Entered
Acc Reg on 25/11/15

Received for thesis on 27/3/67

Awarded Ph.D

231

25-9-95

TH-840

THE CRYSTAL AND MOLECULAR STRUCTURE STUDIES
BY
X-RAY DIFFRACTION

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

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MARCH - 1967

27/3/67

ACKNOWLEDGEMENTS

I am greatly indebted to Dr. A. B. Biswas for suggesting the research problem and his inspiring guidance during the course of this work.

I am grateful to Dr. L. M. Pant and Dr. S. S. Tavale for very valuable help and discussions. Thanks are due to Dr. T. D. Sakore for ungrudging help on many occasions, to the Council of Scientific and Industrial Research, New Delhi, for the award of a Fellowship and to the Director, National Chemical Laboratory for allowing to submit this work for Ph.D. degree.

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ABSTRACT

In the present work the crystal and molecular structures of sodium salts of α-keto valeric acid, α-keto caproic acid, α-keto heptylic acid have been determined by X-ray diffraction. The structure of sodium pyruvate has been recomputed by independent three dimensional data.

The unit cell dimensions, space group and the number of molecules (n) in unit cell are given in the following table.

TABLE

S.No.	Compounds	a in Å	b in Å	c in Å	Space group	(n)
1.	Sodium 2-oxo valerate	34.09	6.14	5.91	Pbcn	8
2.	Sodium 2-oxo caproate	39.46	6.11	5.94	Iba2	8
3.	Sodium 2-oxo heptylate	44.18	6.08	5.91	Pbcn	8
4.	Sodium pyruvate	22.12	5.27	3.68	$P2_1/a$	4

The (001) and (010) projections of all the structures were refined by the usual Fourier syntheses, difference syntheses and least squares methods, and finally by least squares using the general reflexions hkl.

All the bond lengths and angles in these structures have been found to be normal. The two C-O bonds of carboxylic group are equal revealing its existence in ionic form.

In all the structures 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.

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CHAPTER - I

INTRODUCTION

Following the discovery of X-ray by Röngtgen in 1895, a good deal of time had been devoted in establishing its fundamental properties and up to 1912, crystallography was in general confined to descriptive morphological crystallography. However, since the inception of classical diffraction experiments by Laue, Friedrich and Knipping[1], the subject "The crystal structure analysis by X-ray diffraction" started making rapid strides, and in recent years, aided with computing facilities, the veil of mystery of many complex structures is being uncovered. The accomplishment of penicillin[2] (Bunn and others, 1952) and vitamin B_{12}[3] (Hodgkin et. al., 1957) structures are illuminating citations. The detailed refinement of relatively simpler structures on the other hand is equally being emphasized. There is no straight forward method to solve the structure except in very few cases, and particularly in organic compounds (containing only C, N and O) considerable difficulty is encountered. Each crystal affords a problem of its own.

The solution of crystal structure by means of X-ray is ultimately to know the diffracting matter (electrons of the atoms or rather atomic positions) in the unit cell. At each point in the crystal there is certain electron density $\rho(x,y,z)$ which is a function of coordinates (x,y,z) of the atoms. Since the crystal structure is essentially a repeating pattern in three dimensions, therefore, the density function $\rho(x,y,z)$ can be expressed as the sum of suitable Fourier series. W. H. Bragg[4] (1915) was first to realise that each X-ray reflection must correspond to one of the component sinusoidal distributions of density in the medium. Ewald[5] (1921) showed the importance of the series by expressing it for periodic density distribution in an infinite crystal in terms of reciprocal lattice vectors. Epstein and Ehrenfest[6] used a triple Fourier series to represent the density of diffracting matter in a crystal which is expressed as

$$\rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l=-\infty}^{+\infty} F(hkl)\ \exp.\left[-2\pi i\ (hx + ky + lz)\right]$$

where V is volume of unit cell, hkl is Miller's indices, F(hkl) is structure factor of the plane (hkl) and the structure factor is given as

$$F(hkl) = \sum_{j} fo_j\ \exp.-B_j \left(\frac{\mathrm{Sine}}{\lambda}\right)^2\ \exp.2\pi i(hx_j+ky_j+lz_j)$$

where fo_j is the scattering factor of the jth atom at rest. B_j is isotropic temperature factor of jth atom and x_j, y_j and z_j are the corresponding coordinates. The main obstacle in summing the series is the complex nature of F(hkl) which involves amplitudes as well as phases. The magnitude of the structure amplitudes can be measured experimentally, but the knowledge about the relative phases is lost in recording the spectra. This lack of information about the phases prohibits the direct determination of the structure by Fourier series. The determination of these phases thus constitute the central problem in the Fourier method of crystal structure analysis.

