods of analysis on one hand, and the development of a

rigid X-ray diffraction theory (Darwin, 1914 a, b; Ewald, 1918; Waller, 1925) on the other, that X-ray methods became firmly established as a tool for the structure analysis of the crystals.

The methods of recording and interpreting X-ray diffraction photographs were improved later. Weissenberg (1924), introduced the moving film method of recording and indexing the diffraction patterns. Also Bouman and de Jong (1938), and Buerger (1944), developed the moving film methods for getting undistorted pictures.

Crystallographers are indebted to Niggli (1919), for showing how the space group of a crystal could be determined with the aid of extinctions of certain classes of spectra. He also first compiled the results of space group theory in a form useful for X-ray diffraction purposes. Niggli effected a fortunate redirection of crystal structure analysis, and now it is a part of normal routine, to first determine the unit cell and space group of a crystal preliminary to any attempt to locate the atoms.

Ewald (1921), is responsible for applying the elegant method of 'reciprocal lattice' to the X-ray diffraction, and for showing how exactly it is suited to the problem.

A paper by Bernal in 1926, "on the interpretation of X-ray single crystal rotation photographs" has had a great

influence, in introducing general and accurate methods of solution. Wyckoff, in 1922, described the positions of the symmetry elements in the 230 space groups, and gave the coordinates of equivalent points in general and special positions. Space group tables have also been published by Astbury and Yardley (1924).

R.W. James and J. West (1924), introduced the measurements of absolute intensity as a part of the routine of crystal analysis. For their interpretation it was necessary to know the scattering curves (f curves) for all atoms. Hartree (1925) in Cambridge was at this time engaged in calculating the Bohr orbits for a number of atoms, and he applied his results to the calculation of the scattering curves. The much greater power of intensity measurements was immediately shown. The analysis of the orthorhombic crystal aragonite by Bragg (1924) and of the barytes group by James and Wood may perhaps be classed amongst the first successes of the new methods.

The principles of the Fourier analysis were outlined by W.H. Bragg (1915) and were rediscovered by Duane (1925), and applied by Havighurst (1925) to give representation of scattering density in crystals. Compton in his book "X-rays and Electrons (1926)" introduced absolute intensity measurements into the Fourier expression. Their most complete application has been found in the two-dimensional pictures of the crystal density projected upon a plane of which diopside (W.L. Bragg 1929) is

an example amongst inorganic crystals, and anthracene (J.M. Robertson, 1933) amongst organic crystals.

Success with structure determination is wholly dependant upon a success in determining the phases of reflections. The interatomic vector maps afforded by the two-dimensional Patterson (1935) and the Patterson-Harker (1936) syntheses have been very helpful in determining the phases of reflections for quite complex structures having small proportions of relatively heavy atoms and for structures of more limited complexity containing atoms of approximately equal atomic numbers. The importance of three-dimensional Patterson function for the elucidation of trial structure of molecules and crystals is now being fully realized (Donohue and Trueblood 1953).

A highly interesting direct method, devised by Harker and Kasper (1948) and extended by Gillis (1948 a) whereby inequalities connecting the $|F(hkl)|$ values are used to determine phases of reflections has been shown by Gillis (1948 b) to predict correctly the signs of the structure amplitudes for oxalic acid dihydrate. Other phase determining direct methods are Sayre's (1952), Cochran's (1952), Zachriassen's (1952), Karle and Hauptman's (1950) inequality methods.

F_0 synthesis, both two and three dimensional has been widely used for accurate molecular measurements; a good example of their use can be found in work on the structure of anthracene

by Mathieson, Robertson and Sinclair (1950). The difference synthesis methods suggested by Booth (1948) and Cochran (1951); the method of least squares by Hughes (1941); the method of steepest descents by Booth (1947), and improved by Vand (1948) and Quarshi (1949), are the methods used for the refinement of atomic parameters.

Three methods of computing Fourier syntheses by means of strips are commercially available with the names Beevers-Lipson (1936), Robertson (1936), and Patterson-Tunell (1942). They are commonly used only for one- and two-dimensional Fourier syntheses.

Amongst the optical methods of computing, Bragg-Huggins masks (1941); the sand machine (McLachlan and Champayne) the X-ray microscope (W.L. Bragg, 1939); the Fly's eye (W.L. Bragg, 1944) and Eilers optical photosummator (1951) are well known.

There are two large scale electronic computers designed solely for crystallographic calculations named as X-RAC (Pepinsky, 1947) and S-FAC.

Since 1940, crystallographers have also been using general purpose punched-card computing machines of the International Business Machine Company (I.B.M. machines) and of the British Tabulating Machine Company (Hollerith machines). Since about 1952, this use has been extended to electronic digital computers.

The keto acid analogs of amino acids are of considerable biochemical interest as intermediates in the biosynthesis and degradation of amino acids. The α -keto acid analogs of amino acids are formed in the course of enzymatic oxidative deamination and transamination. α -keto acids capable of enolization may theoretically exist in cis and trans enol forms; and this has been demonstrated experimentally in several instances. (Meister, Fraser and Tice (1954); Anderson and Rasford (1953)).

Although considerable work has been done on the structure of amino acids, very little attention has been given to their α -keto acid analogs. The structure analysis of these compounds is difficult, as many of them are unstable.

With a view to providing structural information which might throw light on their chemical characteristics, the structure analyses of the sodium salts of pyruvic acid, $\text{CH}_3\text{COCOONa}$; α -ketobutyric acid, $\text{CH}_3\text{CH}_2\text{COCOONa}$; and α -ketocaprylic acid, $\text{CH}_3(\text{CH}_2)_5\text{COCOONa}$ were undertaken. It was thought that a comparison of the crystal and molecular structure of sodium pyruvate with those of its higher homologues should be of interest.

Part I and II comprise four chapters on crystal and molecular structures of sodium pyruvate and sodium α -ketobutyrate respectively and part III deals in three chapters on the crystal and molecular structure of sodium α -ketocaprylate.

Chapters II, VI and X are devoted for the crystal data and experimental details such as the determination of unit cell dimensions, density, space group and linear absorption coefficient, estimation and correction of intensities. Chapters III and VII deal with the preliminary structures and Patterson projections, Chapters IV, VIII and XI with the electron density projections and refinement of atomic parameters by different methods, such as Fourier and difference Fourier syntheses and least squares methods, while Chapters V, IX and XII deal with the results and discussions such as bond distances and angles, estimation of errors and crystal and molecular structures.

PART-I: CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM PYRUVATE

CHAPTER - II

CRYSTAL DATA AND EXPERIMENTAL DETAILS

(i) The determination of unit cell dimensions:

Sodium pyruvate, $\text{CH}_3\text{COCOONa}$, was crystallised from aqueous solution. The crystals are monoclinic and grow as very thin plates. A clear crystal was examined through the polarizing microscope for sharp extinction. The dimensions of the crystal were approximately 1.1 mm. along c axis and 0.7 mm. along the b axis. This crystal was used to take the rotation photographs along the three axes. The cell dimensions were determined from these rotation photographs. The values are:

$$a = 22.25 \pm 0.02; \quad b = 5.31 \pm 0.01; \quad c = 3.71 \text{ \AA} \quad \text{and} \\ \beta = 98.2^\circ$$

The β angle was determined from a Laue photograph taken with X-rays travelling parallel to the b axis.

Axial length 'a' was obtained from four observations; i.e. from V, VI, VII and VIII layers of the rotation photograph; 'b' was determined only from first two layers; while 'c' from the first layer. The errors quoted are the standard deviations of the mean values.

(ii) The crystal density determination:

The density of sodium pyruvate was measured by flotation method at 25°C by using two solution mixtures. The principle behind this method is as follows:

When a solid neither rises nor falls through a liquid column, in which it is submerged, the densities of the solid and the liquid are equal. It is then only necessary to determine the density of the liquid.

The density of sodium pyruvate obtained from two solution mixtures is as follows:

(1) Ethylene dibromide and carbon tetrachloride.

The density observed ($\rho_{\text{obs.}}$) = 1.721 gm.cm^{-3}

(2) Ethylene dibromide and benzene $\rho_{\text{obs.}} = 1.715 \text{ gm.cm}^{-3}$

The mean $\rho_{\text{obs.}}$ from the two observations = 1.718 gm.cm^{-3}

Number of molecules per unit cell $V\rho = \frac{nM}{N}$,

where N = Avogadro's number; ρ = crystal density in gm.cm^{-3} ;
 V = unit cell volume in \AA^3 and n = number of molecules per unit cell. Calculated density using 4 molecules per unit cell is 1.684 gm.cm^{-3} .

(iii) Linear absorption coefficient μcm^{-1} for $\text{CuK}\alpha$ radiation was calculated by the formula:

$$\mu = \frac{\rho \sum n \mu_a}{\sum n W} \text{cm}^{-1}$$

where ρ = density in gm.cm^{-3}

n = relative number of atoms present

μ_a = gm. atomic absorption coefficient

$\sum n W$ = sum of the atomic weights of the elements present

μ_a for C, O, and Na is 66, 203 and 711 respectively.

μ calculated for $\text{CuK}\alpha$ radiation is 23.7 cm^{-1} .

(iv) Space group determination:

From the diffraction photographs, the crystals are found to be monoclinic and the systematic absences are:

oko for k odd

and hol for h odd

so that the space group is uniquely determined as $P2_1/a$.

(v) Collection of data and estimation of intensity:

The crystal of the size $(0.7 \times 1.1) \text{ mm}^2$ was set roughly by Laue photograph and then accurately by double oscillation photograph [Cole and Weisz (1948), and Davis (1950)] with the c axis, parallel to the oscillation axis. The intensity data for the (hko) zone was collected using $\text{CuK}\alpha$ radiation ($\text{CuK}\beta$ was filtered through Nickel filter) and the multiple film technique, from a series of 10° oscillation photographs. Then a^*b^* section ($a^* = 0.069$; $b^* = 0.290$ r.l.u.) reciprocal lattice was plotted and hko reflections were indexed using Bernal chart. Intensity measurement of hko reflections was done visually, using an intensity scale from the same crystal. For this purpose a suitable reflection which was strong enough in an oscillation photograph, was exposed at different positions of the film, for periods ranging from one minute to twenty minutes at intervals of one minute.

The same crystal was used to collect the intensity data for (010) and (100) projection in the similar manner. The intensity measurements of these reflections were done, with the

intensity scales, prepared from the respective orientations of the crystal. In order to bring the intensities of reflections in different oscillation photographs to a common scale, the photographs were taken in such a way that there was an overlap of 2° in the ranges of oscillation of adjacent photographs.

Of the 153 possible reflections, in the hko zone, 122 were observed; while in the hol and okl zones, 93 and 19 were observed out of possible 105 and 27 respectively.

(vi) Correction factors:

The observed intensities were corrected for Lorentz (L) and polarisation (p) factors. The Lorentz factor arises from the variable time-opportunity for reflection, which is offered to the various planes by the geometry of rotation. The reciprocal points near the origin, obviously move slowly, while those away from the origin move fastly. The polarisation factor arises on account of the uneven loss of intensity of different reflections due to different degree of polarisation of the diffracted X-ray beams.

The integrated intensity (I_{hkl}) of a reflection hkl received by a film from a crystal rotating uniformly in a beam of monochromatic X-radiation is given by

$$I_{hkl} \propto L_{hkl} \cdot P_{hkl} \cdot |F^2|_{hkl} \quad \text{and} \quad |F^2| \propto DI.$$

For equatorial photograph $L.p. = \frac{1 + \cos^2 2\theta}{\sin 2\theta}$ where θ is the Bragg angle.

W. Cochran (1948) gives the curves for D for different values of ξ ; where $D = \frac{(\sin^2\theta - \xi^2)^{\frac{1}{2}}}{1 + \cos^2\theta}$ (for normal beam) and $D = \frac{\cos\theta}{1 + \cos^2\theta}$ (for equi-inclination).

ξ and ξ' are the cylindrical co-ordinates for the corresponding reflections. The intensities were corrected from these curves and corrections for extinction and absorption factors were neglected on account of the flakiness of the crystals used and of the low coefficient of absorption ($\mu = 23.1 \text{ cm}^{-1}$). On account of the flakiness of the crystals, the shapes and sizes of the spots were not uniform, and this seems to be a serious source of error in the estimation of integrated intensities.

Scale factor and the temperature factor:

At all temperatures including absolute zero, atoms have finite amplitude of oscillation. These thermal vibrations of the atoms will cause them to occupy larger volume than they would occupy at rest and will make the scattering factor smaller. Debye (1914) gave the relation between scattering factor f of a vibrating atom and to that f_0 of an atom at rest by the formula $f = f_0 e^{-B(\sin\theta/\lambda)^2}$; where B is the temperature factor of an atom.

Wilson's (1942) method was used to obtain the preliminary values for the scale factors (k) and the temperature factors $B(\text{\AA}^2)$. For a unit cell with a known content of atoms, any arbitrary arrangement of atoms would give a set of reflections of the same average value of $|F^2|$; in other words, whatever the

structure, the average value of $|F^2|$ is the same; Wilson (1942) showed that this average $|F^2|$ is equal to the sum of the squares of the diffracting powers of the atoms $\langle |F^2| \rangle = \sum_{n=1}^N f_n^2$. Also, over reasonably small ranges of Bragg angle θ , the average observed intensity on absolute scale ($K=1$) is equal $\sum_{n=1}^N f_n^2$, i.e. $\langle |F^2| \rangle = \langle I_{\text{abs. obs.}} \rangle = \sum_{n=1}^N f_n^2$; f_n is the atomic scattering factor for the n^{th} atom, with temperature factor B .

Noting that $I_{\text{obs.}} = KI_{\text{abs. obs.}}$; $I_{\text{obs.}}$ is the arbitrary intensity observed on the film and $I_{\text{abs. obs.}}$ is the absolute intensity. Then we have $\langle I_{\text{obs.}} \rangle = K \sum f_0^2 e^{-2B(\sin\theta/\lambda)^2}$, where f_0 is the atomic scattering factor for the atom at rest. Taking logarithms on both sides:

$$\log_e \langle I_{\text{obs.}} \rangle / \sum f_0^2 \text{ or } \log_e C = \log_e K - 2B(\sin\theta/\lambda)^2.$$

By dividing the reflections into groups lying between chosen limits of $(\sin\theta/\lambda)^2$ the mean of the observed intensities was evaluated for each range.

The graph $\log_e C$ against $(\sin\theta/\lambda)^2$ gives the value of $2B \text{ \AA}^2$ (from the slope) and $\log_e K$ (the intercept on the y axis). In this way the scale factors (K) and temperature factors were obtained for all the projections (fig. 1 a, b, c).

The mean values for the intensities ($\langle I_{\text{obs.}} \rangle$) for all the three projections are given in table (1a, 1b and 1c), together with the other data which are needed.

TABLE - 1a

(001) PROJECTION

$(\sin^2\theta/\lambda^2)$	$\langle I_{\text{obs.}} \rangle$	$\sum f_o^2$	$C = \frac{\sum f_o^2}{\langle I_{\text{obs.}} \rangle}$	$\log_e C$
0.0378	62.2	744	11.96	2.48
0.0852	37.2	436	11.72	2.46
0.1270	27.8	318	11.44	2.44
0.1780	19.9	236	11.86	2.47
0.3040	5.8	129	22.24	3.10
0.2370	12.8	168	13.12	2.57

TABLE - 1b

(010) PROJECTION

$(\sin^2\theta/\lambda^2)$	$\langle I_{\text{obs.}} \rangle$	$\sum f_o^2$	$C = \frac{\sum f_o^2}{\langle I_{\text{obs.}} \rangle}$	$\log_e C$
0.0378	218.0	744	3.4	1.224
0.0852	77.0	436	5.7	1.741
0.1270	29.0	318	11.0	2.397
0.1780	17.0	236	13.9	3.294
0.2370	13.0	168	13.0	2.623
0.3040	13.5	129	9.6	2.262

TABLE - 1c

(100) PROJECTION

$(\sin^2\theta/\lambda^2)$	$\langle I_{\text{obs.}} \rangle$	$\sum f_o^2$	$C = \frac{\sum f_o^2}{\langle I_{\text{obs.}} \rangle}$	$\log_e C$
0.0515	8.40	614	73.1	4.29
0.1052	2.52	374	148.4	5.00
0.1515	2.33	268	115.0	4.75
0.2061	0.96	196	204.0	5.32

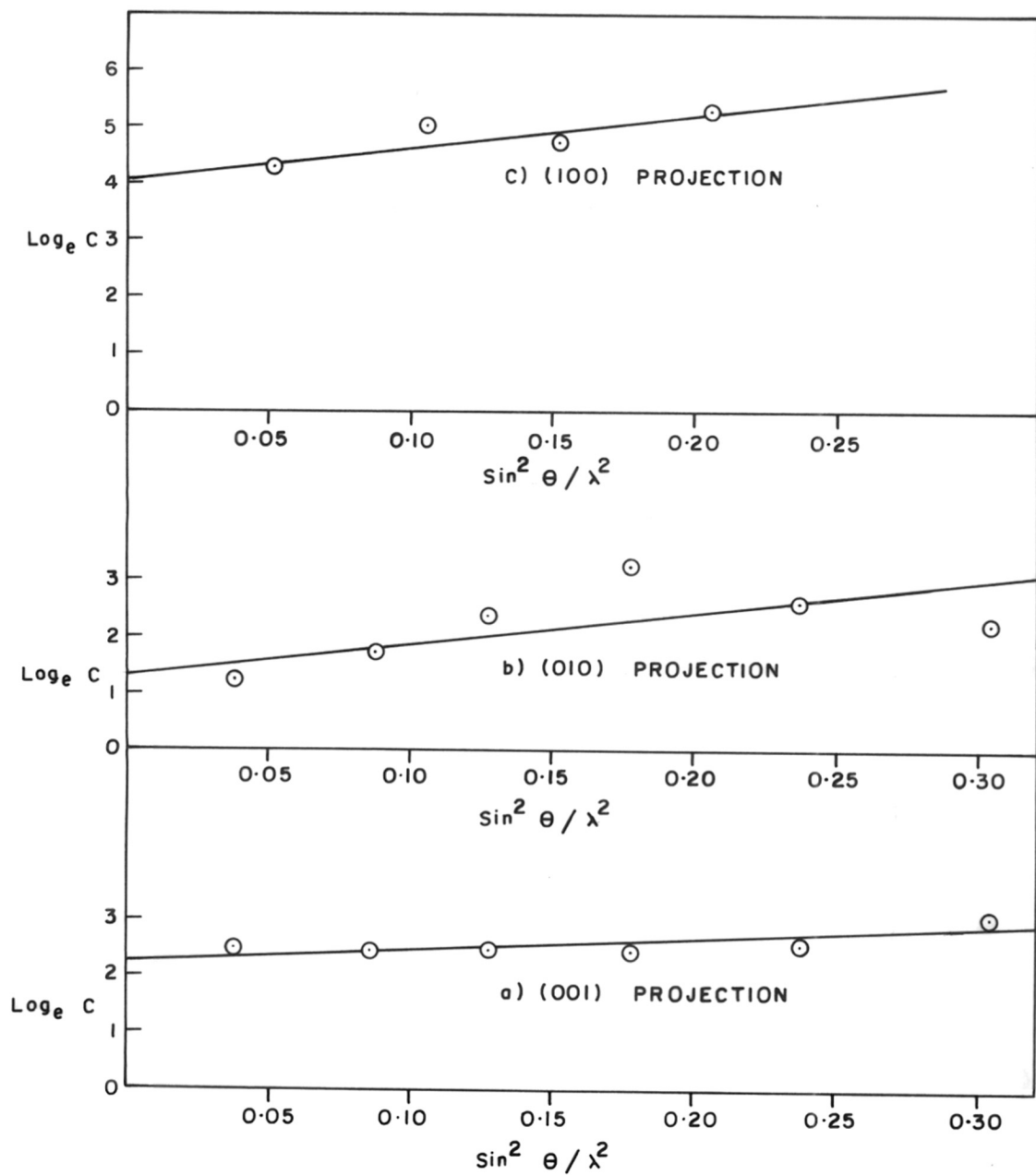


FIG. 1. (a, b, c). DETERMINATION OF PRELIMINARY SCALE AND TEMPERATURE FACTORS BY WILSON'S METHOD.

To get $\sum f_o^2$, Mcweeny's (1951) values of atomic scattering factors were used for carbon and oxygen; and James and Brindley's values (1931) for Na .

The values of scale factors (K) and temperature factors ($B \text{ \AA}^2$) obtained from the graphs (fig. 1) for different projections are as follows:

	K	B
(001)	10.0	1.1 \AA^2
(010)	3.7	2.8
(100)	60.0	2.8

These values were improved during the later stages of refinement (Chapter IV). The final overall temperature factors are 1.1 \AA^2 for F(hko); 2.1 \AA^2 for F(hol) and 3.2 \AA^2 for F(okl).

C H A P T E R - I I I

PATTERSON PROJECTION AND PRELIMINARY STRUCTURE

(i) Patterson synthesis:

Intensities provide the modulus of the structure, but not the phase associated with it; and the determination of the phases of various reflections is the main problem in X-ray crystallography. Patterson function (1934, 1935a, 1935b) is based on the intensity distribution. In 1934, A.L. Patterson discovered the vector representation of crystal structure. In his treatment, the quantity $P(uvw)$ which represents the weighted average of density of scattering matter about a point (x,y,z) in the crystal, is given by the equation:

$$P(uvw) = \int_0^a \int_0^b \int_0^c \rho(xyz) \rho(x+u, y+v, z+w) dx dy dz \dots\dots (1)$$

Here $\rho(x+u, y+v, z+w)$ represents a density distribution at the point $(x+u, y+v, z+w)$ and $\rho(x,y,z)$, that at (x,y,z) . The distribution is weighted according to the amount of scattering matter in the volume element at (x,y,z) ; i.e. $\rho(xyz)dx dy dz$.

Expanding $\rho(xyz)$ and $\rho(x+u, y+v, z+w)$ by expressing them in terms of corresponding Fourier series and after intergration, equation (1) becomes:

$$P(uvw) = \frac{1}{V} \sum_h \sum_k \sum_l \left| F(hkl) \right|^2 \cos 2\pi(hu + kv + lw) \dots\dots (2)$$

The coefficients in this expression are simply related to the actual X-ray intensities and can be measured directly.

The function $P(uvw)$ can be large (equation 1) only when both $\rho(xyz)$ and $\rho(x+u, y+v, z+w)$ are large. This occurs, when there are atoms at both (x,y,z) and $(x+u, y+v, z+w)$, separated by the vector distance (uvw) . Then a peak in the function $P(uvw)$ at (u_1, v_1, w_1) corresponds to an interatomic distance defined by a vector with components u_1, v_1, w_1 . Thus this picture of the crystal structure is not direct but it is a vector map, showing all the interatomic vectors of the crystal. For n atoms in the unit cell, there are $n(n-1)/2$ possible vectors, each of which will result in a separate peak in the distribution function. The height of a peak due to any two atoms will depend on the electron density near each of the atoms. If there are many atoms in the unit cell, many interactions will be possible and several of them will overlap each other. This will cause the difficulty in assigning the positions of the atoms. However, if some of the atoms in the cell have much greater diffracting powers than the others, the vectors between the heavy atoms will stand out, and the information thus gained may lead to a knowledge of the coordinates of these atoms.

In certain cases, when the heavy atom lies on the centre of symmetry, the signs of all the F 's will be positive with respect to the heavy atom, and projected electron densities may be calculated directly.

(ii) (001) Patterson projection and the trial structure:

The formula used after simplification, to compute the (001)

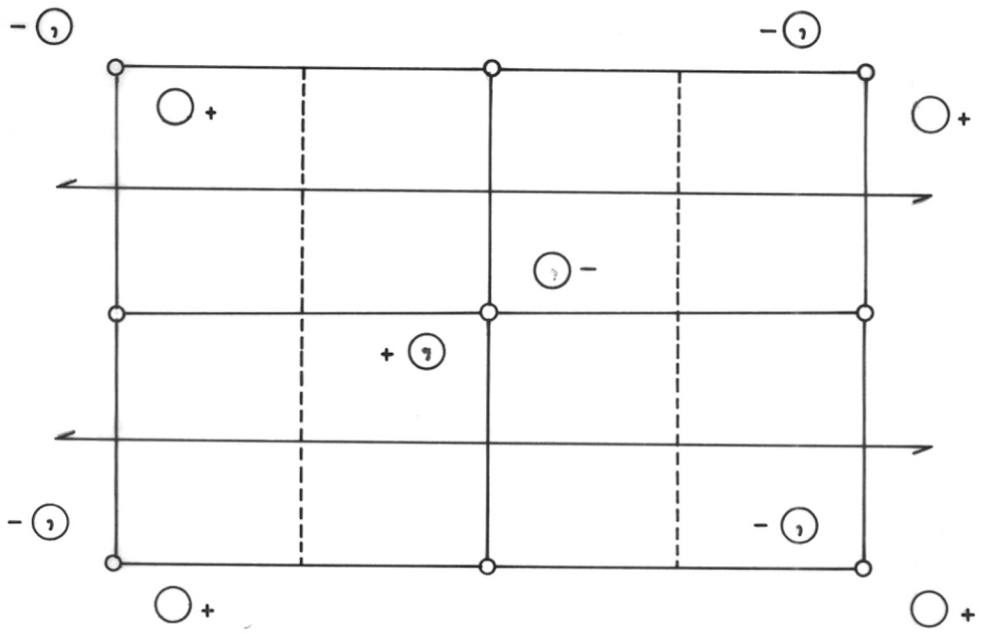


FIG. 2 SPACE GROUP $P2_1/a$

Patterson projection is, $P(uv) = \frac{1}{V} \sum_h \sum_k I(hko) \cos 2\pi hx \cos 2\pi ky$.

A weight half was given to h0c and okc reflections. To compute the (001) Patterson map (fig. 3) the intensities of all the observed reflections were used as the Fourier coefficients. The summation was carried out using Beavers-Lipson strips, along half of the a axis and along half of the b axis, at intervals of $\frac{1}{60}$ th of the cell edge. The rest of the cell could be completed from symmetry considerations. The contours were drawn at arbitrary intervals.

The equivalent points and the symmetry elements for the space group $P2_1/a$ are shown in fig. (2).

The four equivalent positions for the space group $P2_1/a$ are x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}+x, \frac{1}{2}-y, z$ origin being at $\bar{1}$ and unique axis b.

The molecules $\bar{x}, \bar{y}, \bar{z}$ and x, y, z are related by centre of symmetry; $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$ and x, y, z by a two fold screw axis, and $\frac{1}{2}+x, \frac{1}{2}-y, z$ and x, y, z by a glide plane a, \perp to b axis. The general positions for (001) projection are:

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

We could assign the Na-Na peaks only. The assignment is as follows. In fig. (3)

Peak No. 1 is due to the interaction of $\text{Na}(\frac{1}{2}-x, \frac{1}{2}+y)$ and $\text{Na}(x,y)$ falling at $u = \frac{1}{2}-2x$; and $v = \frac{1}{2}$. This gave $x_{\text{Na}} = 0.199$.

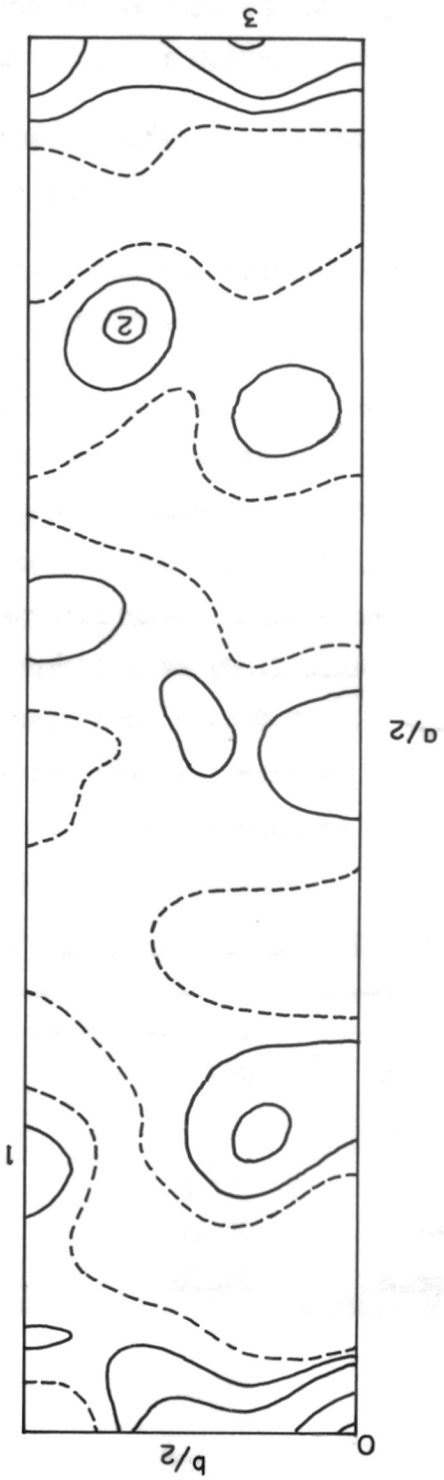


FIG. 3 (001) PATTERSON PROJECTION CONTOURS DRAWN AT ARBITRARY INTERVALS

Peak No.2 is due to Na(x,y) and Na(\bar{x},\bar{y}) falling at (2x,2y). This gave $x_{Na} = 0.199$ and $y_{Na} = 0.179$.

Peak No.3 is due to Na($\frac{1}{2}+x, \frac{1}{2}-y$) and Na(x,y) falling at ($\frac{1}{2}, \frac{1}{2}-2y$) giving $y_{Na} = 0.177$.

From these three peaks the mean co-ordinates of sodium atom were obtained as $x_{Na} = 0.199$ and $y_{Na} = 0.178$.

The signs of F(hko)'s were calculated from sodium position alone; and an electron density projection was obtained. For the trial structure, the bond lengths c-c = 1.50 Å, c-o = 1.25 Å and the angles around carbon of the carboxylic group and carbon of the keto group as 120°, were assumed. Also plane of the molecule was assumed to be nearly parallel to (001) plane. This assumption was made because the shortest axis c is 3.71 Å. With the help of these assumptions and the above electron density map, a trial structure was postulated and set up. The parameters of the atoms for the trial structure are given in table (2).

TABLE - 2 (001) TRIAL STRUCTURE PARAMETERS

	x	y
Na	0.199	0.178
O ₁	0.200	0.480
O ₂	0.100	0.270
O ₃	0.170	0.880
C ₁	0.160	0.620
C ₂	0.110	0.250
C ₃	0.060	0.710

(111) (010) Projection:

The formula used to compute the (010) Patterson projection is $P(uow) = \frac{1}{V} \sum_h \sum_l I(hol) \cos 2\pi(hu + lw)$.

A weight half was given to hoo and ool reflections. To compute the (010) Patterson map (fig. 4), the intensities of all the observed reflections were used as the Fourier coefficients. The summation was carried out using Beever-Lipson strips along one quarter of a axis and along the whole of the c axis, at intervals of 1/60th of the cell edge. The rest of the cell could be completed from symmetry considerations. The contours were drawn at arbitrary intervals.

The general positions for this projection are:

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

The interpretation of (010) Patterson map (fig. 4) is as follows:

It was possible to interpret four peaks only.

Let (x', z') be the fractional co-ordinates of Na and (x_1, z_1) and (x_2, z_2) those of carboxylic oxygens O_1 and O_3 respectively. The four peaks interpreted, correspond to the following atom-atom vectors. In fig. (4)

Peak No.1 is due to $Na(\frac{1}{2}-x', \bar{z}')$ and $Na(x', z')$ falling at $(\frac{1}{2}-2x', 2\bar{z}')$.

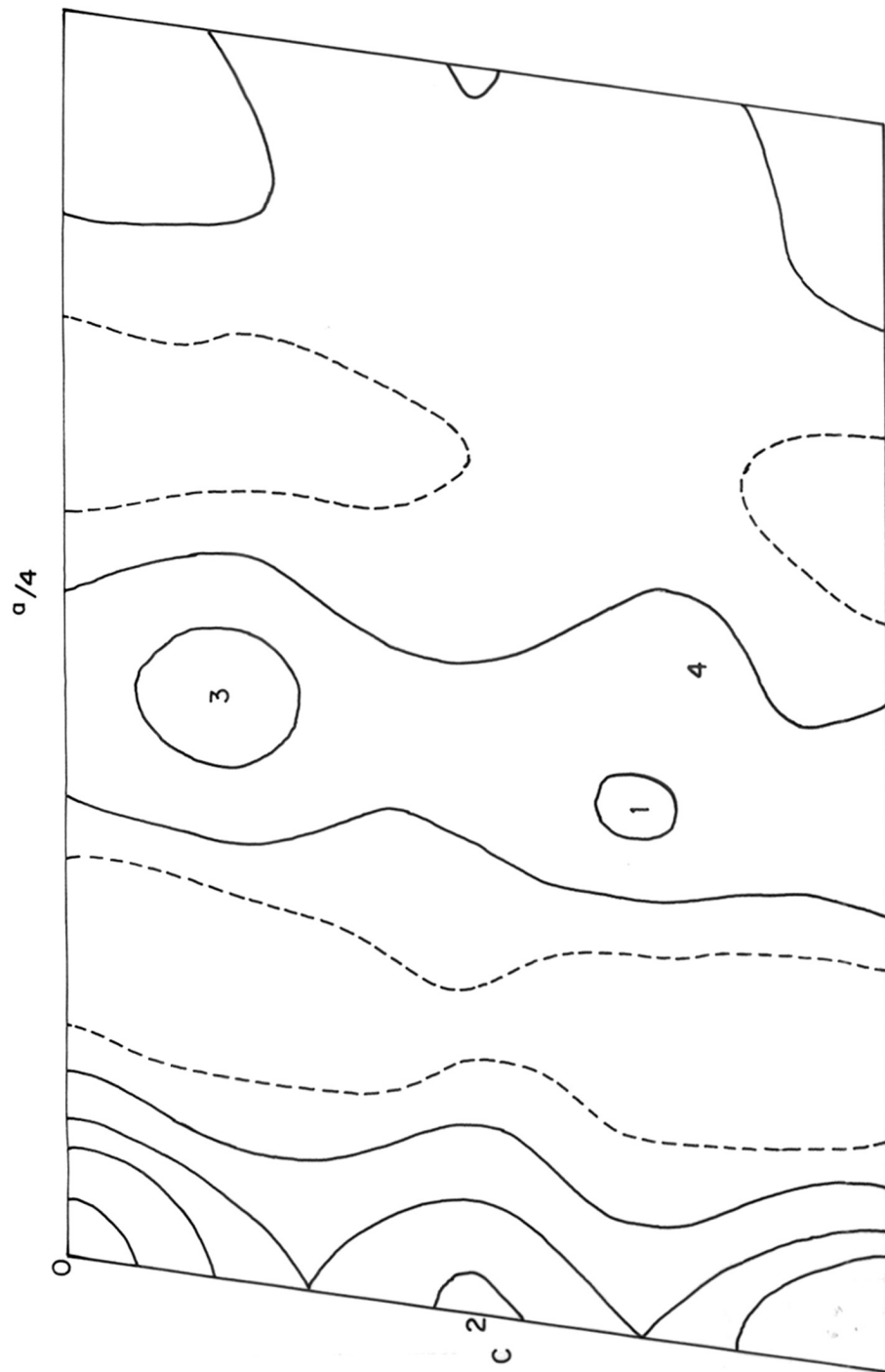


FIG. 4 (010) PATTERSON PROJECTION. CONTOURS DRAWN AT ARBITRARY INTERVALS

Peak No.2 corresponds to $\text{Na}(x', z')$ and $O_1(x_1, z_1)$ falling at $(x_1-x'; z_1-z')$.

Peak No.3 is due to $\text{Na}(\frac{1}{2}-x', \bar{z}')$ and $O_1(x_1, z_1)$ at $(\frac{1}{2}-x'-x_1; \bar{z}'-z_1)$

and peak No.4 corresponds to $\text{Na}(\frac{1}{2}+x', z')$ and $O_3(\bar{x}_2, \bar{z}_2)$ at $(-\frac{1}{2}-x'-x_2, -z'-z_2)$.

From these four peaks the following z parameters were obtained:

$$z_{\text{Na}} = 0.150; \quad z_{O_1} = 0.660 \quad \text{and} \quad z_{O_3} = 0.660.$$

C H A P T E R - I V

ELECTRON DENSITY PROJECTIONS AND REFINEMENT
OF ATOMIC PARAMETERS

The electron density of a crystal at (x,y,z) can be expressed by the Fourier series,

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) e^{-2\pi i(hx+ky+lz)} \quad \dots (1)$$

and if the crystal is centrosymmetric, as is the case with sodium pyruvate, sodium α -ketobutyrate and sodium α -ketocaprylate, the expression (1) simplifies to

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) \cos 2\pi(hx+ky+lz) \quad \dots (2)$$

where h,k,l are the indices associated with each reflection; x, y and z are the fractional co-ordinates of a point at which the electron density is to be evaluated; V is the volume of the unit cell in \AA^3 .

The expression giving the amplitude and the phase of the wave diffracted by the contents of a unit cell in a direction corresponding to the reflection (hkl) is called its structure factor F(hkl). The expression for the structure factor F(hkl) for a centrosymmetrical crystal is

$$F(hkl) = \sum_{n=1}^N f_n \cos 2\pi(hx_n+ky_n+lz_n) \quad \dots (3)$$

f_n is the atomic scattering factor of atom n.

The usual method to solve the crystal structure is to postulate a trial structure based on the consideration of expected

bond lengths, bond angles etc., and calculate the structure factors from it. If there is enough agreement, between the magnitudes of the observed and calculated structure factors; those having definite signs are used to sum the Fourier series of electron density. This Fourier series will yield a better set of co-ordinates than those used for the original structure factor calculations. These new co-ordinates are used, in turn, to calculate a new set of structure factors. The signs of the new set of structure factors are then used to calculate another electron density map. This process is repeated till the structure factors stop changing their phases. The Fourier refinement stops; because the atomic co-ordinates derived from Fourier syntheses are liable to error due to

- (1) experimental errors in the observed structure factors,
- (2) termination of the Fourier series at a finite Θ value, while the coefficients are still appreciable and
- (3) rounding off errors in computation.

Refinement of atomic parameters of sodium pyruvate was done by successive cycles of electron density projections followed by a few cycles of least squares method.

The (001) Projection:

- (1) Calculation of the structure factors:

The space group $P2_1/a$, being centrosymmetric, the calculation of the structure factor involves the calculation of real part only. Taking the centre of symmetry as the origin, the structure factor

formulae for (hko) reflections are

$$\begin{aligned} \text{for } (h+k) = 2n; \quad F(hko) &= 4 \sum_{n=1}^n f_n \cos 2\pi h x_n \cos 2\pi k y_n \\ (h+k) = 2n+1; \quad &= -4 \sum_{n=1}^n f_n \sin 2\pi h x_n \sin 2\pi k y_n \end{aligned}$$

For the calculation of structure factors, McWeeny's (1951) values of atomic scattering factors for carbon and oxygen, and James and Brindley's (1931) values for Na^+ were used. The atomic scattering factor values were obtained for a particular value of B factor by the formula $f = f_0 e^{-B(\sin^2\theta/\lambda^2)}$

f_0 is the atomic scattering factor value at rest and f that for temperature factor B. Preliminary B factor was obtained by Wilson's (1942) method. (Chapter II).

(ii) (001) electron density projection:

Formula used for $\rho(xyo)$ is

$$\begin{aligned} \rho(xyo) = \frac{1}{Ac} \left[F(000) + 2 \left\{ \sum_{h=2}^{\infty} F(h00) \cos 2\pi h x + \sum_{k=2}^{\infty} F(0k0) \cos 2\pi k y \right\} \right. \\ \left. + 4 \left\{ \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} F(hko) \cos 2\pi h x \cos 2\pi k y \right. \right. \\ \left. \left. - \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} F(hko) \sin 2\pi h x \sin 2\pi k y \right\} \right] \end{aligned}$$

where Ac is the area of the projection.

To compute the (001) electron density map, the observed structure amplitudes were used as the Fourier coefficients and the phases were calculated using the trial atomic parameters (table-2); out of 122 observed reflections, 49 were used for the first Fourier synthesis. The summation was carried out using

Beevers-Lipson strips, along one quarter of the a axis and along whole of the b axis, at intervals of 1/60th of the cell edge. The contours were drawn at arbitrary intervals. Starting from the trial structure parameters, (001) projection was refined by six cycles of Fourier synthesis method. After sixth Fourier, the structure factors stopped changing signs; except for a few small ones. The temperature factor used for these refinements was 1.1 \AA^2 and scale factor 10 (both were obtained from Wilson's method). The parameters obtained from sixth electron density projection are given in table (3). R after VI Fourier was ≈ 0.25 ; where R is the reliability factor, defined as $\frac{\sum (|F_o| - |F_c|)}{\sum (|F_o|)}$.

The final (001) electron density projection shown in fig. (5) was obtained by using final calculated signs (i.e. from final parameters) and F_o values for all except, 200, 100 and 510 (table-11) reflections. For these three reflections final F_c values were used.

(iii) Least squares refinement of atomic parameters:

Least squares method, (Hughes 1941) is one of the refinement techniques used for the refinement of atomic parameters. This method may be used after the structure is fairly well determined (i.e. when most of the atomic parameters are well within their correct values). The principle used in this method is to minimise, with respect to the parameters of the structure factor expression, the sum of the squares of the differences between the observed and calculated structure factors. The basic theory is as follows:

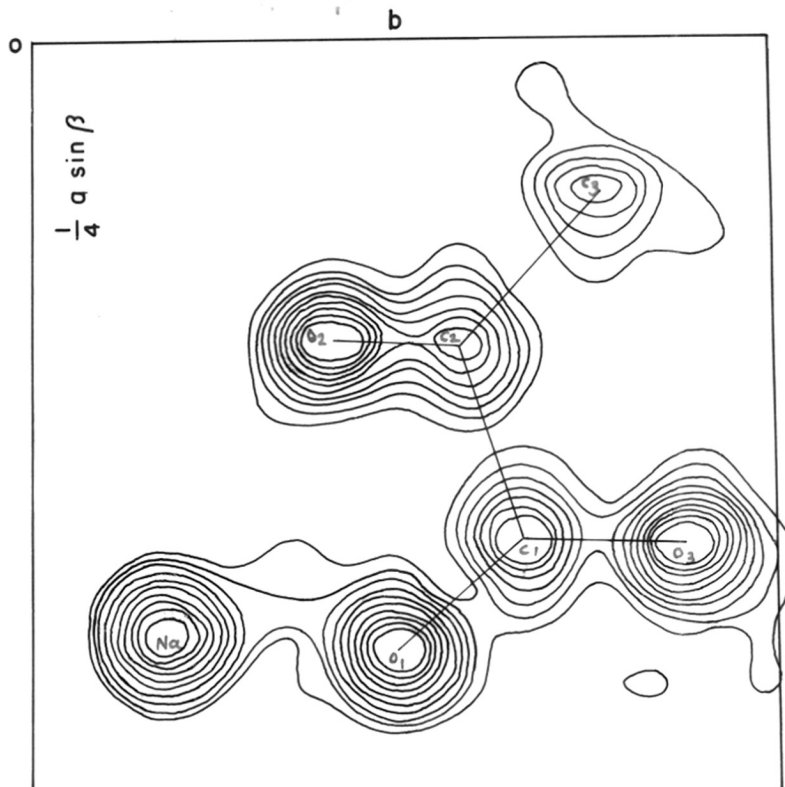


FIG. 5. (001) ELECTRON DENSITY PROJECTION. CONTOURS DRAWN AT INTERVALS OF $1e. \text{A}^{-2}$, STARTING FROM $2e. \text{A}^{-2}$ (FOR Na^+ ALTERNATE CONTOURS ARE DRAWN)

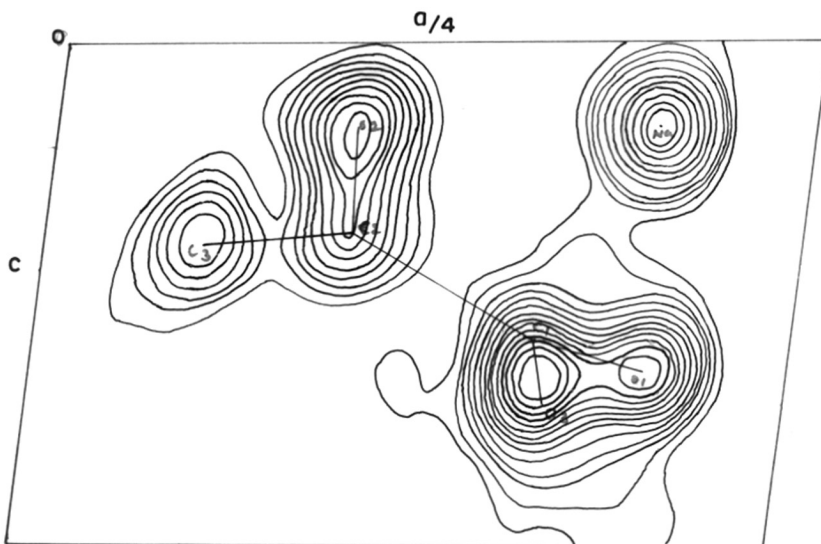


FIG. 7. (010) ELECTRON DENSITY PROJECTION. CONTOURS DRAWN AT INTERVALS OF $1e. \text{A}^{-2}$, STARTING FROM $2e. \text{A}^{-2}$ (FOR Na^+ ALTERNATE CONTOURS ARE DRAWN)

Best parameters are those which result in a minimization of the quantity, $R_1 = \sum w(hkl) (|F_o(hkl)| - |F_c(hkl)|)^2$ where the weight w of a particular term should be taken inversely proportional to the square of the probable error of the corresponding F_o . The summation is taken over all the structure factors, included in the refinement; and it is assumed that F_o and F_c have the same signs.

The corrections $\Delta x, \Delta y, \Delta z$ in the atomic parameters which would make R_1 minimum, are given by the relation,

$$(F_o - F_c) = \Delta F = \frac{\partial F}{\partial x_1} \Delta x_1 + \frac{\partial F}{\partial y_1} \Delta y_1 + \dots = \frac{\partial F}{\partial x_2} \Delta x_2 + \dots$$

Multiplying both sides by $\frac{\partial F}{\partial x_1}$,

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

Summing up for all the observed structure factors one gets

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

Terms such as $\sum \frac{\partial F}{\partial x_1} \frac{\partial F}{\partial y_1}$ are small as compared with $\sum \left(\frac{\partial F}{\partial x_1}\right)^2$; and hence can be neglected; and the equation reduces to

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

$$\text{or } \Delta x = \frac{\sum \Delta F \frac{\partial F}{\partial x}}{\sum \left(\frac{\partial F}{\partial x}\right)^2}$$

Similarly for Δy and Δz .

For (001) projection, the formula for the least squares refinement is derived as follows:

$$F(hko) = \sum_{n=1}^N 4f_n \cos 2\pi hx_n \cos 2\pi ky_n, \quad \text{for } h+k = 2n$$

$$\therefore \frac{\partial F}{\partial x_n} = -8\pi hf_n \sin 2\pi hx_n \cos 2\pi ky_n$$

$$\text{for } (h+k) = 2n+1, F(hko) = -4f_n \sin 2\pi hx_n \sin 2\pi ky_n$$

$$\therefore \frac{\partial F}{\partial x_n} = -8\pi hf_n \cos 2\pi hx_n \sin 2\pi ky_n$$

Substituting the values for $\frac{\partial F}{\partial x}$ one gets,

$$\Delta x_n = -\frac{1}{2\pi} \left\{ \frac{\sum_{\text{for } h+k=2n} h(4f_n) \Delta F(\sin 2\pi hx \cos 2\pi ky)}{\sum h^2 (4f_n)^2 (\sin 2\pi hx \cos 2\pi ky)^2} + \frac{\sum_{\text{for } h+k=2n+1} h(4f_n) \Delta F(\cos 2\pi hx \sin 2\pi ky)}{\sum h^2 (4f_n)^2 (\cos 2\pi hx \sin 2\pi ky)^2} \right\}$$

Similarly Δy could be obtained.

After VI Fourier synthesis, the refinement stopped as there was no further change of signs in $F(hko)$. Therefore the further refinements were carried out, twice by least squares method. For II least squares refinement, four reflections (table 11) 200, 100, 510 and 040 whose F_0 values were considered uncertain, were not included. The maximum shift in the parameters after final refinement was 0.03 Å. The parameters obtained from two cycles of least squares refinement are given in table (3).

R after I cycle and II cycle of least squares refinement was 0.23 and 0.22 respectively.

TABLE - 3

REFINEMENT OF PARAMETERS

	x parameters			y parameters		
	VI Fourier	I least square	II least square	VI Fourier	I least square	II least square
Na	0.199	0.1986	0.1989	0.178	0.1803	0.1802
O ₁	0.205	0.2045	0.2035	0.495	0.4891	0.4887
O ₂	0.101	0.1005	0.1004	0.409	0.4108	0.4100
O ₃	0.170	0.1699	0.1707	0.879	0.8873	0.8843
C ₁	0.167	0.1654	0.1657	0.655	0.6594	0.6608
C ₂	0.103	0.1019	0.1024	0.585	0.5821	0.5803
C ₃	0.055	0.0527	0.0523	0.771	0.7778	0.7722
R \approx	0.25	0.23	0.22			

After I least square, it was tried to correct the scale factor K and the temperature factor ($B \text{ \AA}^2$) by Wilson's method; but they remained unchanged (fig. 6a, table 4).