To overcome the phase problem various methods have been devised. Trial and error is one of them in which a reasonable trial structure is postulated and if a satisfactory agreement between observed and calculated structure amplitudes is obtained then the calculated phases with observed amplitudes are used to sum up the Fourier series.

An attempt to ~~evade~~ overcome the difficulty of phase determination was made by Patterson, A. L.[7] (1934,1935) in which squares of the moduli of Fourier coefficients are used instead of structure factors. Thus the resulting synthesis gives map which gives information about the interatomic vectors rather than the atomic positions. However, it has been proved to be of immense importance as a starting point for deriving the trial structure. One of the important properties of three dimensional Patterson map realised by Harker[8], is the occurrance of peaks corresponding to vectors between the symmetry related atoms. He introduced the method of calculating certain planes (Harker sections) or lines (Harker lines) which give very useful information leading to the determination of phases.

The Patterson method is of particular use in case of heavy atom compounds. The heavy atom-heavy atom peak is easily located and then the coordinates of other atoms are derived by Fourier synthesis using the phases based upon the calculations of heavy atom position alone. Since heavy atom contribution dominates most of the phases of the reflexions, it proves quite effective in most of the cases.

Another powerful method of determining phases is the use of isomorphous replacement. The general principle is that if it is possible to substitute successively two different heavy atoms in a molecule without disturbing the overall crystal structure, then the phase relationship can be determined from a difference effect. For example, a most simple case is when heavy atom happens to occupy a centre of symmetry. Let these atoms be A_1 and A_2 and the remainder of molecule be O. Now if these structures are isomorphous, the contribution of O remains constant and we get

$$FA_1O - FA_2O = FA_1 - FA_2 = \Delta F$$

here ΔF represents the difference in scattering power of the two heavy atoms and this is sufficient to determine the signs of the two structure factors if their magnitudes can be accurately measured. The use of the method has been made in case of Phthalocyanines[9], camphor~~[10]~~ derivatives[10] and suc~~c~~rose derivatives[11].

Recently direct methods of determining phases are being developed. Harker and Kasper[12] (1948) devised certain inequality relations between structure factors thereby predicting the signs of some of the structure amplitudes, on the basis of mathematical physical aspects that the electron density is no where a negative quantity in the crystal and that the electrons can, to a close approximation, be considered to be distributed spherically ar~~r~~ound the atoms. The use in its extended form was made by Gillis[13] (1948 a, b) to determine the signs for oxalic acid structure. D. Sayre[14] (1952) gave a new set of relationships which exists among the structure factors of crystal containing atoms of approximately equal diffracting power such as C, N and O atoms.

The Fourier transform method is making its important place in crystal structure analysis. The Fourier transform of a group of atoms is a function which represents the amplitude and the phase of the radiation scattered by the group of atoms in a particular direction. The process of crystal structure determination is essentially the fitting of the reciprocal lattice on the Fourier transform of the contents of the unit cell so that the modulus of the transform at each reciprocal lattice point is equal~~l~~ to the structure amplitude of the corresponding X-ray reflexion.

Once the approximate coordinates of the atoms in a unit cell are obtained, the next task is to refine these parameters. Various methods are available for refining the structure such as Fourier synthesis, difference synthesis and least squares etc. In the Fourier synthesis the maxima in the electron density map will occur away from the assumed position in the direction of true one. The new atomic positions are used to recalculate the phases and the process is repeated till no further changes of phase~~s~~ occur ~~in structure amplitudes~~. In difference synthesis, difference between observed and calculated structure factors with proper phases are used as Fourier coefficients and the resulting map indicates the incorrect posistioning of atoms if they lie on steep gradients. The least squares method is based on the minimization of a weighted sum of squares of discrepancies between observed and calculated factors.