The theory of the method is as follows:

Let K_1 be the scaling factor to be applied to the present $F_o(hko)$'s and B_1 the temperature factor in \AA^2 from which F_c 's have been calculated, and B_2 the correct temperature factor to be applied to calculate correct F_c 's. It can be written:

$$K_1 \frac{F_o}{F_c} = e^{-(B_2 - B_1)(\sin\theta/\lambda)^2}$$

This equation can be obtained in the form

$$\log_e C = -\Delta B (\sin\theta/\lambda)^2 + \log_e 1/K_1$$

$$\text{where } B_1 - B_2 = \Delta B; \text{ and } F_o/F_c = C.$$

From the graph $(\sin\theta/\lambda)^2$ against $\log_e C$, slope will give $-\Delta B$ i.e. the correction to be applied to the temperature factor and the intercept on y axis will give the scale factor (K_1) to be applied to get correct F_o 's.

TABLE - 4 DETERMINATION OF CORRECT B AND SCALE
FACTORS FROM F_o & F_c VALUES

$\frac{(\sin^2\theta)}{\lambda^2}$	$\sum F_c$	$\sum F_o$	$C = \frac{\sum F_o}{\sum F_c}$	$\log_e C$
0.0378	366	361	0.9863	$\bar{1}.9812$
0.0852	237	223	0.9410	$\bar{1}.9352$
0.1270	212	224	1.0560	0.0545
0.1780	245	247	1.0080	0.0076
0.2370	180	196	1.0890	0.0856
0.3040	159	161	1.0130	0.0129

The final R value obtained for F(hko) was 0.22 [F(hoo) values are the mean values from final F(hko) and F(hol) values]; on including all except very high angle unobserved reflections, at half the minimum observable value. On omitting the (200) reflection, which appears to be subject to extinction, R decreased to 0.215.

The (010) Projection:

(i) Refinement by Fourier synthesis:

Formula for the structure factor calculation is

$$F(\text{hol}) = \sum_1^n 4f_n \cos 2\pi(hx_n + lz_n)$$

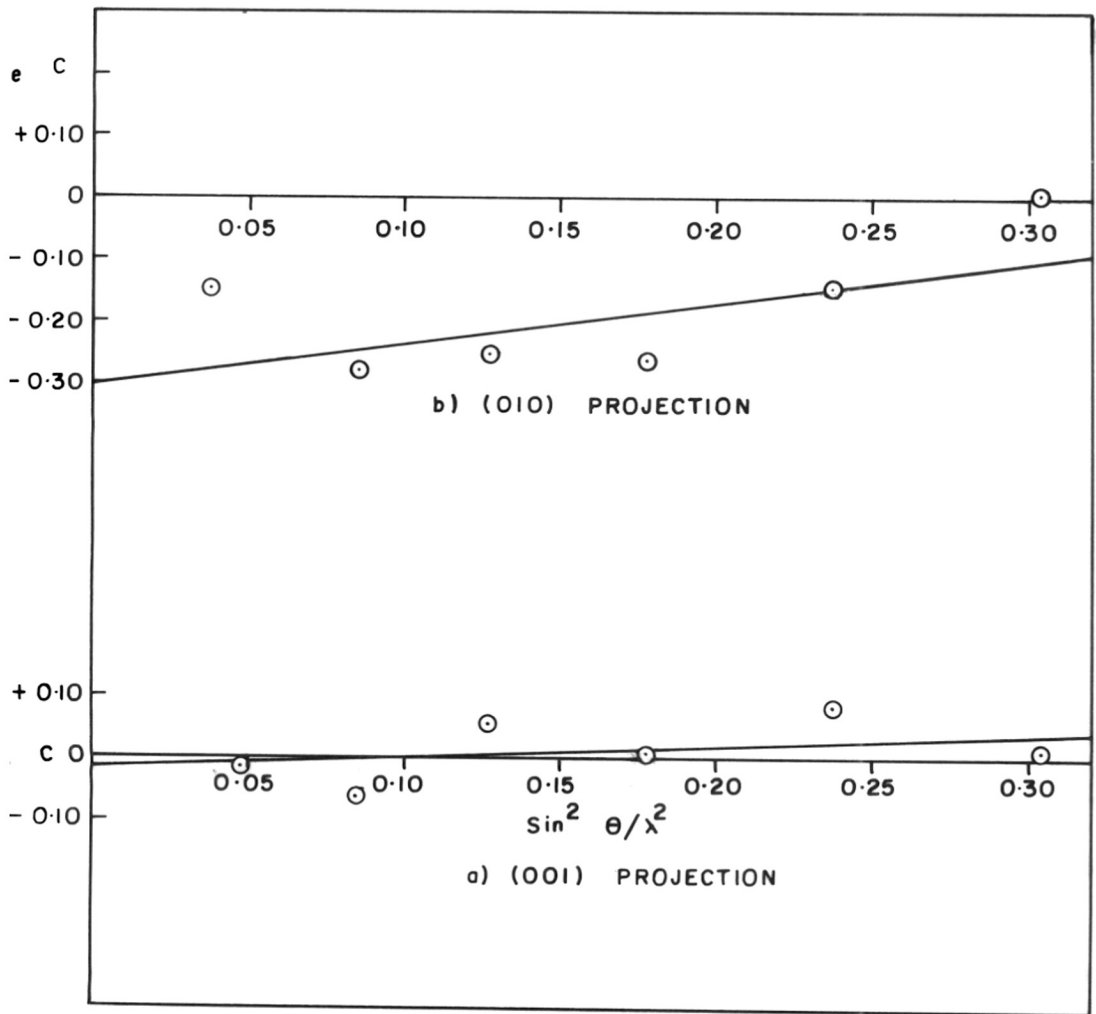


FIG. 6. (a,b) CORRECTION OF SCALE AND TEMPERATURE FACTORS FROM F_0/F_c VALUES.

and that for $\rho(xoz)$ is,

$$\rho(xoz) = \frac{1}{Ac} \left[F(000) + 4 \sum_{h=1}^{\infty} \sum_{l=1}^{\infty} \left\{ F(h0l) \cos 2\pi(hx+lz) + F(h0l) \cos 2\pi(-hx+lz) \right\} \right]$$

Starting from the parameters obtained from (010) Patterson projection, (Chapter III; x parameters taken from (001) projection) the (010) electron density map was computed. The summation was carried out using Beevers-Lipson strips along one quarter of the a axis and along whole of the c axis at intervals of 1/60th of the cell edge. In all four Fourier refinements were done for the refinement of z parameters. At the fourth refinement, structure factors stopped changing signs except for a few small ones. z parameters obtained from IV cycle are given in table (6). R for IV cycle is ≈ 0.31 .

The final (010) electron density projection (fig. 7) was obtained using final calculated signs and F_0 values for all except 200, ~~401~~, ~~40 $\bar{1}$~~ , ~~20 $\bar{2}$~~ and 402 reflections, for which the final F_0 (table 11) values were used.

(ii) Refinement of z parameters by the least square method:

Formula used was derived as follows:

$$F(h0l) = \sum_{n=1}^N 4f_n \cos 2\pi(hx_n + lz_n)$$

$$\therefore \frac{\partial F}{\partial z_n} = -4f_n \sin 2\pi(hx_n + lz_n) 2\pi l$$

$$= -8\pi l f_n (\sin 2\pi h x_n \cos 2\pi l z_n + \cos 2\pi h x_n \sin 2\pi l z_n)$$

$$\therefore z_n = -\frac{1}{2\pi} \frac{\sum (4f_n) l \Delta F (\sin 2\pi h x_n \cos 2\pi l z_n + \cos 2\pi h x_n \sin 2\pi l z_n)}{\sum (4f_n)^2 l^2 (\sin 2\pi h x_n \cos 2\pi l z_n + \cos 2\pi h x_n \sin 2\pi l z_n)^2}$$

z parameters were refined by a few cycles of least squares method. After I least square, the temperature factor and scale factor was corrected from F_o and F_c values from the plot of $\log_e C$ against $(\sin\theta/\lambda)^2$ (fig. 6b, table 5).

TABLE - 5 DETERMINATION OF CORRECT B AND SCALE
FACTORS FROM F_o AND F_c VALUES

$(\sin\theta/\lambda)^2$	ΣF_c	ΣF_o	$C = \frac{\Sigma F_o}{\Sigma F_c}$	$\log_e C$
0.0378	321	277	0.8630	$\bar{1}.8526$
0.0852	235	178	0.7573	$\bar{1}.7220$
0.1270	122	95	0.7785	$\bar{1}.7495$
0.1780	148	114	0.7702	$\bar{1}.7389$
0.2370	81	70	0.8642	$\bar{1}.8540$
0.3040	115	116	1.0090	0.0086

The new temperature factor obtained was 2.1 \AA^2 and $K_1=1.35$. This gave R as 0.24 for I least squares cycle. After one more cycle of least squares, few co-ordinates which were showing large shifts were refined further by least squares method. The details of refinement of z parameters after different cycles of least squares are given in table (6).

TABLE - 6

REFINEMENT OF z PARAMETERS

	IV Fourier	I cycle of least square	II cycle	III cycle	IV cycle
Na	0.164	0.1652	0.1638		
O ₁	0.661	0.6464	0.6491		
O ₂	0.171	0.1511	0.1617	0.1617	
O ₃	0.700	0.7183	0.7144		
C ₁	0.625	0.5831	0.5854		
C ₂	0.341	0.3802	0.3707	0.3685	
C ₃	0.400	0.4161	0.3986	0.3885	0.3882

The final value of R was 0.223 which dropped to 0.192 on omitting 200, ~~401~~, ~~40 $\bar{1}$~~ , ~~40 $\bar{2}$~~ and 402 reflections (table 11). These five reflections appear to be subject to extinction; and were not used for the final refinement.

(100) Projection:

Preliminary B factor for (100) projection obtained from Wilson's method was 2.8 Å² and after correction it became 3.2 Å². R is 0.210 with the final y and z parameters, obtained from (100) and (010) projections.

The final atomic parameters are listed in table (7) and structure factors in table (11).

TABLE - 7 FINAL ATOMIC PARAMETERS

	<u>x</u>	<u>y</u>	<u>z</u>
Na	0.1989 ± 0.0008	0.1802 ± 0.0032	0.1638 ± 0.0054
O ₁	0.2035 ± 0.0010	0.4887 ± 0.0043	0.6491 ± 0.0073
O ₂	0.1004 ± 0.0010	0.4100 ± 0.0043	0.1617 ± 0.0073
O ₃	0.1707 ± 0.0010	0.8843 ± 0.0043	0.7144 ± 0.0073
C ₁	0.1657 ± 0.0013	0.6608 ± 0.0057	0.5854 ± 0.0097
C ₂	0.1024 ± 0.0013	0.5803 ± 0.0057	0.3685 ± 0.0097
C ₃	0.0523 ± 0.0013	0.7722 ± 0.0057	0.3882 ± 0.0097

(Note: x,y,z are the fractional co-ordinates)

C H A P T E R - VRESULTS AND DISCUSSION.

(1) Bond distances and bond angles:

Intramolecular and intermolecular bond distances were calculated using co-ordinates from table (7); by the following formula for monoclinic crystals.

$$d^2 = \sum_1^3 (x_2 - x_1)^2 + 2(x_2 - x_1)(z_2 - z_1)\cos\beta,$$

where d is the bond distance; (x_1, y_1, z_1) and (x_2, y_2, z_2) are the co-ordinates in Å of the atoms. β is the angle between a and c axes.

Bond angles were calculated, using the formula:

$$r_2^2 = (r_1)^2 + (r_3)^2 - 2r_1r_3\cos\hat{r}_1r_2r_3$$

where r_1, r_2, r_3 are the lengths between the atoms 1 and 2, 2 and 3; and 3 and 1 respectively.

The bond lengths and bond angles found in the pyruvate group are shown in fig. (8) and listed in table (8).

TABLE - 8 INTRAMOLECULAR BOND LENGTHS AND ANGLES

	Bond lengths		Bond angles
C ₁ -O ₁	1.242 ± 0.040 Å	O ₁ -C ₁ -O ₃	126.3 ± 3.0°
C ₁ -O ₃	1.278 ± 0.040	O ₁ -C ₁ -C ₂	115.4 ± 2.7
C ₁ -C ₂	1.579 ± 0.045	O ₃ -C ₁ -C ₂	117.8 ± 2.7
C ₂ -O ₂	1.183 ± 0.040	C ₁ -C ₂ -O ₂	119.1 ± 2.9
C ₂ -C ₃	1.518 ± 0.045	C ₁ -C ₂ -C ₃	113.7 ± 2.6
		C ₂ -C ₂ -C ₃	125.8 ± 3.0

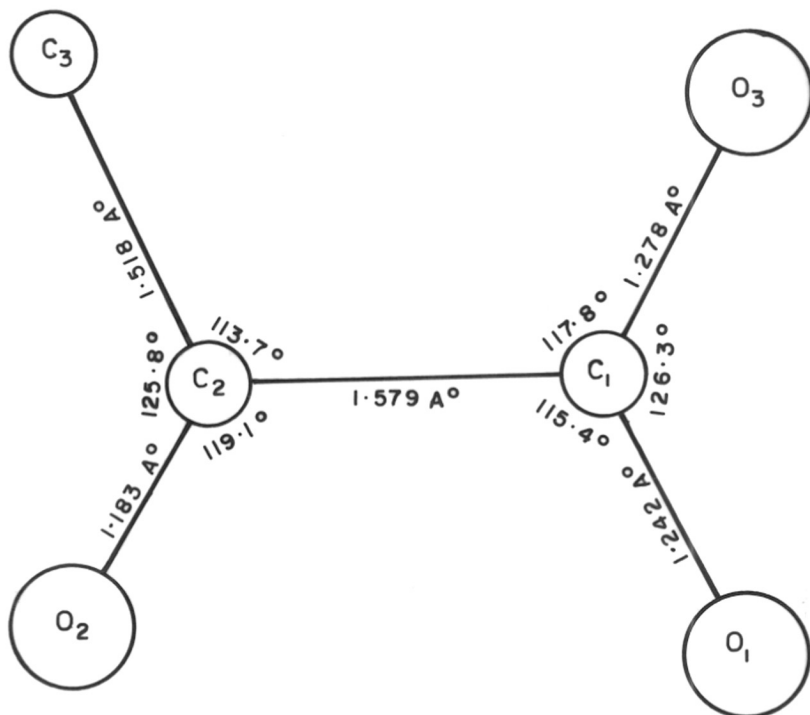


FIG. 8. BOND LENGTHS AND BOND ANGLES IN THE PYRUVATE GROUP, O₁ AND O₃ ARE CARBOXYLIC OXYGENS, O₂ IS KETO GROUP OXYGEN AND C₃ IS METHYL CARBONS.

(ii) Estimation of errors:

The standard deviations (σ) of atomic co-ordinates and the interatomic distances were estimated (Lipson and Cochran, 1953), assuming $\sigma(F) = K|F|$ and $p = 5 \text{ \AA}^2$.

The formula for deviation $\sigma(x_n)$ in \AA in the co-ordinates of the atoms for centresymmetrical, two dimensional synthesis is $\sigma(x_n) = \frac{K}{\sqrt{2} Z_n} \frac{\pi}{2p} \left(\frac{1}{A} \sum_{n=1}^N Z_n^2 \right)^{\frac{1}{2}}$ where $K = R \approx 0.21$; Z_n is the atomic number of the atom n. A is the area of the projection; p is a constant for each atom given by Costain's formula:

$\rho = Z \left(\frac{Z}{\pi} \right)^{3/2} e^{-pr^2}$ where ρ is the density at a distance r from the centre of the atom. The above expression is for three dimensions and reduces to $\rho = \rho_0 e^{-pr^2}$ for two dimensions. The value of p in practice, is taken about 5.0 \AA^2 .

The deviations in the atomic co-ordinates are as follows:

	$\pm \sigma(x_n)$	$\pm \sigma(y_n)$	$\pm \sigma(z_n)$
Na	0.017 \AA	0.017 \AA	0.020 \AA
O	0.023	0.023	0.027
C	0.030	0.030	0.036

A root mean square of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ was taken as the standard deviation (σr) of each atomic position. It comes as 0.018 \AA for Na ; 0.024 \AA for O and 0.032 \AA for C.

The deviation in bond lengths was calculated by the formula $\sigma(l-2) = \sqrt{\sigma(r_1)^2 + \sigma(r_2)^2}$ where $\sigma(r_1)$ and $\sigma(r_2)$ are the deviations in atomic positions for atoms 1 and 2 respectively.

It comes as:

$$\begin{aligned}\sigma(\text{C-C}) &= \pm 0.045 \text{ \AA} \\ \sigma(\text{C-O}) &= \pm 0.040 \\ \sigma(\text{Na-O}) &= \pm 0.030 \\ \sigma(\text{Na-Na}) &= \pm 0.030\end{aligned}$$

The standard deviations $\sigma(\theta)$ in bond angles were calculated by the method of Darlow (1960) and listed in table (8). The formulae involved in the method are as follows:

$$\sigma^2(\theta) = (\ell_1/\ell_1\ell_3 \sin\theta)^2 \times [A_3^2 \sigma^2(x_1) + (A_1+A_3)^2 \sigma^2(x_2) + A_1^2 \sigma^2(x_3) \\ \text{similar terms in y and z}]$$

$$\text{where } A_1 = (x_2-x_1) - (\ell_1/\ell_3)\cos\theta (x_2-x_3)$$

$$A_3 = (x_2-x_3) - (\ell_3/\ell_1)\cos\theta (x_2-x_1)$$

$$B_1 = (y_2-y_1) - (\ell_1/\ell_3)\cos\theta (y_2-y_3) \text{ etc.}$$

ℓ_1 is the bond length between atoms 2 and 1; ℓ_3 that between 2 and 3 and θ is the angle subtended at atom 2 by the bonds (ℓ_1 and ℓ_3) from atoms 1 and 3. (x_1, y_1, z_1) are the co-ordinates in \AA of the atom 1 and so on.

For isotropic standard deviations for each atom, the expression for $\sigma(\theta)$ reduces to

$$\sigma^2(\theta) = \frac{\sigma^2(1)}{\ell_1^2} + \frac{\ell_{13}^2}{\ell_1\ell_3} \frac{\sigma^2(2)}{\ell_2} + \frac{\sigma^2(3)}{\ell_3}$$

where $\sigma(1)$, $\sigma(2)$ and $\sigma(3)$ are the standard deviations of any coordinate for atoms 1, 2 and 3 and ℓ_{13} is the distance between atoms 1 and 3. In case of sodium pyruvate isotropic standard deviations are $\pm 0.018 \text{ \AA}$ for Na ; $\pm 0.024 \text{ \AA}$ for O and $\pm 0.032 \text{ \AA}$

for C, from which $\delta(\theta)$ in each angle was obtained.

(iii) Molecular structure:

The orthogonal co-ordinates x', y, z' of the atoms in sodium pyruvate were calculated by the formulae

$x' = x \sin \beta$; $y' = y$; $z' = z + x \cos \beta$; and are listed in table (9) (β is the angle between a and c).

TABLE - 9 ORTHOGONAL CO-ORDINATES

	$x' \text{ \AA}$	$y \text{ \AA}$	$z' \text{ \AA}$
Na	4.381	0.957	- 0.023
O ₁	4.482	2.595	1.762
O ₂	2.211	2.177	0.281
O ₃	3.759	4.696	2.108
C ₁	3.649	3.509	1.646
C ₂	2.255	3.082	1.042
C ₃	1.152	4.100	1.274

The plane through the atoms C₂, C₁, O₁ and O₃ fig. (8) can be represented by the equation

$$0.3488 x' + 0.2674 y - 0.8978 z' - 0.6916 = 0$$

where x', y and z' are expressed in \AA units and referred to the orthogonal axes a', b and c (table 9). The perpendicular distances of the individual atoms from the mean plane are 0.0146 \AA for O₁, C₂ and O₃; and - 0.0439 for C₁. Referred to the same axes a', b and c the mean plane through the atoms C₁, C₂, O₂ and C₃ can be represented by the equation:

$$0.2488x' + 0.5492y - 0.7980z' - 1.4959 = 0$$

The perpendicular distances of the individual atoms from this plane are 0.0248 \AA for O_2 , C_1 and C_3 ; and -0.0745 \AA for C_2 . These two planes make an angle of 18.1° with each other. The central C_1-C_2 (fig. 8) bond length ($1.579 \pm 0.045 \text{ \AA}$) is not significantly different from the normal single C-C bond length (1.545 \AA). This suggests that there is no appreciable degree of conjugation across this bond. There would thus be a possibility of the free rotation of the two planes across the central C-C bond. This explains the fact that the two planes $C_1C_2O_2O_3$ and $C_2C_1O_3O_1$ are not co-planar but make an angle of 18.1° with each other.

The two bonds C_1-O_1 ($1.242 \pm 0.040 \text{ \AA}$) and C_1-O_3 ($1.278 \pm 0.040 \text{ \AA}$) are of different lengths, although the differences may be within experimental errors. In oxalic acid dihydrate and seven amino acids listed by Ahmed and Cruickshank (1953) the two C-O bonds are always of unequal length. The angle $O_1-C_1-O_3$ ($126.3 \pm 3.0^\circ$) is significantly larger than the angle $C_2-C_1-O_1$ ($115.4 \pm 2.7^\circ$) and $C_2-C_1-O_3$ ($117.8 \pm 2.7^\circ$). This is in agreement with the results found for oxalic acid dihydrate and the aminoacids listed by Ahmed and Cruickshank (1953). The differences in the angles $O_2-C_2-C_3$ ($125.8 \pm 3.0^\circ$); $O_2-C_2-C_1$ ($119.1 \pm 2.9^\circ$) and $C_3-C_2-C_1$ ($113.7 \pm 2.6^\circ$) are also significant. Ahmed and Cruickshank's results are given in table (10).

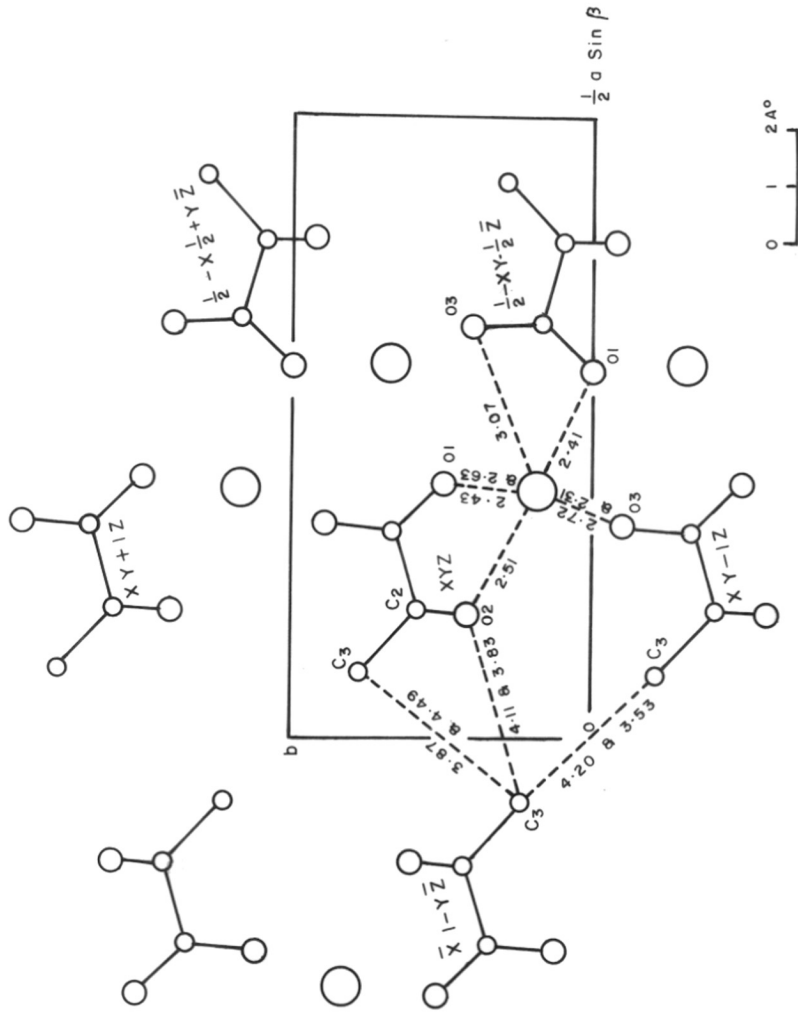


FIG. 9. STRUCTURE PROJECTED ON (001)

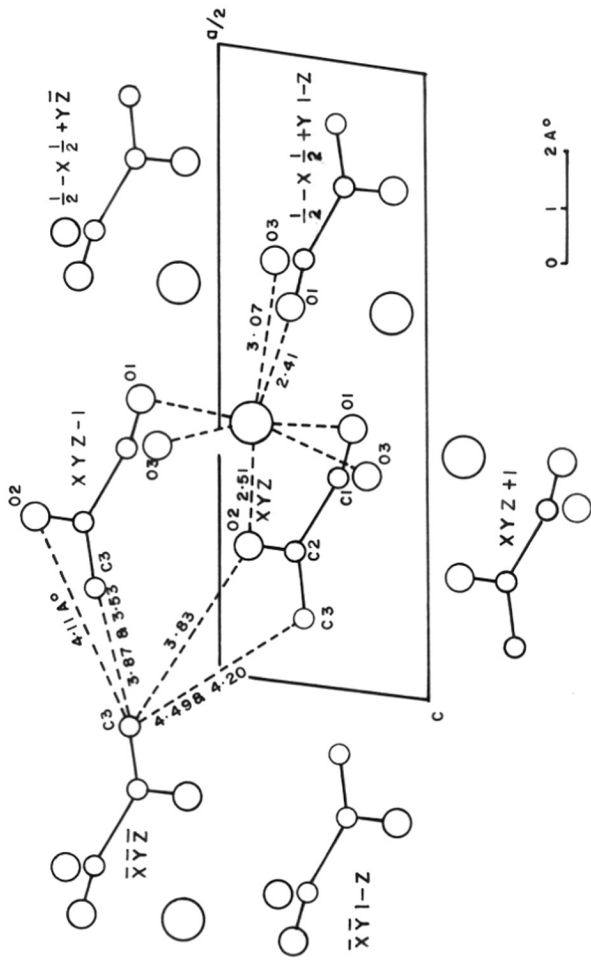


FIG. 10. STRUCTURE PROJECTED ON (010)

	C-C-O	long C-O	Short C-O	C-C-O	O-C-O
Oxalic acid dihydrate	112.6°	1.285 ^o Å	1.187 ^o Å	121.6°	125.8°
Alanine	113	1.27	1.21	121	
Serine	117	1.27	1.26	117	
Threonine	116	1.25	1.24	117	
α-Glycylglycine	115	1.26	1.22	117	
β-Glycylglycine	112	1.27	1.21	123	
Hydroxyproline	115	1.27	1.25	119	
N-acetylglycine	112	1.31	1.19	124	

(iv) Crystal structure:

The projections of the structure along the c and b axes are shown in figs. (9) and (10) respectively. There are six short bonds and one slightly longer bond between Na(x,y,z) and the neighbouring oxygens; these distances are as follows:

Na-O ₁ (x,y,z)	2.43 ± 0.03 Å
Na-O ₁ (x,y,z-1)	2.63 ± 0.03
Na-O ₃ (x,y-1,z)	2.72 ± 0.03
Na-O ₃ (x,y-1,z-1)	2.31 ± 0.03
Na-O ₁ (½-x,y-½,1-z)	2.41 ± 0.03
Na-O ₂ (x,y,z)	2.51 ± 0.03
Na-O ₃ (½-x,y-½,1-z)	3.07 ± 0.03

These Na-O distances are comparable with those of sodium tropolonate (Sasada and Nitta (1956)); and Shiono (1961))

(2.37 to 2.61 Å) and those given in the International tables for X-ray crystallography (1960) (2.22 to 2.78 Å).