This rapidly growing field is difficult to review adequately, but some of the better established and more important methods have been summarized.

Considerable work has been done on the structure of amino acids but there α-keto anologs have so far received a little attention. These acids are of considerable biochemical interest as intermediates in the bio-synthesis and degradation of amino acids. They are formed during the course of enzymatic oxidative deamination and transamination and capable of enolization, may exist theoretically in cis and trans enol form which has been demonstrated experimentally in several cases. (Meister[15], et. al. 1954, Anderson and Rasford[16], 1953). The structure determination of these compounds is difficult owing to the unstable nature of many of them.

Recently structures of sodium salts of some α-keto acids have been determined (Tavale, Pant and Biswas, 1961, 63, 64)[17] by two dimensional data and, therefore, though their results cannot be authenticated, shows an interesting persistent lengthening of C_1-C_2 bond and enolization in case of sodium 2 oxo-butyrate. This aroused an interest to examine whether these observations represent merely ~~xix~~ an error or they are real structural features. These prompted us to carry out structure determination work on similar compounds as accurately as possible to provide reliable structural information which might throw light on their chemical behaviour.

The work has been incorporated in four parts, describing the crystal and molecular structures of sodium 2 oxo-valerate, sodium 2-oxo caproate, sodium 2-oxo heptylate and sodium pyruvate respectively. Each part comprises three chapters describing "Crystal data and experimental details", "Trial structure and its refinement" and "Results and discussion" respectively.

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PART-I: CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM 2-OXO VALERATE

CHAPTER - II

CRYSTAL DATA AND EXPERIMENTAL DETAILS

(A) Sodium 2-oxo valerate ($C_5H_7O_3Na$) prepared by adding concentrated solution of sodium hydroxide to the alcoholic solution of α-keto valeric acid, is highly soluble in water. Crystals were grown from water-alcohol mixture as very thin flakes. The preliminary X-ray photographs showed these crystals to belong to the orthorhombic system.

(i) The determination of unit cell dimensions:

A suitable crystal after examining through the polarising microscope was mounted along the needle axis. The crystal was set first visually and then accurately by double oscillation[1] (Davies, 1950). Axial lengths a, b and c were measured from high angle reflexions in equatorial Weissenberg photographs[2]. These values are

$a = 34.08\ A^{o}$ $b = 6.14$ Å $C = 5.91$ Å

(ii) The crystal density determination:

The density of the crystal was measured at 25°C by usual flotation method using the mixture of organic liquids. The mean value is 1.47 gm cm^{-3}.

(iii) Number of molecules per unit cell:

The number of molecules per unit cell is given by

$$n = \frac{V.N.\rho}{M}$$

where n is number of molecules per unit cell; V is volume of the unit cell; N is Avagadro's number; ρ is observed density and M is molecular weight.

This gave 8 molecules per unit cell and calculated density 1.48 gm cm^{-3}.

(iv) **Linear absorption coefficient:**

μ cm^{-1} for Cukα radiation was calculated by the formula

$$\mu = \frac{\rho \Sigma n \mu g}{\Sigma n \omega} \text{ cm}^{-1}$$

where ρ is density in gm cm^{-3}, n is relative number of atoms present, μg is gm atomic absorption coefficient, and Σnw is sum of the atomic weights of the elements present. μg for carbon, oxygen and sodium is 66,203 and 711 respectively. Thus μ calculated for Cukα radiation is 17.6 cm^{-1}.

(B) **Collection of data and estimation of intensities:**

The three dimensional data were collected from equi-inclination Weissenberg photographs taken with Cukα radiations. The crystal used was roughly of 0.5 x 1.0 mm^2 area. The longer side being c axis; zero to fourth layers were taken along this axis as oscillation axis, using usual multiple film techniques[3], while zero layer only was collected with 'b' axis as oscillation axis.

In all 71, 70, 96, 103, 63 and 64 reflexions of the type hko, hol, hk1, hk2, hk3 and hk4 respectively were observed out of 189, 169, 324, 335, 283 and 262 corresponding theoretically possible reflexions. Some of the low angle reflexions were cut off because of the beam-stop.