There are van der Waals bonds between the methyl carbons C₃ and keto group oxygens O₂, and between carbons and carbons of the neighbouring molecules. The more significant distances are as follows:

C ₃ ($\bar{x}, 1-y, \bar{z}$) - C ₃ (x, y, z)	4.49 ± 0.06 Å
C ₃ ($\bar{x}, 1-y, \bar{z}$) - C ₃ (x, y, z-1)	3.87 ± 0.06
C ₃ ($\bar{x}, 1-y, \bar{z}$) - C ₃ (x, y-1, z)	4.20 ± 0.06
C ₃ ($\bar{x}, 1-y, \bar{z}$) - O ₂ (x, y, z-1)	4.11 ± 0.04
C ₃ ($\bar{x}, 1-y, \bar{z}$) - C ₃ (x, y-1, z-1)	3.53 ± 0.06
C ₃ ($\bar{x}, 1-y, \bar{z}$) - O ₂ (x, y, z)	3.83 ± 0.04
C ₃ (x, y-1, z) - O ₂ (x, y, z)	3.68 ± 0.04
C ₃ (x, y, z-1) - O ₂ (x, y, z)	3.49 ± 0.04

The strong Na-O bonds tie the molecules into infinite layers parallel to the (100) plane. Any one layer of molecules is linked with the neighbouring layers tightly on one side by Na-O bonds and loosely on the other side by van der Waals bonds. This arrangement explains the presence of strong cleavage parallel to the (100) face. Similar arrangement of layers of molecules has also been observed in the crystal structures of potassium caprate, (Vand, Lomer and Lang (1949)) potassium caproate (Lomer, 1952) and the potassium salt of o-nitrophenol hemihydrate (Richards, 1961).

The short Na-Na contact distances obtained are as follows:

Na(x,y,z) - Na($\frac{1}{2}$ -x, $\frac{1}{2}$ +y, \bar{z})	3.81 ± 0.03 Å
- Na($\frac{1}{2}$ -x,y- $\frac{1}{2}$, \bar{z})	3.81 ± 0.03
- Na(x,y,z-1)	3.71 ± 0.03
- Na(x,y,z+1)	3.71 ± 0.03

The refinement of the temperature factors has not been attempted. The differences in the overall temperature factors for the three projections, however, suggest that the mean amplitude of the thermal vibration of atoms has the largest component along the c axis and the smallest component along the a axis, since the overall temperature factor is least for the (001) projection (1.1 Å²) and maximum for the (100) projection (3.2 Å²). This is also indicated by the (010) electron-density projection (fig.7) where the atomic contours, especially those of the methyl carbon atom, appear distinctly elongated nearly along the c axis. This can be understood from the orientation of the molecule (x,y,z) with respect to the neighbouring molecules in fig. 9. The atom O₁ is strongly bonded to the two sodium atoms (x,y,z) and (x,y,z+1), and atom O₃ is strongly bonded to the two sodium atoms (x,y+1,z) and (x,y+1,z+1). The methyl carbon C₃ and ketogroup oxygen O₂ are bonded to the neighbouring molecules by weak forces only. The oscillation of the molecule about the line O₁-O₃ should therefore be most likely, and so the components of the thermal vibration amplitudes of the atoms C₂, C₃ and O₂ will be maximum along the c axis and will be least along the a axis.

The bond between $\text{Na}(x,y,z)$ and $\text{O}_2(x,y,z)$ is quite strong (distance 2.51 \AA), but since the movement of the atom O_2 would take place nearly perpendicular to the Na-O_2 bond, the Na-O_2 distance is not expected to alter appreciably during the oscillation. Besides, there is a possibility of free rotation about the central C-C bond, so that the plane $\text{C}_3\text{-C}_2\text{-O}_2$ may keep turning suitably during the oscillation so that the Na-O_2 distance is not affected.

TABLE - 11 OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
2	0	0	36	- 52	11	1	0	15	- 9
4	0	0	38	- 38	12	1	0	28	- 23
6	0	0	30	20	13	1	0	10	8
8	0	0	77	- 65	14	1	0	31	22
10	0	0	63	56	15	1	0	18	10
12	0	0	18	- 11	16	1	0	28	- 33
14	0	0	22	- 21	17	1	0	16	13
16	0	0	12	- 7	18	1	0	17	11
18	0	0	7	7	19	1	0	18	- 17
20	0	0	30	29	20	1	0	18	11
22	0	0	18	- 13	21	1	0	7	- 6
24	0	0	8	5	22	1	0	14	- 13
26	0	0	12	- 11	23	1	0	5	6
28	0	0	8	- 8	24	1	0	15	14
1	1	0	16	- 29	25	1	0	5	5
2	1	0	13	15	26	1	0	< 4	0
3	1	0	11	13	27	1	0	4	2
4	1	0	17	17	0	2	0	4	3
5	1	0	20	34	1	2	0	< 6	- 6
6	1	0	12	- 12	2	2	0	8	- 7
7	1	0	18	19	3	2	0	16	20
8	1	0	48	50	4	2	0	9	- 10
9	1	0	40	- 40	5	2	0	< 3	- 2
10	1	0	18	- 20	6	2	0	13	- 13

h	k	l	F ₀	F _c	h	k	l	F ₀	F _c
7	2	0	8	- 8	5	3	0	32	- 40
8	2	0	16	17	6	3	0	< 3	0
9	2	0	8	9	7	3	0	34	32
10	2	0	16	21	8	3	0	7	9
11	2	0	18	- 16	9	3	0	8	- 7
12	2	0	2	4	10	3	0	8	- 9
13	2	0	15	17	11	3	0	3	- 6
14	2	0	< 3	- 3	12	3	0	3	4
15	2	0	5	- 4	13	3	0	19	23
16	2	0	14	- 12	14	3	0	< 2	6
17	2	0	16	- 12	15	3	0	21	- 25
18	2	0	< 3	1	16	3	0	< 2	- 1
19	2	0	15	11	17	3	0	15	14
20	2	0	< 3	- 1	18	3	0	5	6
21	2	0	13	- 10	19	3	0	4	- 5
22	2	0	5	- 2	20	3	0	5	2
23	2	0	8	7	21	3	0	4	- 6
24	2	0	5	- 3	22	3	0	7	- 7
25	2	0	4	5	23	3	0	8	9
26	2	0	5	- 4	24	3	0	6	- 4
1	3	0	9	- 14	25	3	0	8	- 9
2	3	0	6	3	0	4	0	20	- 11
3	3	0	21	30	1	4	0	21	28
4	3	0	20	- 27	2	4	0	< 9	3

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
3	4	0	11	- 14	5	5	0	12	- 14
4	4	0	19	19	6	5	0	8	8
5	4	0	8	- 9	7	5	0	10	- 10
6	4	0	8	- 8	8	5	0	7	- 7
7	4	0	16	14	9	5	0	12	12
8	4	0	< 3	- 4	10	5	0	6	6
9	4	0	17	- 20	11	5	0	4	3
10	4	0	5	- 3	12	5	0	< 3	1
11	4	0	11	13	13	5	0	9	- 10
12	4	0	16	- 21	14	5	0	9	- 13
13	4	0	< 3	1	15	5	0	< 3	1
14	4	0	10	15	16	5	0	4	5
15	4	0	3	2	17	5	0	4	- 4
16	4	0	5	8	18	5	0	4	- 3
17	4	0	4	5	19	5	0	4	7
18	4	0	11	- 8	0	6	0	3	3
19	4	0	9	- 8	1	6	0	< 6	- 6
20	4	0	4	6	2	6	0	15	- 18
21	4	0	9	7	3	6	0	< 6	3
22	4	0	3	- 1	4	6	0	8	10
1	5	0	< 10	10	5	6	0	< 3	7
2	5	0	< 10	- 1	6	6	0	11	14
3	5	0	< 10	4	7	6	0	< 3	- 2
4	5	0	7	7	8	6	0	10	- 11

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
9	6	0	< 3	5	$\overline{12}$	0	1	15	14
10	6	0	4	4	$\overline{14}$	0	1	11	- 14
11	6	0	< 3	- 2	$\overline{16}$	0	1	12	9
12	6	0	9	- 7	$\overline{18}$	0	1	24	- 27
13	6	0	6	- 8	$\overline{20}$	0	1	7	- 5
0	0	1	30	- 32	$\overline{22}$	0	1	15	21
2	0	1	18	- 18	$\overline{24}$	0	1	7	- 6
4	0	1	28	- 44	$\overline{26}$	0	1	< 4	1
6	0	1	11	- 7	0	0	2	26	- 30
8	0	1	42	49	2	0	2	14	- 14
10	0	1	5	3	4	0	2	39	51
12	0	1	23	- 23	6	0	2	24	- 27
14	0	1	18	17	8	0	2	23	25
16	0	1	5	- 3	10	0	2	9	- 8
18	0	1	5	- 1	12	0	2	12	- 15
20	0	1	8	8	14	0	2	9	8
22	0	1	23	- 18	16	0	2	18	- 11
24	0	1	7	- 3	18	0	2	15	9
26	0	1	7	9	20	0	2	14	- 6
$\overline{2}$	0	1	12	17	22	0	2	5	4
$\overline{4}$	0	1	36	54	$\overline{2}$	0	2	35	52
$\overline{6}$	0	1	14	- 17	$\overline{4}$	0	2	38	- 47
$\overline{8}$	0	1	31	- 31	$\overline{6}$	0	2	14	16
$\overline{10}$	0	1	34	36	$\overline{8}$	0	2	7	- 4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\overline{10}$	0	2	26	- 27	$\overline{12}$	0	3	5	6
$\overline{12}$	0	2	19	23	$\overline{14}$	0	3	8	- 2
$\overline{14}$	0	2	< 3	- 1	$\overline{16}$	0	3	7	- 9
$\overline{16}$	0	2	14	16	$\overline{18}$	0	3	14	9
$\overline{18}$	0	2	7	- 6	$\overline{20}$	0	3	8	- 7
$\overline{20}$	0	2	5	- 2	$\overline{22}$	0	3	7	4
$\overline{22}$	0	2	< 5	2	$\overline{24}$	0	3	4	11
$\overline{24}$	0	2	11	- 11	0	0	4	17	- 15
$\overline{26}$	0	2	12	12	2	0	4	11	10
0	0	3	< 3	- 4	4	0	4	7	- 5
2	0	3	7	- 4	6	0	4	8	11
4	0	3	9	- 7	8	0	4	3	- 2
6	0	3	5	2	10	0	4	8	- 10
8	0	3	4	1	$\overline{2}$	0	4	8	- 7
10	0	3	9	- 9	$\overline{4}$	0	4	8	8
12	0	3	5	2	$\overline{6}$	0	4	7	- 5
14	0	3	< 5	2	$\overline{8}$	0	4	12	12
16	0	3	4	4	$\overline{10}$	0	4	7	- 8
18	0	3	9	7	$\overline{12}$	0	4	< 4	0
$\overline{2}$	0	3	7	8	$\overline{14}$	0	4	7	7
$\overline{4}$	0	3	4	7	$\overline{16}$	0	4	4	- 2
$\overline{6}$	0	3	< 4	5	0	1	1	37	- 41
$\overline{8}$	0	3	< 4	- 1	0	2	1	10	- 7
$\overline{10}$	0	3	12	- 15	0	3	1	12	- 12

h	k	l	{F ₀ }	F _c	h	k	l	{F ₀ }	F _c
0	4	1	3	- 5	0	1	3	3	3
0	5	1	17	10	0	2	3	9	9
0	6	1	<2	- 1	0	3	3	3	2
0	1	2	25	- 26	0	4	3	3	4
0	2	2	<2	- 4	0	5	3	<2	4
0	3	2	<3	- 2	0	1	4	6	5
0	4	2	10	5	0	2	4	<2	- 1
0	5	2	9	- 6	0	3	4	<2	1
0	6	2	<2	1					

PART-II: CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM α -KETOBYRATE

C H A P T E R - V I

CRYSTAL DATA AND EXPERIMENTAL DETAILS

(i) The determination of unit cell dimensions:

Sodium α -ketobutyrate, $\text{CH}_3\text{CH}_2\text{COCOONa}$ crystals were grown from aqueous solution. The crystals are orthorhombic and grow as very thin plates, parallel to the (100) face. The unit cell dimensions were determined from the zero layer Weissenberg photographs. The unit cell dimensions are as follows:

$$a = 29.28 \pm 0.04; \quad b = 6.04 \pm 0.01; \quad c = 5.90 \overset{\circ}{\text{A}}$$

Axial length a was obtained from 22,00; 24,00; 26,00; 28,00; 30,00 and 36,00 reflections; b was determined from 040 and 060 while c from 004 and 006 reflections.

(ii) The crystal density determination:

The density of sodium α -ketobutyrate was obtained by flotation method at 24°C , by using two solution mixtures.

(1) Ethylene dichloride and ethylene dibromide.

(2) Ethylene dichloride and carbon tetrachloride.

First gave the density ($\rho_{\text{obs.}}$) as 1.563 gm.cm^{-3} ; while second as 1.560 gm.cm^{-3} . The mean density obtained from the two is 1.562 gm.cm^{-3} and that calculated for eight molecules of $\text{CH}_3\text{CH}_2\text{COCOONa}$ per unit cell is 1.578 gm.cm^{-3} .

(iii) Linear absorption coefficient $\mu_{\text{cm}^{-1}}$ for $\text{CuK}\alpha$ radiation (formula is given in Chapter-II) obtained is 20.0 cm^{-1} .

(iv) Space group determination:

From the diffraction photographs the crystals are found to be orthorhombic and the systematic absences are:

okl for k odd

hol for l odd

and hko for h+k odd,

so that the space group is uniquely determined as Pbcn.

(v) Collection of data and estimation of intensities;

The hko and hol reflections were collected from zero layer Weissenberg photographs along the c and b axis respectively. The crystals used to collect hko and hol reflections were of the size (0.5 x 0.7) mm² area; the longer side being the oscillation axis. Of the 127 possible hko reflections and 112 possible hol reflections, 92 and 76 respectively were observed. Intensities were estimated with the intensity scales, prepared from the same crystals, in the respective orientations, using a pack of three films.

(vi) Correction factors:

The observed intensities were corrected for Lorentz and polarisation factors in the same way as sodium pyruvate. Correction for absorption was neglected on account of the flakiness of the crystals and the low coefficient of absorption ($\mu = 20.0 \text{ cm}^{-1}$).

Scale factor (K) and the temperature factor ($B \text{ \AA}^2$)

Wilson's (1942) method was used to obtain preliminary values for the scale and temperature factors; for both the zones, from the graph of $(\sin\theta/\lambda)^2$ against $\log_e C$ (fig. 11a, 11b). The scale

and temperature factors obtained were as follows:

	Scale factor	Overall temperature factor
hko zone	100	2.44 Å ²
hol zone	164	2.48

The necessary data to obtain K and B factors is given in tables 12a and 12b.

TABLE - 12a (001) PROJECTION

$(\sin\theta/\lambda)^2$	$\langle I_{\text{obs.}} \rangle$	$\langle f_o^2 \rangle$	$C = \frac{\langle f_o^2 \rangle}{\langle I_{\text{obs.}} \rangle}$	$\log_e C$
0.0378	17.94	1552	86.5	4.46
0.0852	9.55	846	93.8	4.54
0.1270	2.67	672	251.7	5.53
0.1780	3.21	480	149.5	5.01
0.2370	2.00	368	184.0	5.22
0.3040	0.83	280	337.0	5.82

TABLE - 12b (010) PROJECTION

$(\sin\theta/\lambda)^2$	$\langle I_{\text{obs.}} \rangle$	$\langle f_o^2 \rangle$	$C = \frac{\langle f_o^2 \rangle}{\langle I_{\text{obs.}} \rangle}$	$\log_e C$
0.0378	10.20	1552	152.2	5.11
0.0852	5.10	896	175.7	5.17
0.1270	1.34	672	501.5	6.22
0.1780	1.28	480	375.0	5.93
0.2370	0.84	368	438.0	6.08

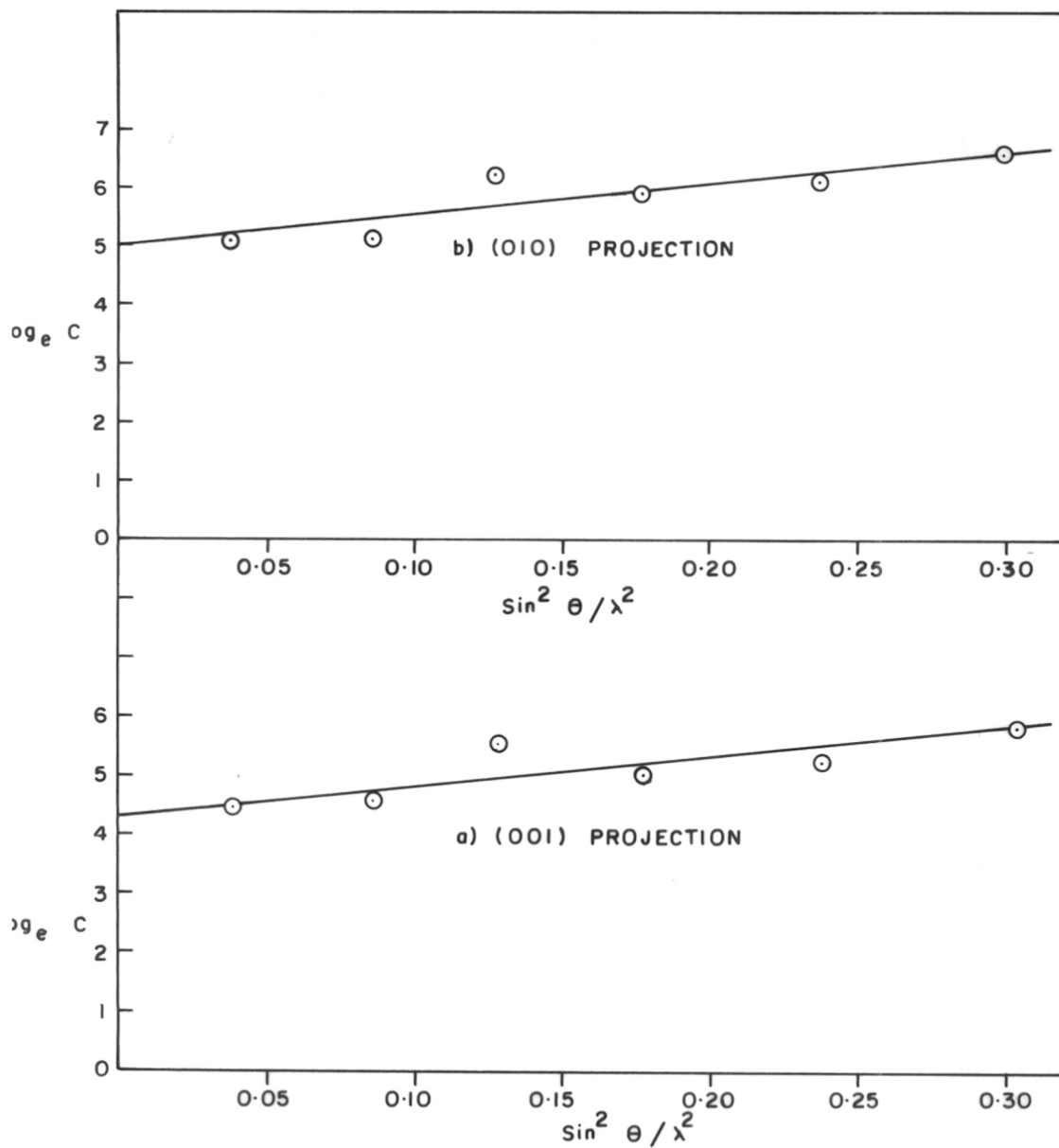


FIG. II. (a,b) DETERMINATION OF PRELIMINARY SCALE AND TEMPERATURE FACTORS BY WILSON'S METHOD.

From the square root of (the corrected intensities X scale factor) $|F_0|$ could be calculated. The values of the scale and temperature factors were improved in the later stages of refinement.

C H A P T E R - V I I

PATTERSON PROJECTION AND PRELIMINARY STRUCTURES

(1) The sharpened Patterson function:

If the individual peaks in the Patterson map are resolved as best as possible, the interpretation of these peaks will be easier. For the sharpening of the peaks, the Patterson function itself should be modified so that the modification makes the individual peaks as sharp as possible and at the same time does not give large subsidiary maxima and minima, which will distort the neighbouring peaks.

A possible modification was suggested by Patterson (1935b) and was used by him to increase the resolution of peaks in the two-dimensional Patterson function of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This consists in taking

$$M(S) = \left(\frac{1}{\hat{f}}\right)^2 e^{-\frac{\pi^2}{p} S^2}$$

where $M(S)$ is the modifying factor, \hat{f} is the unitary scattering factor, taking account of the temperature factor, p is a constant given by Costain's (1941) formula; and $S = |2\sin\theta/\lambda|$. Another modification suggested by Schomaker and Shoemaker (unpublished) consists in taking

$$M(S) = \left(\frac{1}{\hat{f}}\right)^2 S^2 e^{-\left(\frac{\pi^2}{p} S^2\right)}$$

This type of modification reduces greatly the influence of low angle terms on the Patterson function, which is advantageous when they are likely to be in error through extinction.

A modification by Shoemaker, Barieu, Donohue and Lu (1953), in preparing the two dimensional Patterson function, the values of $F(hkl)^2$ were sharpened (Patterson, 1935); and multiplied by a modification function of the form $(2\sin\theta/\lambda)^4 e^{-B(2\sin\theta/\lambda)^2}$. This function has a zero value at $\theta = 0$ and a very small value at the limit of the data; and has a maximum value at about half the maximum value of $\sin\theta$.

For sharpening of the Patterson function, we multiplied the corrected intensities of each reflection by S^2 , where S is the length of the corresponding reciprocal lattice vector from the origin. ($S = 2\sin\theta$; where θ is the Bragg angle).

The principle involved is as follows:

$$P(uv) = \sum_h \sum_k |F^2(hk)| \cos 2\pi(hu + kv)$$

Second positional derivative of this is,

$$\left(\frac{\partial^2 P}{\partial r^2}\right) = K(\sin\theta)^2 = \frac{K}{4}(S^2) \text{ where } k \text{ is a constant.}$$

The sharpened Patterson function obtained in this way will give the peaks of which the central maximum is accompanied by a minimum; and this makes the accompanying peaks diffuse. Also this modification makes the low angle reflections negligible. But as we were interested in locating the sodium atom position, this modification was used.

(ii) The "Photosummator" (G.V. Eller)

Electron density for any centrosymmetrical projection is given by $\rho(x,y) = \frac{1}{AC} \sum_h \sum_k F(hk) \cos 2\pi(hx + ky)$.

In this equation, the term $\cos 2\pi(hx+ky)$ represents a diagonally fluctuating function which can be represented photographically by variation in blackening of a film. If such a function is projected on to a photographic paper, with an exposure proportional to $|F(hk)_{\text{obs.}}|$; the result is the photographic Fourier summation.

A most convenient and commercially available device is the "Photosummator", designed by Eller (1955). A vertical slit source of light passing through a specially designed grating produces a sinusoidal distribution of intensity on a photographic plate mounted at the centre of a movable disc. The intensity depends on the exposure time, and the correct orientation of the Fourier terms relative to each other is achieved by rotating the disc carrying the photographic plate. The spacing is altered by varying the distance between grating and source, the grating being geared to a cursor which permits the settings to be made directly from a drawing of the reciprocal lattice, mounted on the rotating disc. The phase is introduced by an eccentric spindle which enables the grating which produces the vertical fringes to be translated horizontally by any amount up to one complete period 2π . It is thus just as easy to perform non-centrosymmetric summations as centrosymmetric one.

(iii) (001) sharpened Patterson projection and the trial structure:

A reciprocal lattice section (a^*b^*) was plotted on the scale 1 r.l.u. = 20 cms for a^* and 1 r.l.u. = 10 cms for b^* ; and the corresponding lattice points (only for 92 observed reflections)

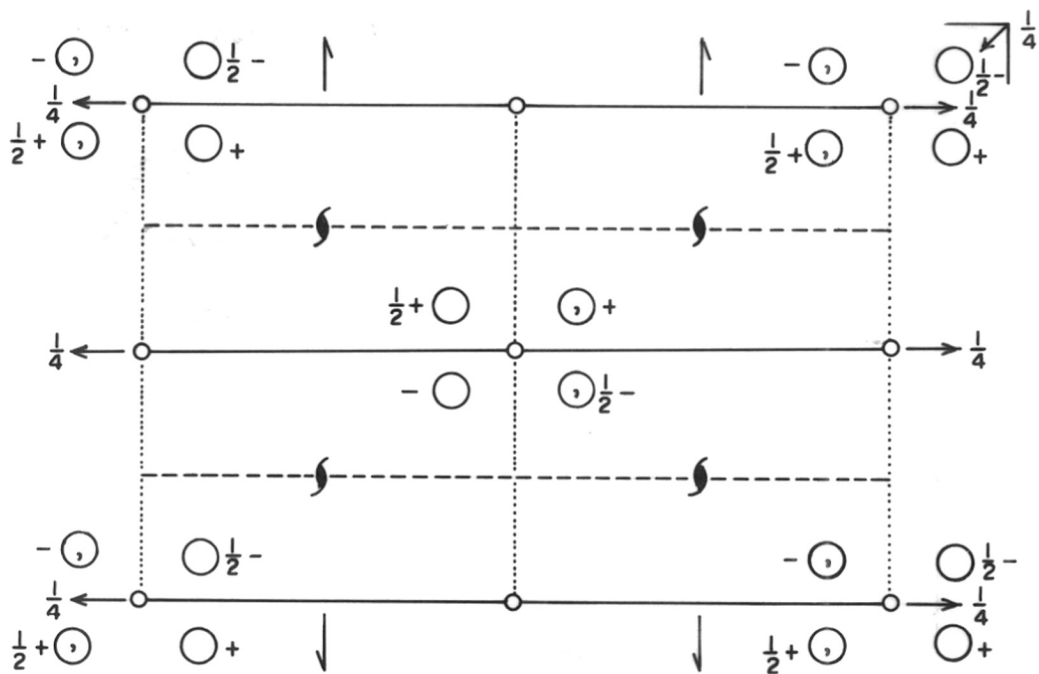


FIG. 12 SPACE GROUP Pbcn

were exposed. The exposures given were proportional to the products of corrected intensities and S the corresponding reciprocal vectors from the origin. In this way the sharpened Patterson photograph for (001) projection was obtained (fig. 13).

The equivalent points and the symmetry elements for the space group $Pbcn$ are shown in fig. (12).

The eight equivalent points for this space group are:

$$\begin{aligned} x, y, z; & \quad \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z; & \quad \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; & \quad \bar{x}, y, \frac{1}{2}-z \\ \bar{x}, \bar{y}, \bar{z}; & \quad \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z; & \quad \frac{1}{2}-x, \frac{1}{2}+y, z; & \quad x, \bar{y}, \frac{1}{2}+z \end{aligned}$$

origin being at $\bar{1}$.

x and y co-ordinates of Na atom were obtained from the following three peaks in the Patterson map (fig. 13).

Peak No.1 due to $Na(x, y)$ and $Na(x, \bar{y})$ falling at $(0, 2y)$
No.2 due to $Na(x, y)$ and $Na(\bar{x}, y)$ at $(2x, 0)$
and No.3 corresponds to $Na(x, y)$ and $Na(\bar{x}, \bar{y})$ at $(2x, 2y)$

Approximate $x_{Na} = 0.209$ and $y_{Na} = 0.250$ was obtained from these three peaks.

From the unit cell dimensions and expected bond lengths in the molecules, it became clear that the molecules must be arranged nearly parallel to the a axis, in sequence. On plotting the sodium atoms in the (001) projection, it seemed likely that, as in the structure of sodium pyruvate, the Na-O bonds tie the molecules into infinite layers parallel to the (100) planes. Bearing these facts in mind and assuming usual bond lengths and bond angles

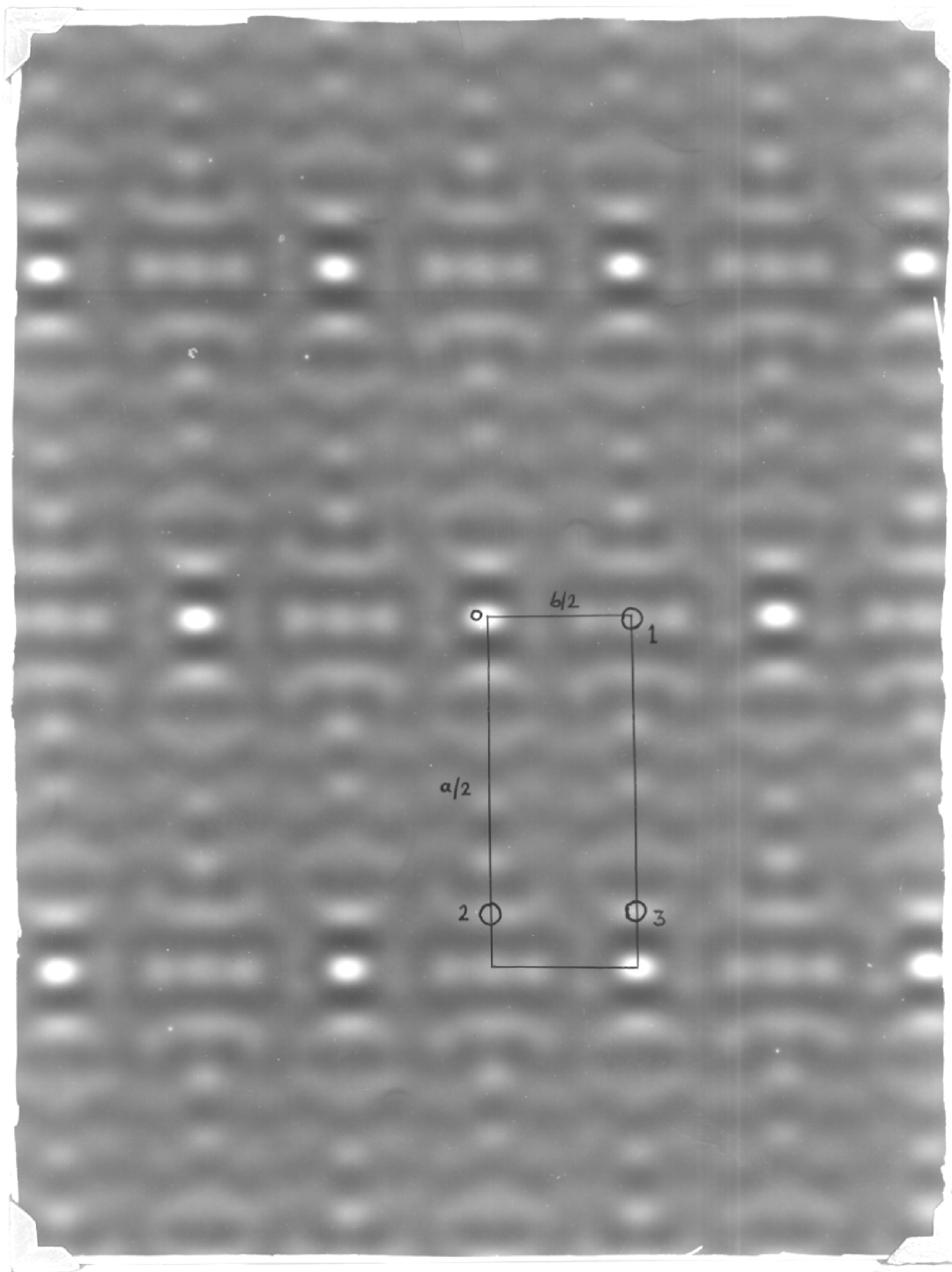


Fig. 13 (001) Sharpened Patterson Projection

(C-C = 1.50 Å; C-O = 1.25 Å and all the angles as 120°(approx.) were assumed); as well as taking the help of the Fourier synthesis obtained with the Eller Photosummator, (Phases for this Fourier synthesis were obtained only from sodium position from the sharpened Patterson) a trial structure was postulated. The x and y parameters of the trial structure are given in table (13).

TABLE - 13

	x	y
Na	0.209	0.250
O ₁	0.214	0.182
O ₂	0.138	0.159
O ₃	0.179	0.389
C ₁	0.174	0.248
C ₂	0.136	0.209
C ₃	0.092	0.283
C ₄	0.054	0.188

(iv) (010) sharpened Patterson projection and the trial z parameters:

(010) sharpened Patterson projection (x axis halved for convenience) was obtained. As the Eller's machine was not set properly at that time the peaks in the photograph were not clear and the z parameter (zNa = 0) obtained from the same was completely in error (Final zNa = 0.076). The sharpened map (fig. 14) given, was obtained after setting the Eller machine.

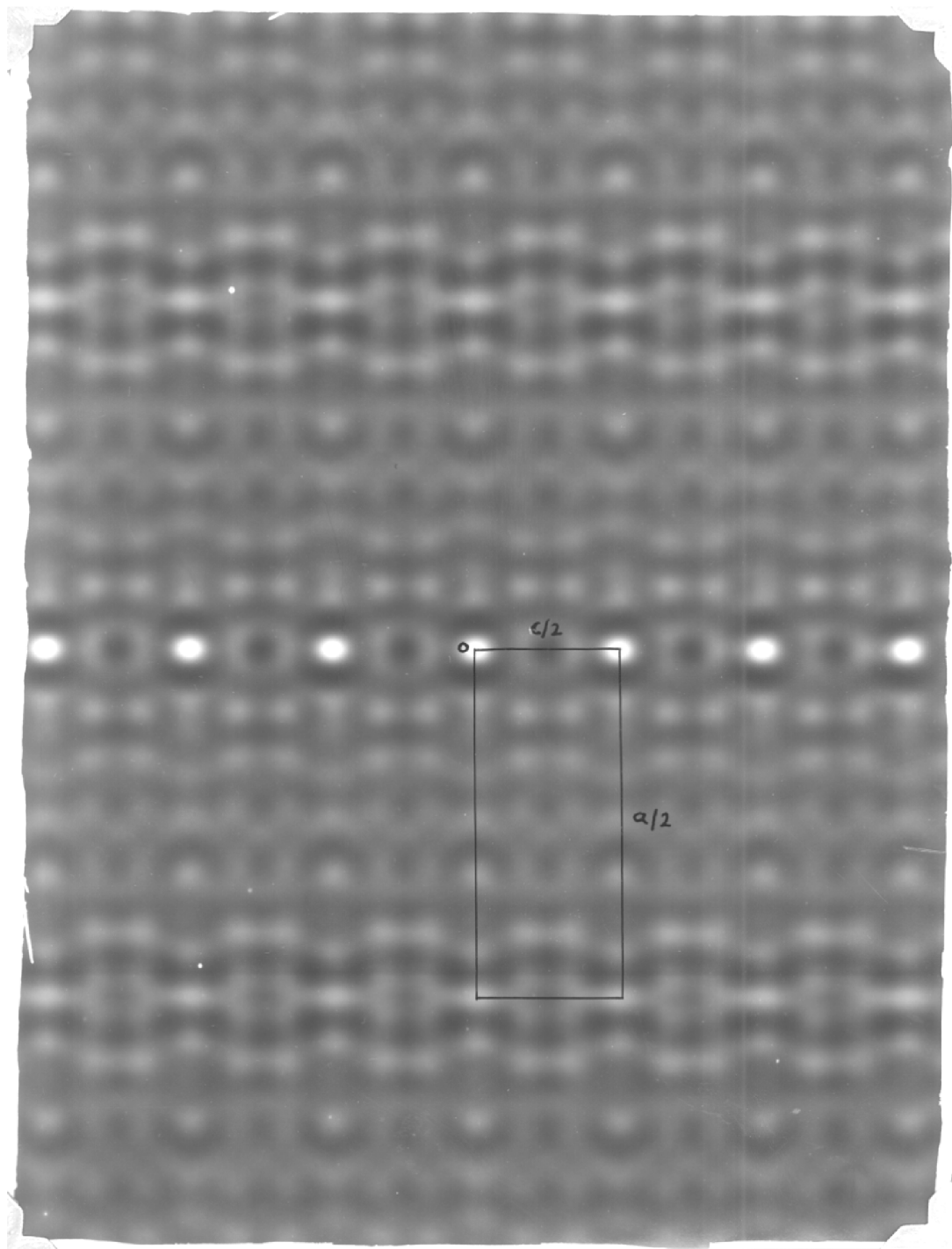


Fig. 14 (010) Sharpened Patterson Projection

Using known x parameters from (001) projection and assuming the bond lengths and angles as mentioned previously the trial z' parameters for the (010) projection were obtained. They are as follows:

	<u>z'</u>
Na	0.000
O ₁	0.819
O ₂	0.466
O ₃	0.328
C ₁	0.000
C ₂	0.819
C ₃	0.110
C ₄	0.849

z' are the parameters with respect to the axis $c' = c/2$. As there are absent reflections such as $h0l$ absent for $l = 2n+1$; for calculation purposes $l' = l/2$ was taken throughout the refinements.

C H A P T E R - V I I I

ELECTRON DENSITY PROJECTIONS AND REFINEMENT OF ATOMIC PARAMETERS

(001) PROJECTION

(i) Structure factor and electron density expressions are as follows:

$$F(hko) = \sum_{n=1}^N 8f_n \cos 2\pi hx_n \cos 2\pi ky_n$$

and

$$\rho(xyo) = \frac{1}{Ac} \left[F(000) + 4 \left\{ \sum_{h=2}^{\infty} F(h00) \cos 2\pi hx + \sum_{k=2}^{\infty} F(0k0) \cos 2\pi ky \right\} + 8 \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} F(hko) \cos 2\pi hx \cos 2\pi ky \right]$$

structure factors were calculated using Mcweeny's (1951) values of atomic scattering factors for carbon and oxygen; and James and Brindley's (1931) values for Na^+ .

(ii) Refinement of x parameters by $\rho(x00)$ i.e. line synthesis:

Starting from the trial structure parameters, x parameters were refined twice by $\rho(x00)$ synthesis, using Beevers-Lipson strips, by the formula,

$$\rho(x00) = \frac{bc}{V} \sum_h F(h00) \cos 2\pi hx$$

where V is the volume in \AA^3 of the unit cell; and b, c the axial lengths.

II line synthesis is shown in fig. (15); and was calculated from the axial reflections 200; 400; 600; 800; 10,00; 12,00; 14,00; 16,00; 18,00; 20,00; 22,00; 24,00 and 26,00. For the 200

reflection, as it seems to be subject to extinction, the calculated F_{200} value was used.

From II line synthesis fig. (15) one could see that the values of C_4 and C_3 are changed. For others, as there was overlapping, it was difficult to assign the proper x co-ordinate. And as C_0 peak is sharp, it seems that both x_{C2} and x_{O2} have the same value as 0.133.

[Note:- Some reflections, hko and hol with $h > 30$ were observed; but these were left out from all calculations.)

The x parameters obtained from the two line syntheses are given in table (14).

(iii) Refinement of x parameters by one-dimensional least square:

The x parameters obtained from the II line synthesis were refined by the method of least squares using the axial reflections, 100, 600, 800, 10,00; 12,00; 14,00; 16,00; 18,00; 20,00; 24,00 and 26,00 by the formula

$$\Delta x_n = -\frac{1}{2\pi} \frac{\sum h(8f_n) \Delta F(\sin 2\pi h x_n)}{\sum h^2 (8f_n)^2 (\sin 2\pi h x_n)^2}$$

The parameters obtained from the same are given in table (14).

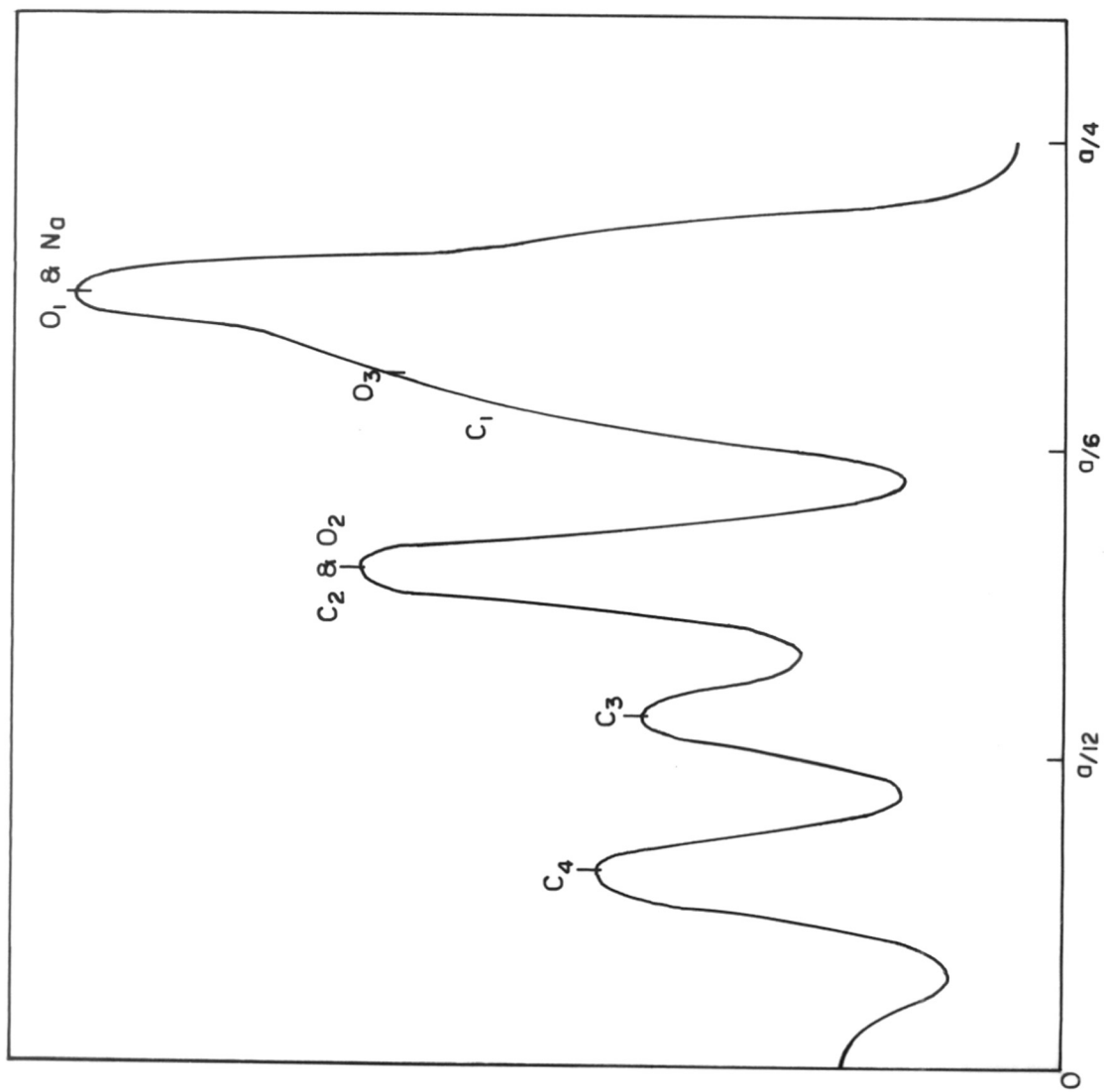


FIG. 15. SECOND LINE SYNTHESIS Q (X00). CONTOURS DRAWN AT ARBITRARY INTERVALS.

TABLE - 14

REFINEMENT OF x PARAMETERS

	1st line synthesis	2nd line synthesis	One dimensional least square
Na	0.209	0.209	0.2100
O ₁	0.209	0.211	0.2130
O ₂	0.133	0.133	0.1330
O ₃	0.190	0.192	0.1905
C ₁	0.180	0.180	0.1770
C ₂	0.133	0.133	0.1330
C ₃	0.097	0.094	0.0960
C ₄	0.047	0.052	0.0535

(iv) Preliminary refinement of y parameters:

After calculating $F(hko)$'s with x parameters from one dimensional least square and trial y parameters, the y parameters were refined twice by Fourier synthesis obtained on Eller Photosummator followed by a difference synthesis (with Eller machine) and then by two dimensional least squares method. The details of y refinement are given in table (15).

For parameters from least square $R \approx 0.28$ with $B = 2.45 \text{ \AA}^2$. Reflections with $h > 30$, 200, 022 and unobserved reflections were excluded for calculating R.

TABLE - 15

REFINEMENT OF γ PARAMETERS

	I Fourier	II Fourier	($F_o - F_c$) synthesis	Least square
Na	0.240	0.230	0.240	0.249
O ₁	0.182	0.177	0.170	0.158
O ₂	0.172	0.184	0.160	0.162
O ₃	0.389	0.395	0.395	0.382
C ₁	0.248	0.241	0.265	0.255
C ₂	0.193	0.202	0.210	0.243
C ₃	0.283	0.304	0.304	0.293
C ₄	0.210	0.246	0.255	0.271

(v) The difference Fourier synthesis:

The difference synthesis is also one of the methods used for the parameter refinement. In this method instead of using the observed structure factors, in the Fourier series, the difference ($F_o - F_c$) with proper phase is used.

The difference synthesis is expressed by the formula (for centrosymmetrical structures)

$$(\rho_o - \rho_c)_{x,y} = \frac{1}{Ac} \sum_h \sum_k (F_o - F_c) \cos 2\pi(hx + ky)$$

The resulting contour map gives the idea about atomic shifts, temperature factors and positions of the hydrogen atoms. If the co-ordinates of the atoms from which F_c 's are calculated are marked on the map the directions of steepest ascent at the assumed atomic positions give the directions of the atomic shifts.

The magnitude of the shift is given by the formula (Lipson and Cochran, 1953)

$$\Delta r_n = \frac{\left(\frac{\partial D}{\partial r}\right)_n}{2p(\rho_0)_n}$$

where r is the distance measured in the direction in which $D = \sigma^* c$ increases most rapidly. $(\rho_0)_n$ is the electron density and $p=5.0$. (p is defined in Chapter V(11)).

Before proceeding to $(\rho_0 - \rho_c)$ synthesis, x and y parameters were refined by difference synthesis using the Eller photosummator followed by the least squares method. The x and y parameters were refined twice by $(\rho_0 - \rho_c)$ synthesis using Beevers-Lipson strips. The summation was carried out along one quarter of the a axis and along half of the b axis, at intervals of $1/120$ th along a and $1/60$ th along b . The difference Fourier maps failed to reveal the hydrogen atom positions with certainty. The parameters from II $(\rho_0 - \rho_c)$ synthesis (fig. 16) are given in table (16).

(Note:- x parameters were refined simultaneously from (100) and (010) projections; and x values are the mean from the two).

TABLE - 16 PARAMETERS FROM II $(\rho_0 - \rho_c)$ SYNTHESIS

	x	y
Na	0.2111	0.2459
O ₁	0.2137	0.1523
O ₂	0.1330	0.1590
O ₃	0.1860	0.3822
C ₁	0.1832	0.2398
C ₂	0.1336	0.2525
C ₃	0.0924	0.2870
C ₄	0.0407	0.2520

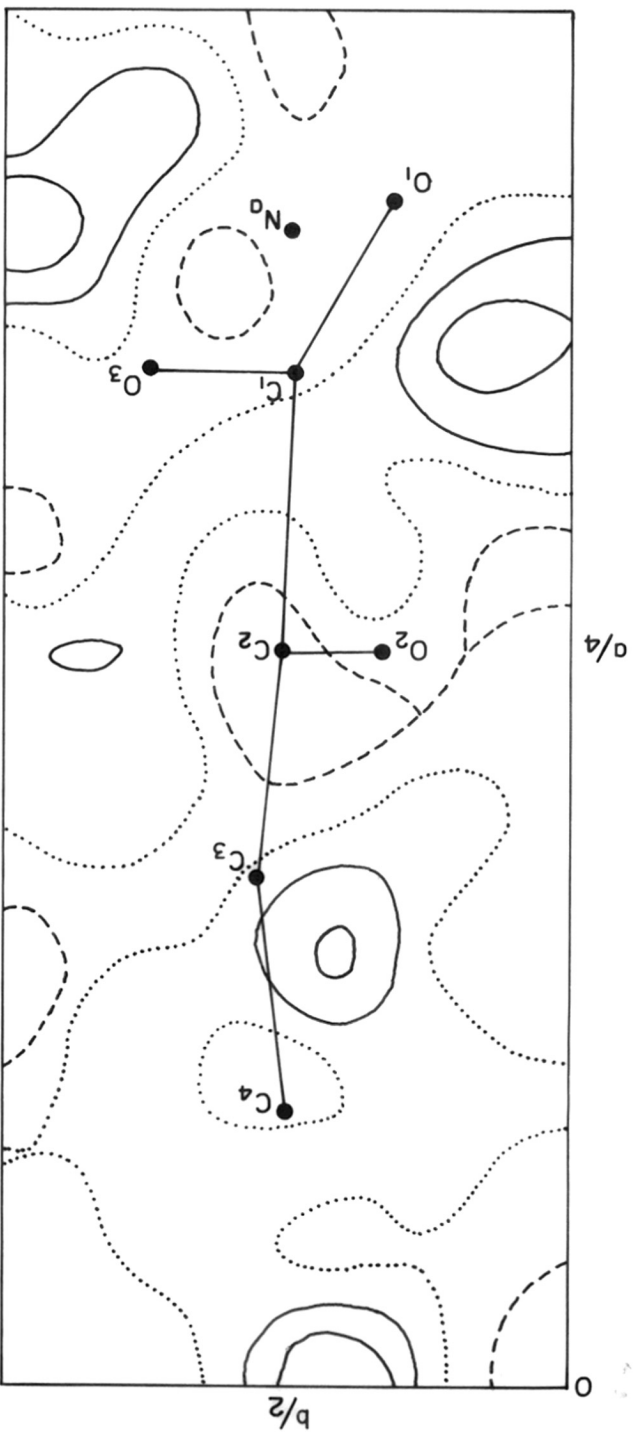


FIG. 16. II^{nd} ($F_0 - F_c$) SYNTHESIS PROJECTED ON (001) CONTOURS DRAWN AT INTERVALS OF $\pm 0.50 e/A^2$, ZERO CONTOURS ARE DOTTED, WHILE -0.5 CONTOURS ARE DASHED. ASSUMED ATOMIC POSITIONS FROM PREVIOUS SYNTHESIS ARE INDICATED BY DOTS.

$R \approx 0.187$ with $B = 2.1 \text{ \AA}^2$ neglecting 020 and 200 reflections.
 $B = 2.1 \text{ \AA}^2$ is a revised temperature factor obtained from F_0 and F_c values.

(vi) Least squares refinement of atomic parameters for overlapping atoms.

If the two atoms are overlapping and are not resolved in projection, their co-ordinates can be refined by taking the cross terms into account. The reason for this is as follows:

In the expression, (Chapter IV (iii))

$$\sum \Delta F \frac{\partial F}{\partial x} = \Delta x \sum \left(\frac{\partial F}{\partial x} \right)^2 + \Delta y \sum \frac{\partial F}{\partial x} \frac{\partial F}{\partial y}$$

For well resolved atoms the cross terms such as $\sum \frac{\partial F}{\partial x} \frac{\partial F}{\partial y}$ are very small as compared with $\sum \left(\frac{\partial F}{\partial x} \right)^2$ and can be neglected; but for overlapping atoms they will be appreciable and hence must be accounted for refinement.

If the x parameters of the two overlapping atoms m and n are to be refined by this method, we have

$$\Delta F = \frac{\partial F}{\partial x_m} \Delta x_m + \frac{\partial F}{\partial x_n} \Delta x_n.$$

Multiplying both the sides of the equation by $\left(\frac{\partial F}{\partial x_m} \right)$ and $\left(\frac{\partial F}{\partial x_n} \right)$ respectively and summing for all the reflections, one gets

$$\sum \Delta F \frac{\partial F}{\partial x_m} = \Delta x_m \sum \left(\frac{\partial F}{\partial x_m} \right)^2 + \Delta x_n \sum \frac{\partial F}{\partial x_m} \frac{\partial F}{\partial x_n}$$

$$\sum \Delta F \frac{\partial F}{\partial x_n} = \Delta x_n \sum \frac{\partial F}{\partial x_m} \frac{\partial F}{\partial x_n} + \Delta x_n \sum \left(\frac{\partial F}{\partial x_n} \right)^2$$

These two simultaneous equations can be solved, after obtaining the numerical values of $(\frac{\partial F}{\partial x_m})^2$; $(\frac{\partial F}{\partial x_n})^2$ and $\frac{\partial F}{\partial x_m} \frac{\partial F}{\partial x_n}$ for Δx_m and Δx_n .

Similarly Δy_m and Δy_n can be obtained.

(vii) Least squares refinement of the temperature factors:

We have,

$$(F_o - F_c) = \Delta F = \frac{\partial F}{\partial B_1} \Delta B_1 + \frac{\partial F}{\partial B_2} \Delta B_2 + \dots$$

where $\Delta B_1, \Delta B_2$ etc. are the corrections to be applied to the temperature factors B_1, B_2 etc.

Multiplying both the sides of the equation by $\frac{\partial F}{\partial B_1}$ we get

$$\Delta F \frac{\partial F}{\partial B_1} = (\frac{\partial F}{\partial B_1})^2 \Delta B_1 + \frac{\partial F}{\partial B_1} \frac{\partial F}{\partial B_2} \Delta B_2 + \dots$$

Summing up for all the observed structure factors, one gets

$$\sum \Delta F \frac{\partial F}{\partial B_1} = \Delta B_1 \sum (\frac{\partial F}{\partial B_1})^2 + \Delta B_2 \sum \frac{\partial F}{\partial B_1} \frac{\partial F}{\partial B_2} + \dots$$

Terms such as $\sum \frac{\partial F}{\partial B_1} \frac{\partial F}{\partial B_2}$ are small as compared with $\sum (\frac{\partial F}{\partial B_1})^2$; and hence can be neglected; and the equation reduces to

$$\sum \Delta F \frac{\partial F}{\partial B_1} = \Delta B_1 \sum (\frac{\partial F}{\partial B_1})^2$$

$$\text{or } \Delta B_1 = \frac{\sum \Delta F \frac{\partial F}{\partial B_1}}{\sum (\frac{\partial F}{\partial B_1})^2}$$

Similarly ΔB_2 etc. could be obtained.

The method of calculation:

$$\begin{aligned} \text{For } F(hko) \text{ we have } F &= \sum 8f_o e^{-B(\sin\theta/\lambda)^2} \cos 2\pi hx \cos 2\pi ky \\ &= e^{-B(\sin\theta/\lambda)^2} \sum 8f_o \cos 2\pi hx \cos 2\pi ky \end{aligned}$$

where f_0 is the atomic scattering factor for the atom at rest.

$$\begin{aligned} \therefore \frac{\partial F}{\partial B} &= - (\sin\theta/\lambda)^2 e^{-B(\sin\theta/\lambda)^2} \sum 8f_0 \cos 2\pi hx \cos 2\pi ky \\ &= - F(\sin\theta/\lambda)^2 = - F(S/2\lambda)^2 \text{ where } S = 2\sin\theta \end{aligned}$$

\therefore After substituting one gets

$$\Delta B = - 4 \lambda^2 \frac{\sum \Delta F F(S)^2}{\sum F^2 S^4}$$

(viii) Refinement of B factors and the atomic parameters by least squares method for (001) projection:

After the II ($\rho_0 - \rho_c$) hko synthesis x and y parameters were refined thrice by the least squares method; Off diagonal terms were included for the overlapping atoms (for (001) projection C_2 and O_2 ; and Na, O_1 and C_1 atoms are overlapping (fig. 17)). After the II least square the individual temperature factors were refined by the least squares method. Final atomic parameters as well as individual temperature factors are given in table (19).

Final R value is 0.159 with individual temperature factors and excluding 020, 200 and 20,00 reflections and including all except very high angle unobserved reflections at half the minimum observable value. Also reflections with $h > 30$ were excluded for the calculation of R. Reflections 200 and 020 were excluded as they appear to be subject to extinction, and 20,00 was left out because it coincides with the 22,00 reflection of CuK_β radiation in the photograph; and hence its observed value is uncertain.

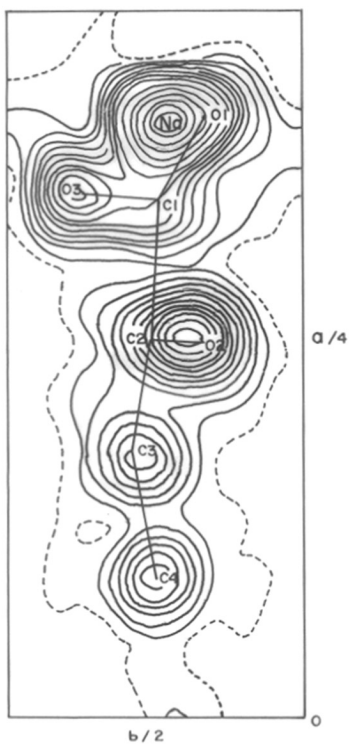


FIG. 17.

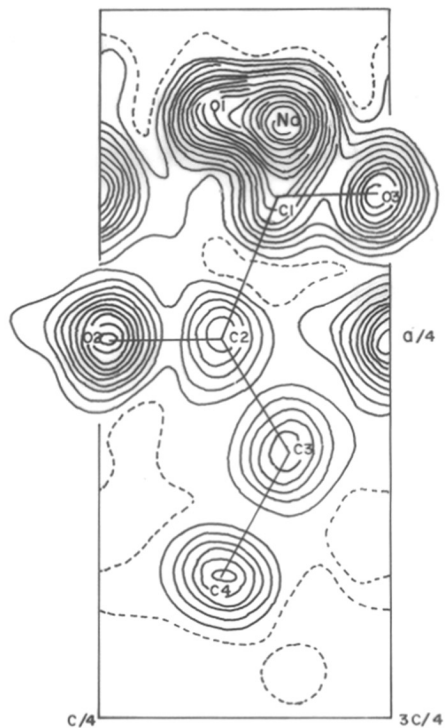


FIG. 19.

FIG. 17. ELECTRON DENSITY PROJECTED ON (001). FIG. 19. THAT ON (010). CONTOURS ARE DRAWN AT INTERVALS OF $1e/A^2$. $1e/A^2$ CONTOURS IS DASHED. FOR Na^+ ALTERNATE CONTOURS ARE DRAWN.

The (001) electron density projection shown in fig. (17) was obtained, using final calculated signs and F_o values for all except $F(200)$ and $F(020)$ for which final F_c (table 21) values were used. The summation was carried out using Beever-Lipson strips, along one quarter of the a axis and along half of the b axis at intervals of 1/120th along a and 1/60th along b.

(010) PROJECTION

(i) Structure factor and electron density expressions:

$$F(ho1) \text{ for } h+l = 2n$$

$$= \sum_{n=1}^N 8f_n \cos 2\pi hx_n \cos 2\pi lz_n$$

$$\text{for } h+l = 2n+1$$

$$= \sum_{n=1}^N -8f_n \sin 2\pi hx_n \sin 2\pi lz_n$$

$$\text{and } \rho(xoz) = \frac{1}{Ac} \left[F(00) + 4 \left\{ \sum_{h=2}^{\infty} F(hoo) \cos 2\pi hx + \sum_{l=1}^{\infty} F(ool) \cos 2\pi lz \right\} \right. \\ \left. + 8 \left\{ \sum_{h=2}^{\infty} \sum_{l=1}^{\infty} \begin{array}{l} h+l = 2n \\ F(ho1) \cos 2\pi hx \cos 2\pi lz \\ - \sum_{h=1}^{\infty} \sum_{l=1}^{\infty} \begin{array}{l} h+l = 2n+1 \\ F(ho1) \sin 2\pi hx \sin 2\pi lz \end{array} \end{array} \right\} \right]$$

(ii) Refinement of z' parameters by line difference, ($\rho_o - \rho_c$) synthesis and least squares method:

Before proceeding to the refinement of z' parameters by line difference synthesis, the trial z' parameters were refined by a difference Fourier and twice by $F_o - F_{Na}$ synthesis taken on Eller photosummator. The z' parameters were refined by difference

line synthesis four times. After I line difference three suitable changes were made in z' parameters of Na, O_1 , O_3 and C_1 ; and then structure started refining. The parameters from I line synthesis with three suitable changes and those from IV line synthesis are given in table (17).

TABLE - 17 REFINEMENT OF z' PARAMETERS

	I line synthesis	I change	II change	III change	IV line synthesis
Na	0.017	0.080	0.110	0.120	0.151
O_1	0.900	-	0.930	0.940	0.912
O_2	0.573	-	-	-	0.531
O_3	0.420	-	0.450	0.460	0.463
C_1	0.150	0.120	0.150	0.160	0.129
C_2	0.963	-	-	-	0.917
C_3	0.233	-	-	-	0.165
C_4	0.963	-	-	-	0.919

$R \approx 0.195$ for the IV line synthesis excluding 200 reflection.

Before proceeding to two dimensional ($\theta-\epsilon$) synthesis B and scale factors were corrected from F_0 and F_c values. The z' parameters were refined twice by ($\theta-\epsilon$) synthesis and then twice by the least squares method. The off diagonal terms were included, wherever necessary, to account for the overlap of atoms. After I cycle of least square individual temperature factors were refined by least squares method.

The z' parameters from II($\rho_0 - \rho_c$) synthesis (fig. 18) and I least squares method are given in table (18) and those from II least squares method (final z parameters) with individual temperature factors are given in table (19).

TABLE - 18 REFINEMENT OF z' PARAMETERS

	II ($\rho_0 - \rho_c$) synthesis	I least square
Na	0.1510	0.1502
O ₁	0.9137	0.9196
O ₂	0.5260	0.5136
O ₃	0.4610	0.4698
C ₁	0.1290	0.1145
C ₂	0.9127	0.9181
C ₃	0.1593	0.1550
C ₄	0.9153	0.9199

The final value of $R(ho1)$, on including all except very high angle unobserved reflections at half the minimum observable value was 0.141 with individual temperature corrections. In obtaining $R(ho1)$, reflections 200 was excluded as it appears to be subject to extinction; and 20,00 was left because it coincides with the 22,00 reflection of $CuK\beta$ radiation in the photograph; and hence its observed value is uncertain.

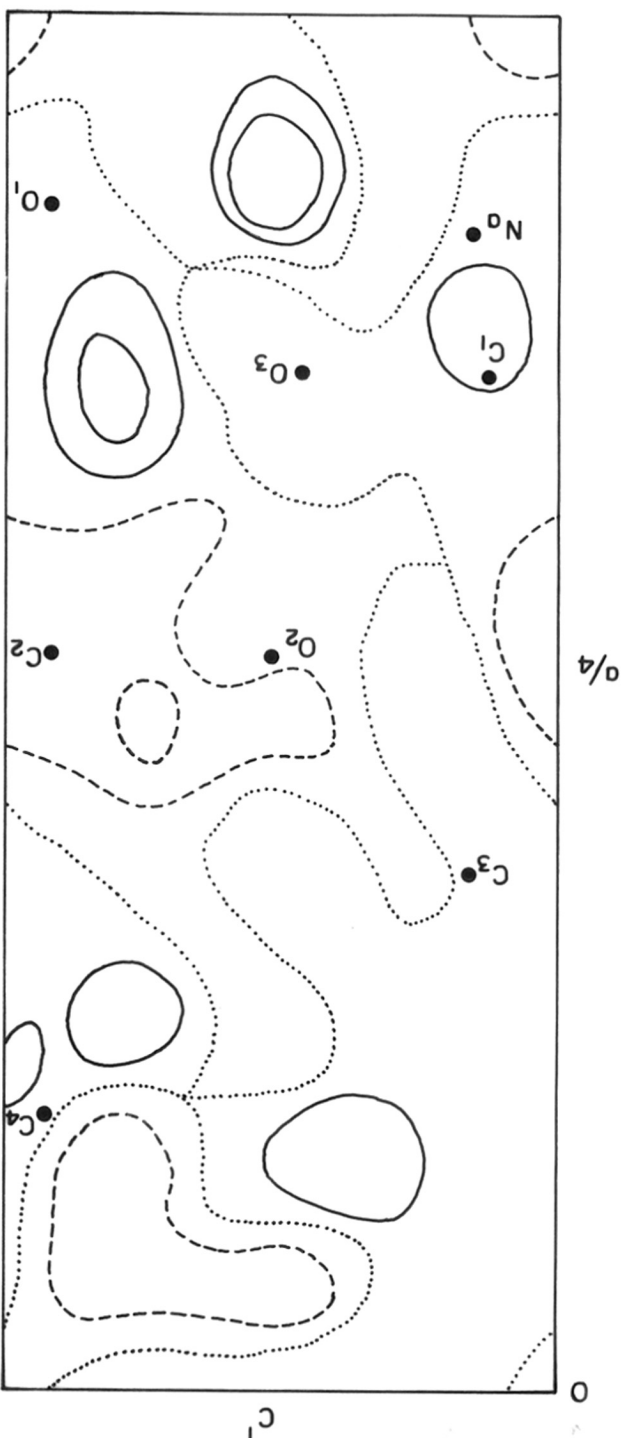


FIG. 18. II^{nd} ($F_0 - F_c$) SYNTHESIS PROJECTED ON (010). CONTOURS DRAWN AT INTERVALS OF $+0.25 e/\text{\AA}^2$. ZERO CONTOURS ARE DOTTED, WHILE $-ve$ CONTOURS ARE DASHED. ASSUMED ATOMIC POSITIONS FROM PREVIOUS SYNTHESIS ARE INDICATED BY DOTS.

The (010) electron density projection shown in fig. (19) was obtained using final calculated signs and F_o values for all except F(200); for which final F_c value was used. The summation was carried out, using Beevers-Lipson strips along one quarter of the a axis and along half of the c axis at intervals of $\frac{1}{120}$ th of the a axis and $\frac{1}{60}$ th of the c axis.

The final atomic parameters and the individual temperature factors are listed in table (19); and the observed and calculated structure factors in table (21). Final z' parameters are converted to z parameters (table 19).

TABLE - 19 FINAL ATOMIC AND THERMAL PARAMETERS

	x	y	z	B(hko)	B(hol)
Na	0.2111 ± 0.0005	0.2450 ± 0.0025	0.0762 ± 0.0025	2.0 \AA^2	1.8 \AA^2
O ₁	0.2136 ± 0.0007	0.1578 ± 0.0033	0.4599 ± 0.0034	2.4	2.3
O ₂	0.1330 ± 0.0007	0.1642 ± 0.0033	0.2584 ± 0.0034	2.9	2.8
O ₃	0.1855 ± 0.0007	0.3769 ± 0.0033	0.7312 ± 0.0034	2.2	2.4
C ₁	0.1838 ± 0.0009	0.2381 ± 0.0045	0.5566 ± 0.0046	1.6	1.4
C ₂	0.1336 ± 0.0009	0.2542 ± 0.0045	0.4564 ± 0.0046	3.4	3.2
C ₃	0.0938 ± 0.0009	0.2865 ± 0.0045	0.5758 ± 0.0046	2.5	2.9
C ₄	0.0488 ± 0.0009	0.2481 ± 0.0045	0.4568 ± 0.0046	2.4	2.7

C H A P T E R - I XRESULTS AND DISCUSSION

(1) Bond distances and angles:

Intramolecular and intermolecular bond distances were calculated by using the co-ordinates from table (19) (after converting them into Å units) by the formula

$$d^2 = \sum_1^3 (x_2 - x_1)^2$$

where d is the bond distance in Å between the two atoms (x_1, y_1, z_1) and (x_2, y_2, z_2) .

Bond lengths and bond angles found in the α -ketobutyrate group are shown in fig. (20) and listed in table (20).

TABLE - 20 INTRAMOLECULAR BOND LENGTHS & BOND ANGLES

Bond lengths		Bond angles	
C ₁ -O ₁	1.149 ± 0.034 Å	O ₁ -C ₁ -O ₃	128.6 ± 2.6°
C ₁ -O ₃	1.330 ± 0.034	O ₁ -C ₁ -C ₂	123.0 ± 2.5
C ₁ -C ₂	1.587 ± 0.038	O ₃ -C ₁ -C ₂	106.5 ± 2.2
C ₂ -O ₂	1.289 ± 0.034	C ₁ -C ₂ -C ₃	127.2 ± 2.4
C ₂ -C ₃	1.376 ± 0.038	C ₁ -C ₂ -O ₂	109.0 ± 2.2
C ₃ -C ₄	1.511 ± 0.038	C ₃ -C ₂ -O ₂	120.8 ± 2.5
		C ₂ -C ₃ -C ₄	118.6 ± 2.4

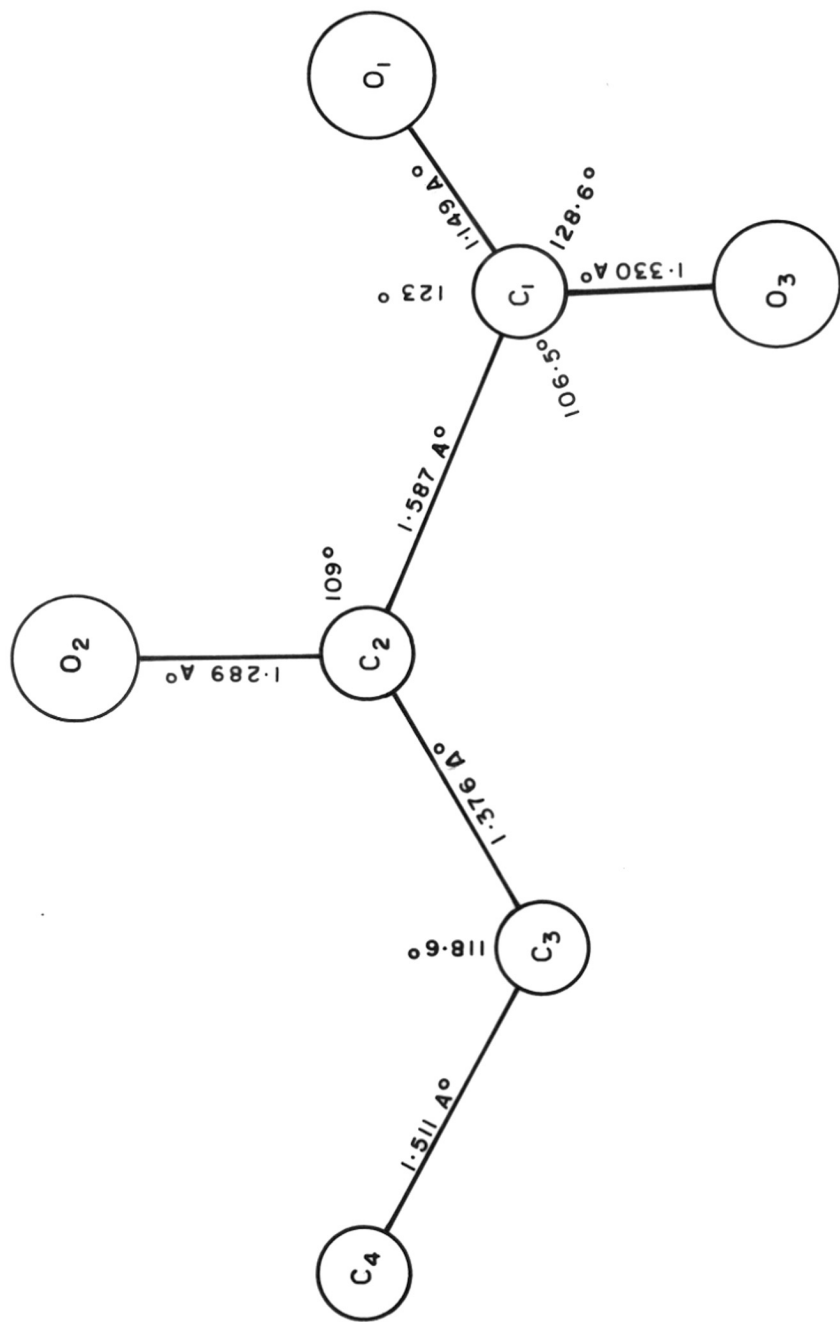


FIG. 20. BOND LENGTHS AND BOND ANGLES IN THE α -KETOBUTYRATE GROUP; O_1 AND O_3 ARE CARBOXYLIC OXYGENS. O_2 IS KETO GROUP OXYGEN, C_3 AND C_4 ARE METHYLENE AND METHYL CARBONS RESPECTIVELY.

(ii) Estimation of errors:

The standard deviations (σ) of atomic co-ordinates and the interatomic distances were estimated (Lipson and Chochran, 1953) assuming $\sigma(F) = 0.15 |F|$ and $p = 5 \text{ \AA}^2$. The deviations in the co-ordinates $\sigma(x_n)$ and those in the positions $\sigma(r)$ of the atoms are as follows: (Method of calculation is given in Chapter V(11)).

	$\pm\sigma(x_n) = \sigma(y_n) = \sigma(z_n)$	$\pm\sigma(r_n)$
Na	0.015 $\overset{\circ}{\text{A}}$	0.015 $\overset{\circ}{\text{A}}$
O	0.020	0.020
C	0.027	0.027

The deviations in bond lengths are:

$$\begin{aligned} \sigma(\text{C-C}) &= \pm 0.038 \overset{\circ}{\text{A}} \\ \sigma(\text{C-O}) &= \pm 0.034 \\ \sigma(\text{Na-O}) &= \pm 0.025 \\ \text{and } \sigma(\text{Na-Na}) &= \pm 0.022 \end{aligned}$$

The standard deviations in bond angles were estimated by the method of Darlow (1960) using isotropic standard deviations for each atom. The bond angle deviations are listed in table (21).

(iii) Molecular structure:

The bond lengths and bond angles found in the α -ketobutyrate group are shown in fig. (20) and listed in table (21).

The mean plane through the atoms O_1, O_3, C_1 and C_2 can be represented by the equation

$$- 0.2046 X - 0.8028 Y + 0.5589 Z + 0.5022 = 0$$

where X, Y and Z are expressed in Å units and referred to the axes of the unit cell. The normal distances of the individual atoms from the mean plane are 0.027 Å for atoms O₁, O₃ and C₂; and -0.80 Å for C₁. The rest of the molecule is non planar. The atoms O₂ and C₄ are 0.426 Å and 0.299 Å away respectively, from the plane containing the atoms C₁, C₂ and C₃.

The observed bond lengths and angles show that sodium α-ketobutyrate is enolized to a great extent in the crystalline state. In the pure keto form, one would expect the C₂-C₃ bond lengths to be about 1.5 Å (the expected distance between two bonded carbon atoms in the sp² state and sp³ state respectively) and the C₂-O₂ bond lengths to be 1.2 Å (the corresponding bond lengths to be about 1.183 ± 0.040 Å). Further the expected value of the angle C₂-C₃-C₄ is about 109.5° (the tetrahedral angle). In the pure enol form, however, the expected C₂-C₃ bond length is about 1.33 Å (the C=C bond length in ethylene) and the expected C₂-O₂ distance is about 1.42 Å, the normal C-O single bond length. Further, the angle C₂-C₃-C₄ is expected to have a value of about 120°. The observed bond lengths (1.376 ± 0.038 Å for C₂-C₃ bond and 1.289 ± 0.034 Å for C₂-O₂ bond) and the observed value of the angle C₂-C₃-C₄ (118.6 ± 2.4°) lie in between the expected values for the keto and enol forms, thereby indicating large percentage of enolization of the compound. It is likely that, the keto and the enol forms are randomly distributed in the crystal. This may be the reason for the larger observed B values for atoms O₂ and C₂ (table 19). It is difficult to account for the larger B values

of these atoms on the basis of rigid-body vibrations or oscillations of the molecule. Intramolecular vibrations are also not expected to be large enough to account for these B values.

The C₂-O₂ bond length ($1.587 \pm 0.038 \text{ \AA}$) in sodium α -keto-butyrate is close to the corresponding bond length in sodium pyruvate ($1.579 \pm 0.045 \text{ \AA}$). It is possible that this increase from the standard single bond length (1.545 \AA) is in both cases significant. Such increase in the C-C bond length has been observed by Chaudhuri and Hargreaves (1956) in the structure of bishydroxydurylmethane where C-C bond distance increases to 1.60 \AA . Unusually long C-C bond lengths have also been reported by Kitaigorodskii (1949) in the structure of acenaphthalene, where the distance between two bonded methylene carbons comes out to be 1.64 \AA ; and by Lemaire and Livingstone (1950) in the structure of octafluorocyclobutane where the C-C bond length is found to lie between 1.57 and 1.62 \AA . In each case, the increase in bond length is attributed to intramolecular strain.

Note:- Kitaigorodskii (1961) reports that the C-C bond ($1.64 \pm 0.04 \text{ \AA}$) in acenaphthalene cannot be considered reliable because CH₂ is poorly resolved in the electron density map.

(iv) Crystal structure:

The projections of the structure along the c and b axes are shown in fig. (21) and fig. (22) respectively.

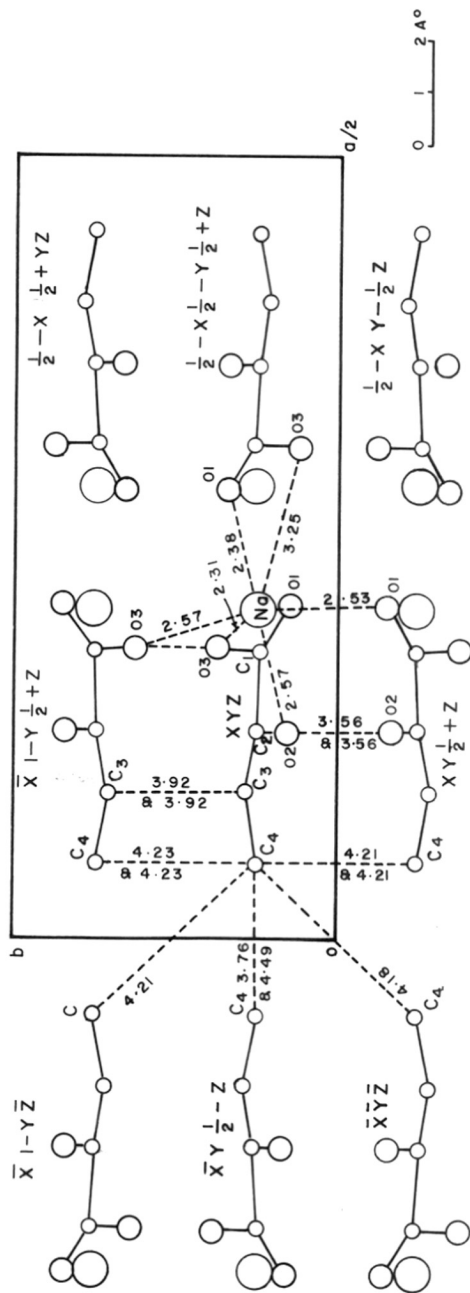


FIG. 21. STRUCTURE PROJECTED ON (001)

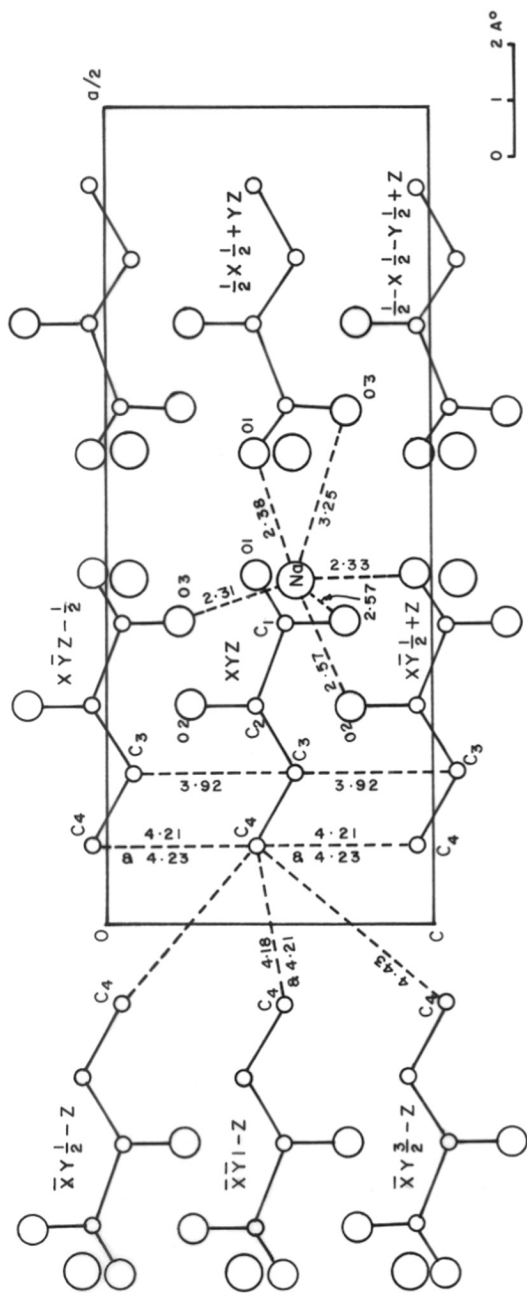


FIG. 22. STRUCTURE PROJECTED ON (010)

There are six short bonds between Na(x,y,z) and the neighbouring oxygens. These distances are as follows:

Na-O ₁ (x,y,z)	2.33 ± 0.03 Å ^o
Na-O ₁ (x, \bar{y} ,z- $\frac{1}{2}$)	2.53 ± 0.03
Na-O ₃ (x,1-y,z- $\frac{1}{2}$)	2.57 ± 0.03
Na-O ₃ (x,y,z-1)	2.31 ± 0.03
Na-O ₁ ($\frac{1}{2}$ -x, $\frac{1}{2}$ -y,z- $\frac{1}{2}$)	2.38 ± 0.03
Na-O ₂ (x,y,z)	2.57 ± 0.03

These distances are comparable to those in sodium pyruvate (2.5 ± 0.2 Å^o).

The more significant van der Waals distances are as follows:

C ₄ (x, \bar{y} ,z+ $\frac{1}{2}$ or z- $\frac{1}{2}$) - C ₄ (x,y,z)	4.21 ± 0.04 Å ^o
C ₄ (\bar{x} ,y, $\frac{1}{2}$ -z) - C ₄ (x,y,z)	3.76 ± 0.04
C ₄ (\bar{x} ,y, $\frac{3}{2}$ -z) - C ₄ (x,y,z)	4.49 ± 0.04
C ₄ (x,1-y, $\frac{1}{2}$ +z or z- $\frac{1}{2}$) - C ₄ (x,y,z)	4.23 ± 0.04
C ₄ (\bar{x} ,1-y,1-z) - C ₄ (x,y,z)	4.21 ± 0.04
C ₄ (\bar{x} , \bar{y} ,1-z) - C ₄ (x,y,z)	4.18 ± 0.04
C ₃ (x, \bar{y} , $\frac{1}{2}$ +z or z- $\frac{1}{2}$) - C ₃ (x,y,z)	4.55 ± 0.04
C ₃ (x,1-y, $\frac{1}{2}$ +z or z- $\frac{1}{2}$) - C ₃ (x,y,z)	3.92 ± 0.04

The structure of sodium α -ketobutyrate is similar to that of sodium pyruvate. In both, strong Na-O bonds tie the molecules into infinite layers parallel to the (100) plane. Any one layer of molecules is linked with the neighbouring layers tightly by Na-O bonds on one side, and loosely on the other by van der Waals bonds.

The short Na-Na contact distances obtained are as follows:

$$\text{Na}(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z) - \text{Na}(x, y, z) \quad 3.73 \pm 0.02 \overset{\circ}{\text{A}}$$

$$\text{Na}(\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}) - \text{Na}(x, y, z) \quad 3.73 \pm 0.02$$

Those observed in sodium pyruvate are ($3.7 \pm 0.1 \overset{\circ}{\text{A}}$).

In sodium pyruvate as well as sodium α -ketobutyrate there are six short distances ($2.5 \pm 0.2 \overset{\circ}{\text{A}}$) between a sodium atom and the neighbouring oxygens; five of these oxygen atoms belong to the carboxylic groups, while one atom belongs to the keto group. It seems plausible to assume that the close approach of the sodium atom to the keto group oxygen produces strain in the molecule and causes the lengthening of the C_1-C_2 bond.

TABLE - 21 OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	F _o	F _c	h	k	l	F _o	F _c
2	0	0	53	- 157	19	1	0	17	17
4	0	0	39	- 45	21	1	0	18	- 22
6	0	0	39	39	23	1	0	16	16
8	0	0	89	- 77	25	1	0	< 6	0
10	0	0	94	87	27	1	0	8	- 10
12	0	0	145	- 143	29	1	0	8	10
14	0	0	59	58	0	2	0	123	-230
*16	0	0	21	3	2	2	0	48	65
18	0	0	12	- 17	4	2	0	12	13
20	0	0	—	- 2	6	2	0	< 3	4
22	0	0	53	46	8	2	0	29	31
24	0	0	26	25	10	2	0	37	- 41
26	0	0	58	- 58	12	2	0	69	85
28	0	0	29	27	14	2	0	51	- 46
30	0	0	22	- 25	16	2	0	23	19
1	1	0	5	5	18	2	0	6	0
3	1	0	6	- 6	20	2	0	6	- 9
5	1	0	6	- 9	22	2	0	23	- 22
7	1	0	7	7	24	2	0	25	- 25
9	1	0	32	43	26	2	0	37	43
11	1	0	53	- 66	28	2	0	17	- 15
13	1	0	16	21	30	2	0	15	14
15	1	0	22	20	1	3	0	16	- 13
17	1	0	17	- 19	3	3	0	26	28

*

h	k	l	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c
5	3	0	14	- 13	22	4	0	< 6	1
7	3	0	< 4	- 3	24	4	0	22	15
9	3	0	39	- 37	26	4	0	21	- 19
11	3	0	58	62	1	5	0	9	5
13	3	0	13	- 10	3	5	0	24	- 22
15	3	0	32	- 29	5	5	0	24	27
17	3	0	18	15	7	5	0	< 6	- 4
19	3	0	14	- 12	9	5	0	< 6	- 5
21	3	0	21	24	11	5	0	14	- 2
23	3	0	22	- 19	13	5	0	8	- 12
25	3	0	8	4	15	5	0	17	13
27	3	0	5	6	0	6	0	26	- 23
29	3	0	12	- 11	2	6	0	17	7
0	4	0	25	36	4	6	0	9	- 9
2	4	0	< 6	0	6	6	0	14	- 3
4	4	0	12	11	8	6	0	23	20
6	4	0	14	- 17	10	6	0	9	- 7
8	4	0	14	- 12	12	6	0	9	8
10	4	0	10	6	14	6	0	< 6	4
12	4	0	24	- 25	16	6	0	7	- 1
14	4	0	21	20	0	0	2	62	82
16	4	0	20	- 19	1	0	2	54	- 52
18	4	0	8	9	2	0	2	21	- 24
24	4	0	16	15	3	0	2	27	33

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
4	0	2	60	61	28	0	2	11	14
5	0	2	<6	- 1	29	0	2	<10	- 10
6	0	2	49	- 52	30	0	2	17	- 17
7	0	2	12	- 11	0	0	4	50	49
8	0	2	38	- 35	1	0	4	< 9	- 20
9	0	2	65	72	2	0	4	14	- 14
10	0	2	37	33	3	0	4	15	15
11	0	2	38	- 32	4	0	4	20	- 22
12	0	2	50	- 49	5	0	4	10	2
13	0	2	18	- 18	6	0	4	21	24
14	0	2	44	44	7	0	4	< 9	4
15	0	2	18	- 17	8	0	4	< 9	- 1
16	0	2	60	- 62	9	0	4	30	32
17	0	2	14	6	10	0	4	10	- 10
18	0	2	37	37	11	0	4	21	- 18
19	0	2	<9	6	12	0	4	20	- 17
20	0	2	17	20	13	0	4	9	- 9
21	0	2	<9	- 5	14	0	4	<10	- 3
22	0	2	16	- 13	15	0	4	20	- 19
23	0	2	11	4	16	0	4	22	28
24	0	2	26	29	17	0	4	14	4
25	0	2	<10	- 7	18	0	4	10	- 13
26	0	2	26	- 27	19	0	4	<10	3
27	0	2	11	15	20	0	4	11	- 10

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
21	0	4	<10	- 5	7	0	6	12	- 10
22	0	4	25	22	8	0	6	<10	11
0	0	6	50	- 45	9	0	6	23	20
1	0	6	<10	- 1	10	0	6	21	- 19
2	0	6	27	23	11	0	6	10	0
3	0	6	<10	9	12	0	6	15	16
4	0	6	12	2	13	0	6	23	- 22
5	0	6	<10	8	14	0	6	9	- 9
6	0	6	12	- 4	15	0	6	9	9

PART-III: CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM α -KETOCAPRYLATE

C H A P T E R - 2

CRYSTAL DATA AND EXPERIMENTAL DETAILS

(i) The determination of unit cell dimensions:

Sodium α -ketocaprylate $\text{CH}_3(\text{CH}_2)_5\text{COCOONa}$ crystals were grown from aqueous solution, containing a trace of acetic acid. The crystals are orthorhombic and grow as fine needles elongated along the c axis. a and b axes were measured from zero level Weissenberg photographs and c from the rotation photograph along the c axis. The unit cell dimensions are as follows:

$$a = 49.57 \pm 0.06; \quad b = 6.05 \pm 0.02 \quad \text{and} \quad c = 5.97 \pm 0.02 \text{ \AA}$$

Axial length a was obtained from 20,00; 22,00; 24,00; 38,00; 42,00; 44,00 and 46,00 reflections; b was obtained from 020 and 040 reflections; while c was obtained from the first two layer lines of the rotation photograph.

(ii) The crystal density determination:

The density obtained by flotation method at 28.5°C is 1.317 gm.cm^{-3} ; and that calculated for eight molecules of $\text{CH}_3(\text{CH}_2)_5\text{COCOONa}$ per unit cell is 1.336 gm.cm^{-3} .

(iii) Linear absorption coefficient μ for $\text{CuK}\alpha$ radiation is 13.5 cm^{-1} .

(iv) Space group determination:

From the diffraction photographs, the crystals are found to be orthorhombic and the systematic absences are

okl for k odd

hol for l odd and

hko for h+k odd.

so that the space group is uniquely determined as Pbcn.

(v) Collection of data and estimation of intensities:

Intensity data was collected from the equi-inclination photographs of higher layers as well as zero layer (from $\lambda = 0$ to $\lambda = 4$) using $\text{CuK}\alpha$ radiation, as well as multiple film technique. The specimen used to collect the intensity data was of the size, roughly $(0.3 \times 4.2 \text{ mm}^2)$ area; the longer side being the oscillation axis. The reflections $h+k+l = 2n$ are found to be sharp and those $h+k+l = 2n+1$ diffuse; thereby suggesting the crystals are disordered. Pant (1964) considers the case of disorder in sodium α -ketocaprylate to be of one-dimensional disorder because the diffusion of intensity takes place along the a^* reciprocal axis.

The structure analysis was carried out with the help of sharp reflections only. Of the 215 possible reflections of the type, hko, 73 were observed; while 56, 84, 22 and 40 sharp reflections of the type hk_1 , hk_2 , hk_3 and hk_4 , respectively, were observed out of possible 176, 204, 155 and 161 respectively. The low angle reflections 200, 400, 600, 800, 110 and 310 could not be recorded as they were cut off by the beam stop. Intensities were measured visually with the intensity scale prepared from sodium α -ketobutyrate crystal.

(vi) Correction factors:

Intensities were corrected for L_p factors in the way as discussed by Cochran (1948). All Weissenberg photographs other than zero level, show elongation of the spots on one half of the film and a contraction of the spots on the other half. The effect is arising from the divergence of the X-ray beam and the movement of the film in either direction, as well as rotation of the crystal (Buerger, 1942; Phillips, 1954). The intensities of higher layer spots were measured from the extended spots and were corrected for the effect of spot-extension by the Phillips method (1956) using the formula $I = WI_e$ where W is the correction factor to be applied to the observed intensities I_e of the elongated spots. Phillips (1956) gives the curves for constant W for normal beam and equi-inclination photographs. No correction was applied for some reflections for which only contracted spots were available. The correction for absorption was neglected on account of the low coefficient of absorption ($\mu = 13.5 \text{ cm}^{-1}$).

Scale and Temperature factors

The structure factors were calculated from the rough structure parameters and the rough scale factor (28) was obtained from $\sum F_{\text{Obs.}} (= \sum \sqrt{I_{\text{Obs.}}})$ and $\sum F_{\text{C}}$. Temperature factor 2.45 \AA^2 was used for calculating the structure factors in the first instance. McWeeny's (1951) values of atomic scattering factors were used for C and O; and James and Brindley's (1931) values for Na^+ .

C H A P T E R - X I

PRELIMINARY STRUCTURE AND THE REFINEMENT OF ATOMIC PARAMETERS

(i) Structure factor expressions (for sharp reflections only)

For

$$\begin{aligned} h+k &= 2n \\ l &= 2n \end{aligned} \quad F(hkl) = \sum_{n=1}^N 8f_n \cos 2\pi hx_n \cos 2\pi ky_n \cos 2\pi lz_n$$

$$\begin{aligned} h+k &= 2n+1 \\ l &= 2n+1 \end{aligned} \quad F(hkl) = \sum_{n=1}^N -8f_n \sin 2\pi hx_n \sin 2\pi ky_n \cos 2\pi lz_n$$

(001) Projection

(ii) Preliminary structure:

The unit cell dimensions of sodium α -keto caprylate are, $a = 49.57 \pm 0.06$; $b = 6.05 \pm 0.02$ and $c = 5.97 \pm 0.02 \text{ \AA}$; and those of sodium α -ketobutyrate are, $a = 29.28 \pm 0.04$; $b = 6.04 \pm 0.01$ and $c = 5.90 \text{ \AA}$. From this data one can see that the two axes in both i.e. b and c are similar; and a axis in sodium α -ketocaprylate has increased by about 20 \AA . Assuming usual bond lengths and angles this is the expected increase in a axis, for a structure isotypic with sodium α -ketobutyrate; because in the latter there are four molecules (fig. 24) in a cell, arranged in sequence nearly parallel to a axis. An increase of about 5 \AA in the length of each molecule (the expected increase in a axis of sodium α -ketocaprylate) will thus mean an increase of 20 \AA in a . A trial

structure was postulated on the above basis for (001) projection. The parameters of the same are given in table (22).

TABLE - 22

	x	y
Na	0.2268	0.2450
O ₁	0.2283	0.1578
O ₂	0.1808	0.1642
O ₃	0.2116	0.3769
C ₁	0.2106	0.2381
C ₂	0.1813	0.2542
C ₃	0.1576	0.2865
C ₄	0.1319	0.2438
C ₅	0.1066	0.2893
C ₆	0.0811	0.2438
C ₇	0.0556	0.2865
C ₈	0.0289	0.2481

(iii) Refinement of (001) projection:

Starting from the trial parameters the structure was refined by a direct Fourier, difference Fourier (both taken on Eller photosummator) and finally by the least squares method. y parameters were refined by 5 cycles of least squares while x parameters by 4 cycles. At the intermediate stage, isotropic temperature factors were obtained for each atom by the least squares method but did not seem to improve the agreement index; so an average

value of 3.6 \AA^2 was used to calculate F_o , for all atoms for further refinements. Final parameters are listed in table (23). Final R for (001) projection is 0.128.

(iv) Refinement of z parameters from (010) projection:

A trial structure was similarly postulated for (010) projection. F(hol)'s were obtained from the 2nd and 4th layer Weissenberg photographs. With the trial z parameters and known final x parameters (from (001) projection) $R \approx 0.30$. The (010) projection refined to $R \approx 0.20$, after three cycles of least squares; but there were serious discrepancies between F_o and F_c for the following reflections.

16,04	$ F_o = 38$	$F_c = 0$
18,04	$= 30$	$= - 6$
14,04	$= 17$	$= - 3$

These discrepancies could not be removed; therefore the trial structure was suitably modified and this refined $R \approx 0.16$. At this stage some of the bond lengths appeared unlikely (fig. 23) $C_1-O_1 = 1.06$; $C_2-O_3 = 1.46$; $C_2-C_3 = 1.43 \text{ \AA}$; so the trial structure was altered again. The modified structural z parameters are as follows:

Na	0.036	C ₁	0.521	C ₅	0.528	
O ₁	0.433	C ₂	0.437	C ₆	0.463	
O ₂	0.220	C ₃	0.541	C ₇	0.554	R = 0.164
O ₃	0.680	C ₄	0.428	C ₈	0.447	

These parameters were refined by six cycles of least squares. z parameters after VI cycle are as follows:

Na	0.032	C ₁	0.521	C ₅	0.554	
O ₁	0.434	C ₂	0.419	C ₆	0.445	R = 0.119
O ₂	0.197	C ₃	0.534	C ₇	0.556	
O ₃	0.673	C ₄	0.449	C ₈	0.444	

Some of the bond lengths at this stage specially C₁-O₁ (1.14 Å), C₁-O₂ (1.17 Å) and C₂-O₃ (1.40 Å) still appeared unlikely (fig. 23); since there were only 41 observed sharp reflections (ho2+ho4) for z refinement and as x parameters were already well refined, it was felt that the z parameters might not be accurate in spite of the low value of R (0.119). So further refinements were carried out with sharp hkl reflections.

(v) Refinement of z parameters from sharp hkl reflections:

To start with, R was 0.275 including unobserved reflections, and it dropped down to 0.265 (0.230 for observed reflections only) after two cycles of least squares refinement. In obtaining R, hko reflections were excluded. 022 reflection shows serious disagreement between F_o and F_c and was also excluded. The 022 reflection appears at the edge of the range of oscillation in the photograph and its estimated intensity is likely to be uncertain. The reflections (table 25) 121; 321; 18,11; 20,11; 24,11; 26,11; 231; 431; 18,13 and 20,13 gave bad agreement between F_o and F_c and if these are excluded R for observed reflections only comes

down to 0.206. It seems probable that the unsatisfactory agreement for some reflections is due to the neglect of hydrogen atoms. There are 104 hydrogen atoms per unit cell; (13 H per molecule) and their neglect could cause an appreciable difference in the value of F_c of some reflections.

The final atomic parameters are listed in table (23); and F_o and F_c (for observed reflections only) in table (25).

TABLE - 23 FINAL ATOMIC PARAMETERS

	x	y	z
Na	0.2274	0.2315	0.029
O ₁	0.2285	0.1579	0.427
O ₂	0.1817	0.1589	0.202
O ₃	0.2109	0.3773	0.682
C ₁	0.2118	0.2557	0.527
C ₂	0.1828	0.2334	0.409
C ₃	0.1577	0.2992	0.545
C ₄	0.1319	0.2132	0.434
C ₅	0.1077	0.2992	0.546
C ₆	0.0808	0.2109	0.436
C ₇	0.0559	0.2849	0.563
C ₈	0.0287	0.2343	0.434

C H A P T E R - X I IR E S U L T S A N D D I S C U S S I O N

(1) Bond distances and angles:

The bond lengths and angles calculated in α -ketocaprylate group are shown in fig. (23) and listed in table (24).

TABLE - 24 INTRAMOLECULAR BOND LENGTHS AND ANGLES

Bond lengths		Bond angles	
C ₁ -O ₁	1.180 ± 0.023 Å	O ₁ -C ₁ -O ₃	137.2 ± 1.9°
C ₁ -O ₃	1.184 ± 0.023	O ₁ -C ₁ -C ₂	111.3 ± 1.6
C ₁ -C ₂	1.607 ± 0.025	O ₃ -C ₁ -C ₂	111.1 ± 1.6
C ₂ -O ₂	1.317 ± 0.023	C ₁ -C ₂ -C ₃	118.1 ± 1.5
C ₂ -C ₃	1.538 ± 0.025	C ₁ -C ₂ -O ₂	118.5 ± 1.5
C ₃ -C ₄	1.532 ± 0.025	C ₃ -C ₂ -O ₂	123.4 ± 1.6
C ₄ -C ₅	1.468 ± 0.025	C ₂ -C ₃ -C ₄	111.0 ± 1.5
C ₅ -C ₆	1.580 ± 0.025	C ₃ -C ₄ -C ₅	111.4 ± 1.5
C ₆ -C ₇	1.516 ± 0.025	C ₄ -C ₅ -C ₆	112.4 ± 1.5
C ₇ -C ₈	1.583 ± 0.025	C ₅ -C ₆ -C ₇	112.3 ± 1.5
		C ₆ -C ₇ -C ₈	113.1 ± 1.5

(ii) Estimation of errors:

The standard deviations (σ) of atomic co-ordinates and the interatomic distances were estimated (Lipson and Cochran, 1953) assuming $\sigma(F) = 0.13 |F|$ and $p = 5 \text{ \AA}^2$ for hkl $\sigma(F) = 0.24 |F|$.

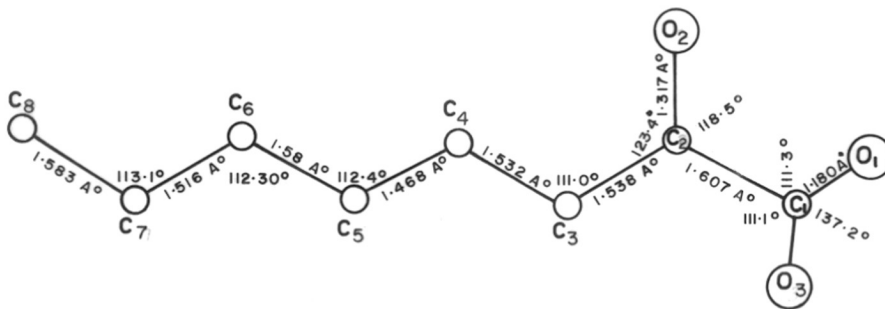


FIG. 23. BOND LENGTHS AND BOND ANGLES IN THE α -KETOCAPRYLATE GROUP. O₁ AND O₃ ARE CARBOXYLIC OXYGENS, O₂ IS KETO GROUP OXYGEN; C₃, C₄, C₅, C₆, C₇ ARE METHYLENE CARBONS AND C₈ IS METHYL CARBON.

The deviations in co-ordinates $\sigma(x_n)$ of the atoms are as follows:

	$\pm\sigma(x_n) = \sigma(y_n)$	$\pm\sigma(z_n)$
Na	0.011 Å	0.009 Å
O	0.015	0.012
C	0.019	0.017

The deviations in bond lengths are

$\sigma(\text{C-C})$	0.025 Å
$\sigma(\text{C-O})$	0.023
$\sigma(\text{Na-O})$	0.017
$\sigma(\text{Na-Na})$	0.015

The standard deviations in bond angles were estimated by Darlow's (1960) method and listed in table (24). These estimates do not take account of the fact that the z parameters have been refined using reflections of the type $h+k+l = 2n$ only. For crystals of space group Pbcn, the neglect of the reflections $h+k+l = 2n+1$ amounts to weighting the structure by half and superposing it on its reflection on (001) and although the right structure from the two possible positions of each atom could be deduced from bond length considerations; the accuracy of z parameters was reduced, specially for atoms near $z = 0.5$ because the structure factor formulae involve a term $\cos 2\pi lz$ which changes very slowly near $z = 0.5$.

(111) Molecular structure:

The bond lengths and angles found in the α -ketocaprylate group are shown in fig. (23) and listed in table (24). The mean plane through the atoms O_3 , O_1 , C_1 and C_2 can be represented by the equation,

$$0.187X + 0.791Y - 0.583Z - 1.381 = 0$$

where X, Y, Z are expressed in \AA units and referred to the axes of the unit cell. The normal distances of the individual atoms from the mean plane are 0.009\AA for O_1 , O_3 and C_2 and -0.025\AA for C_1 .

Referred to the same axes, the mean plane through the atoms, C_1 , C_2 , O_2 and C_3 can be represented by the equation

$$0.078X + 0.936Y - 0.343Z - 1.190 = 0$$

The normal distances of the individual atoms from the mean plane are -0.001\AA for C_1 , O_2 and C_3 ; and 0.002\AA for C_2 . The two planes make an angle of 17.3° with each other. The corresponding angle for sodium pyruvate is 18.1° .

The least squares plane through the atoms C_2 , C_3 , C_4 , C_5 , C_6 , and C_7 obtained by the method of Schomaker, Waser, Marsh and Bergman (1959) can be represented by the equation

$$0.033X - 0.835Y + 0.549Z - 0.502 = 0$$

The normal distances of the individual atoms from this plane are -0.039\AA for C_2 ; 0.031\AA for C_3 ; 0.061\AA for C_4 ; -0.046\AA for C_5 ; -0.005\AA for C_6 ; -0.004\AA for C_7 and -0.216\AA for the methyl carbon C_8 . The angle between this plane and the one passing

Unlike sodium α -ketobutyrate, enolization does not seem to occur in sodium α -ketocaprylate. This is clear from the length of the C_2-C_3 bond (1.538 \AA) which is close to the single C-C bond length (1.545 \AA) and the angle $C_2-C_3-C_4$ (111.0°) which is close to the tetrahedral angle; the corresponding values for sodium α -ketobutyrate are 1.376 \AA and 118.6° respectively. It is seen that the atoms C_1 , C_2 , O_2 and C_3 are co-planar within experimental error in the cases of sodium pyruvate and sodium α -ketocaprylate; while in sodium α -ketobutyrate, the atom O_2 is 0.426 \AA away from the plane containing atoms C_1 , C_2 and C_3 . It seems reasonable to conclude that this distortion from planarity in sodium α -ketobutyrate is caused by the enolization of the molecule.

The C_2-O_2 bond length (1.317 \AA) is larger than that expected in pure keto form (1.183 \AA in sodium pyruvate). It may be, that, this increase is related to the shortening of the C-O bonds of the carboxylic group. (1.180 \AA and 1.184 \AA).

The observed C_1-C_2 bond length (1.607 \AA) in sodium α -ketocaprylate is longer than single C-C bond lengths (1.545 \AA) as is the case with sodium pyruvate (1.579 \AA) and sodium α -ketobutyrate (1.587 \AA).

(iv) Crystal structure:

The projections of the structure along the c and b axes are shown in fig. (24) and fig. (25) respectively. The structure is isotypic with that of sodium α -ketobutyrate. There are six short

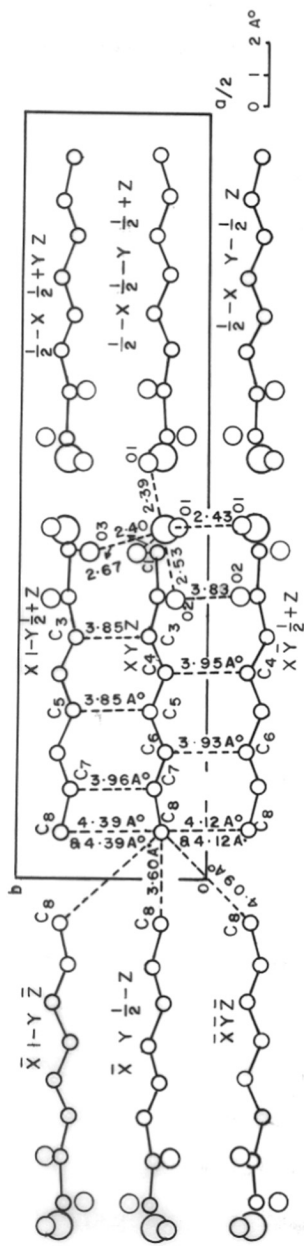


FIG. 24. STRUCTURE PROJECTED ON (001)

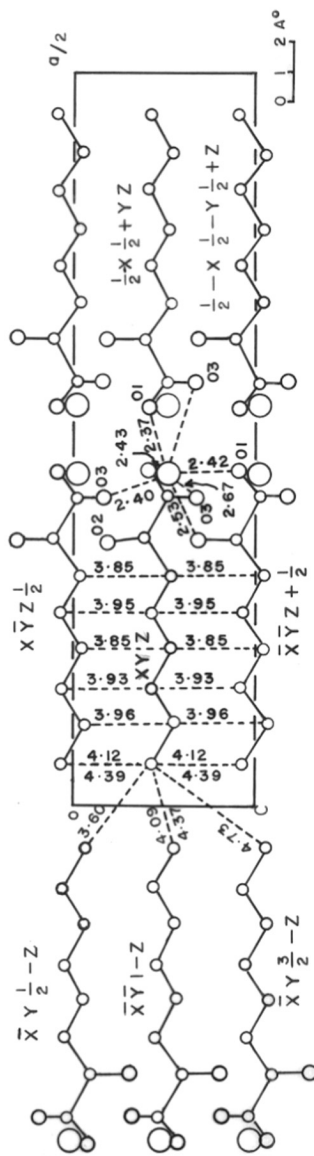


FIG. 25. STRUCTURE PROJECTED ON (010)

bonds between Na(x,y,z) and the neighbouring oxygens. These Na-O distances are as follows:

Na-O ₁ (x,y,z)	2.42 ± 0.02 Å ^O
Na-O ₁ (x,ȳ,z-½)	2.43 ± 0.02
Na-O ₃ (x,1-y,z-½)	2.67 ± 0.02
Na-O ₃ (x,y,z-1)	2.40 ± 0.02
Na-O ₁ (½-x,½-y,z-½)	2.37 ± 0.02
Na-O ₂ (x,y,z)	2.53 ± 0.02

These distances are comparable to those of sodium pyruvate (2.5 ± 0.2 Å^O) and sodium α-ketobutyrate (2.5 ± 0.2 Å^O). In all the three, strong Na-O bonds tie the molecules into infinite layers parallel to the (100) plane; anyone layer of molecules is linked with the neighbouring layers tightly on one side by Na-O bonds and loosely on the other side by van der Waals bonds. More significant van der Waals distances in sodium α-ketocaprylate are as follows:

C ₈ (x,y,z) - C ₈ (x,ȳ,½+z or z-½)	4.12 ± 0.03 Å ^O
C ₈ (x,y,z) - C ₈ (x̄,y,½-z)	3.60
C ₈ (x,y,z) - C ₈ (x̄,y,¾-z)	4.73
C ₈ (x,y,z) - C ₈ (x̄,ȳ,1-z)	4.09
C ₈ (x,y,z) - C ₈ (x,1-y,½+z or z-½)	4.39
C ₈ (x,y,z) - C ₈ (x̄,1-y,1-z)	4.37
C ₁ (x,y,z) - C ₁ (x,1-y,½+z or z-½)	4.20
C ₁ (x,y,z) - C ₁ (x,ȳ,½+z or z-½)	4.30
C ₂ (x,y,z) - C ₂ (x,1-y,½+z or z-½)	4.40

$C_2(x,y,z) - C_2(x,\bar{y},\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.11
$C_3(x,y,z) - C_3(x,\bar{y},\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.69
$C_3(x,y,z) - C_3(x,1-y,\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	3.85
$C_4(x,y,z) - C_4(x,\bar{y},\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	3.95
$C_4(x,y,z) - C_4(x,1-y,\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.58
$C_5(x,y,z) - C_5(x,\bar{y},\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.69
$C_5(x,y,z) - C_5(x,1-y,\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	3.85
$C_6(x,y,z) - C_6(x,\bar{y},\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	3.93
$C_6(x,y,z) - C_6(x,1-y,\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.60
$C_7(x,y,z) - C_7(x,\bar{y},\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.56
$C_7(x,y,z) - C_7(x,1-y,\frac{1}{2}+z \text{ or } z-\frac{1}{2})$	3.96

The short Na-Na contact distances obtained are:

$Na(\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z) - Na(x,y,z)$	$3.74 \pm 0.02 \overset{\circ}{\text{Å}}$
$Na(\frac{1}{2}-x,\frac{1}{2}-y,z-\frac{1}{2}) - Na(x,y,z)$	3.74 ± 0.02

Those observed in sodium pyruvate are $(3.7 \pm 0.1 \overset{\circ}{\text{Å}})$ and in sodium α -ketobutyrate $(3.73 \pm 0.02 \overset{\circ}{\text{Å}})$.

In all the three, there are six short distances between a sodium atom and the neighbouring oxygens; five of these oxygen atoms belong to the carboxylic groups while one atom belongs to the keto group.

TABLE - 25 OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
10	0	0	43	41	23	1	0	20	11
12	0	0	81	- 82	27	1	0	34	29
14	0	0	42	41	29	1	0	25	- 25
16	0	0	85	- 85	31	1	0	22	22
18	0	0	92	88	33	1	0	20	- 18
20	0	0	121	-131	35	1	0	19	17
22	0	0	78	84	37	1	0	19	- 18
24	0	0	73	- 72	0	2	0	291	-325
26	0	0	22	15	2	2	0	79	78
30	0	0	25	- 22	4	2	0	25	- 25
38	0	0	74	72	6	2	0	25	27
42	0	0	61	- 57	8	2	0	20	18
44	0	0	31	36	12	2	0	25	28
46	0	0	34	- 38	16	2	0	39	40
48	0	0	23	21	18	2	0	46	- 43
50	0	0	20	- 20	20	2	0	78	78
5	1	0	15	15	22	2	0	57	- 54
7	1	0	9	1	24	2	0	50	55
11	1	0	12	12	26	2	0	26	- 24
13	1	0	17	20	28	2	0	17	12
15	1	0	34	- 35	34	2	0	19	- 4
17	1	0	44	56	36	2	0	19	- 16
19	1	0	107	- 99	38	2	0	31	- 40
21	1	0	36	37	42	2	0	36	41

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
44	2	0	23	- 21	23	5	0	23	25
46	2	0	23	22	2	1	1	165	193
3	3	0	29	27	4	1	1	30	25
5	3	0	34	- 38	6	1	1	23	32
7	3	0	22	23	8	1	1	27	16
13	3	0	20	- 24	10	1	1	14	10
15	3	0	31	28	12	1	1	30	17
17	3	0	49	- 47	14	1	1	25	- 26
19	3	0	96	108	16	1	1	39	40
21	3	0	35	- 29	18	1	1	68	- 40
23	3	0	28	- 28	20	1	1	63	36
25	3	0	23	21	22	1	1	19	- 25
27	3	0	31	- 32	24	1	1	26	- 11
29	3	0	22	23	26	1	1	27	5
31	3	0	19	- 19	28	1	1	37	- 30
35	3	0	20	- 18	30	1	1	26	16
37	3	0	20	22	32	1	1	36	- 40
39	3	0	20	- 20	34	1	1	20	17
0	4	0	43	43	36	1	1	41	- 46
24	4	0	31	- 17	38	1	1	21	29
5	5	0	23	24	40	1	1	41	42
7	5	0	23	- 22	1	2	1	48	- 16
9	5	0	23	23	3	2	1	23	- 9
19	5	0	32	- 40	5	2	1	25	23

h	k	l	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c
7	2	1	27	- 28	17	4	1	23	- 31
9	2	1	26	22	21	4	1	23	35
11	2	1	14	- 9	6	5	1	19	- 5
17	2	1	31	32	8	5	1	21	27
21	2	1	55	- 50	10	5	1	30	- 26
23	2	1	15	10	12	5	1	34	32
25	2	1	16	- 11	14	5	1	24	- 25
27	2	1	18	19	16	5	1	24	20
29	2	1	17	- 17	18	5	1	19	- 8
2	3	1	35	- 60	2	0	2	26	- 24
31	2	1	18	13	4	0	2	27	25
4	3	1	14	- 30	6	0	2	68	- 86
6	3	1	25	15	8	0	2	46	64
8	3	1	35	- 51	10	0	2	42	- 48
10	3	1	39	39	12	0	2	22	- 21
12	3	1	41	- 47	14	0	2	44	43
14	3	1	37	38	16	0	2	76	- 73
16	3	1	33	- 30	18	0	2	56	57
18	3	1	16	15	20	0	2	54	- 48
28	3	1	27	22	22	0	2	39	25
30	3	1	28	- 15	24	0	2	45	- 49
32	3	1	35	35	26	0	2	54	51
34	3	1	35	- 22	28	0	2	49	- 52
36	3	1	36	35	30	0	2	41	32

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
32	0	2	14	- 7	27	1	2	12	- 7
34	0	2	17	- 13	29	1	2	12	2
36	0	2	35	38	0	2	2	65	-153
40	0	2	19	19	2	2	2	35	44
42	0	2	36	- 34	4	2	2	27	- 27
44	0	2	13	12	6	2	2	28	45
46	0	2	14	- 13	8	2	2	16	- 20
48	0	2	13	10	12	2	2	22	28
50	0	2	16	- 15	14	2	2	33	- 34
52	0	2	12	10	16	2	2	45	50
54	0	2	11	- 6	18	2	2	36	- 38
1	1	2	6	- 5	20	2	2	28	36
3	1	2	9	3	22	2	2	22	- 17
5	1	2	15	17	24	2	2	21	24
7	1	2	35	- 33	26	2	2	21	- 18
9	1	2	47	47	28	2	2	19	19
11	1	2	42	- 41	30	2	2	13	- 10
13	1	2	30	27	42	2	2	21	24
15	1	2	8	4	44	2	2	14	- 9
17	1	2	24	- 19	46	2	2	14	11
19	1	2	14	0	48	2	2	14	- 8
21	1	2	15	- 12	1	3	2	12	7
23	1	2	17	10	3	3	2	12	- 8
25	1	2	12	5	5	3	2	10	- 12

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
7	3	2	25	31	8	1	3	43	46
9	3	2	35	- 50	10	1	3	47	- 46
11	3	2	35	46	12	1	3	49	44
13	3	2	24	- 35	14	1	3	27	- 24
19	3	2	13	18	16	1	3	16	7
23	3	2	13	- 15	18	1	3	26	- 3
31	3	2	15	- 13	20	1	3	25	3
33	3	2	15	16	1	2	3	29	29
35	3	2	17	- 14	3	2	3	16	- 23
0	4	2	45	73	5	2	3	17	1
2	4	2	29	- 30	7	2	3	17	21
4	4	2	16	19	9	2	3	17	- 27
8	4	2	16	- 13	11	2	3	18	20
10	4	2	17	11	13	2	3	17	- 9
12	4	2	15	- 19	21	2	3	21	- 13
14	4	2	14	12	13	3	3	24	22
16	4	2	16	- 16	15	3	3	29	- 29
18	4	2	13	11	17	3	3	35	33
20	4	2	13	- 20	19	3	3	30	- 26
26	4	2	14	- 9	2	0	4	23	- 26
28	4	2	15	9	4	0	4	9	13
2	1	3	29	39	6	0	4	11	- 12
4	1	3	16	16	8	0	4	11	8
6	1	3	24	- 26	10	0	4	10	2

h	k	l	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c
12	0	4	6	- 6	2	2	4	13	23
14	0	4	11	10	4	2	4	13	- 14
16	0	4	22	- 21	6	2	4	12	14
18	0	4	20	24	8	2	4	6	- 9
20	0	4	16	- 9	12	2	4	7	8
22	0	4	10	5	14	2	4	16	- 15
24	0	4	8	- 10	16	2	4	21	21
26	0	4	10	9	18	2	4	16	- 21
28	0	4	11	- 3	20	2	4	8	7
1	1	4	4	0	1	3	4	8	3
5	1	4	5	5	3	3	4	7	2
7	1	4	5	- 4	17	3	4	12	- 4
9	1	4	5	- 1	19	3	4	13	6
11	1	4	5	2	21	3	4	8	- 1
15	1	4	7	2	14	4	4	11	15
17	1	4	12	1	16	4	4	16	- 15
19	1	4	13	- 3	18	4	4	13	13
0	2	4	20	- 26					

C H A P T E R - XIII

SUMMARY

(i) Sodium pyruvate, $\text{CH}_3\text{COCOONa}$, crystallised from aqueous solution, is monoclinic, space group $\text{P}2_1/\text{a}$, with four molecules per unit cell of dimensions

$$a = 22.25 \pm 0.02; \quad b = 5.31 \pm 0.01 \quad \text{and} \quad c = 3.71 \overset{\circ}{\text{\AA}};$$
$$\beta = 98.2^\circ$$

The detailed structure has been determined by two dimensional Fourier syntheses, and refined by the method of least squares.

The plane containing the methyl carbon, the keto group and the carbon of the carboxylic group makes an angle of 18.1° with the plane of the C-COO group. This suggests that there is no appreciable conjugation across the central C-C bond length ($1.579 \pm 0.045 \overset{\circ}{\text{\AA}}$) which is close to the standard single C-C bond length ($1.545 \overset{\circ}{\text{\AA}}$).

Strong Na-O bonds tie the molecules into infinite layers parallel to the (100) planes. Any layer of molecules is linked with the neighbouring layers by strong Na-O bonds on one side and van der Waals bonds on the other.

(ii) Sodium α -ketobutyrate, $\text{CH}_3\text{CH}_2\text{COCOONa}$, crystallised from aqueous solution, is orthorhombic, space group Pbcn , with eight molecules per unit cell of dimensions

$$a = 29.28 \pm 0.04; \quad b = 6.04 \pm 0.01 \quad \text{and} \quad c = 5.90 \overset{\circ}{\text{\AA}}$$

The detailed structure has been determined by two dimensional Fourier, difference Fourier and least squares methods.

The observed bond lengths and angles (table 20) show that sodium α -ketobutyrate is enolized to a great extent in the crystalline state. The crystal structures of sodium α -ketobutyrate and sodium pyruvate are similar.

(iii) Sodium α -ketocaprylate $\text{CH}_3(\text{CH}_2)_5\text{COCOONa}$ is orthorhombic, space group Pbcn, with eight molecules per unit cell of dimensions, $a = 49.57 \pm 0.06$; $b = 6.05 \pm 0.02$ and $c = 5.97 \pm 0.02 \text{ \AA}$.

The structure is isotypic with that of sodium α -ketobutyrate. Unlike sodium α -ketobutyrate, however, enolization does not seem to occur in this compound. In all the three compounds the Na-O bonds tie the molecules into infinite double layers; any double layer is linked with the neighbouring layers by van der Waals bonds. In all the three, there are six short distances ($2.5 \pm 0.2 \text{ \AA}$) between a sodium atom and the neighbouring oxygens; five of these oxygen atoms belong to the carboxylic groups, while one atom belongs to the keto group. It seems plausible to assume that the close approach of the sodium atom to the keto group oxygen produces strain in the molecule and causes the lengthening of the $\text{C}_1\text{-C}_2$ bond. (sodium pyruvate, $1.579 \pm 0.045 \text{ \AA}$; sodium α -ketobutyrate, $1.587 \pm 0.038 \text{ \AA}$; sodium α -ketocaprylate, $1.607 \pm 0.025 \text{ \AA}$).

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