The reflexions with indices h + k + l = 2n + 1 were found to be diffuse and those with h + k + l = 2n sharp; suggesting the same type of disorder as was observed in sodium 2 oxo-caprylate (Pant[4] (1964).)

The intensities of zero layers as well as higher layers photographs were estimated visually with the help of intensity scale prepared from the same crystal as follows:

After taking (hko) Weissenberg photograph, a fairly strong reflexion-spot which at the same time was well separated from other spots was chosen and the crystal was oscillated through 10° about the angle giving this reflexion spot keeping the film stationary. The relative scale was prepared by recording X-ray diffraction spot when the crystal passed once through the particular reflecting position, then the camera was moved by about 3 mm distance and the next spot was recorded when the crystal passed twice through the reflecting position and so on. Thus a set of diffraction spots of known relative intensities was obtained and was used for estimating the intensities of zero as well as higher layer photographs. The visually estimated intensities were corrected for Lp and spot extension as follows:

(1) Lorentz and polarisation (Lp) factor:

The integrated intensity (I) of diffraction spots on the oscillation and Weissenberg photographs is given as

$$I \propto F^2 \times Lp$$

where F^2 is structure amplitude and L and p are Lorentz and polarisation factor respectively.

In general the X-ray beam is unpolarised i.e. azimuth of the electric vector assumes all direction with time. The effective amplitude of the radiation after it is reflected by the crystal at the angle 2θ consists only of the components of

$* \quad p = \frac{1}{2}(1 + \cos^2 2\theta)$

The factor 'L' is Lorentz factor which is expressed in terms of cylinderical coordinates ζ and ξ_ζ as follows:

these azimuth after reflection. This feature has the effect of reducing the intensity of X-ray beam by a factor 'p' called polarisation factor and is given by $\overset{*}{\wedge}L = (\xi_\zeta \cos\theta)^{-1}$ for equi-inclination photographs and $L = (\sin^2 2\theta - \zeta)^{-1/2}$ for normal beam photographs, for zero layer $\zeta = 0$ and $\xi_\zeta = 2 \sin\theta$

$$L = (\sin 2\theta)^{-1}$$

This can be interpreted as the relative time opportunity for the various planes of crystal to reflect. Reciprocal points do not move at the same rate through the sphere of reflection. Those near the origin obiviously move slowly than those which are away.

Since both Lorentz and polarisation factors always occur together, it is therefore convenient to combine them putting

$$F^2 \propto DI$$

where $\quad D = \dfrac{(\sin^2 2\theta - \zeta^2)^{\frac{1}{2}}}{1 + \cos^2 2\theta}$ for normal beam photographs

and $\quad D = \dfrac{(\xi_\zeta \cos\theta)}{1 + \cos^2 2\theta}$ for equi-inclination

All the intensities were corrected for the Lp factor with the help of curves given by Cochran[5] (1948).

Since the calculated absorption coefficient μ for CuKα radiation of the compound is quite small, therefore, absorption correction was neglected.

(ii) <u>Correction for spot extension:</u>

In upper-level Weissenberg photograph the corresponding reflexions are extended on one side of the film and contracted on the otherside. The degree of distortion vary from reflexion to reflexion ~~to reflexion~~ in a way which depends on the experimental arrangements.

The variation in spot area arises from the divergence of the X-ray beam incident upon the crystal. The effect could be explained by supposing the crystal to be devided into small elements of length which receive X-rays at angles of incidence depending upon their position in the crystal. All the elements giving particular reflexion are not brought into the reflecting position at the same time but they come in turn by the rotation of the crystal. During the time taken to complete as reflexion in this way the film is moved a distance depending upon the camera constants; so that the reflexion spots are contracted or extended according to whether the film motion is in the same direction as the spot growth or in the opposite direction.

The fractional increase in the area of reflexion is given by Phillips[6] (1954) as

$$W = \frac{A + \Delta A}{A} \qquad \text{for equi-inclination setting.}$$

When distortions are small i.e. less than 1.5 the intensity is corrected measuring intensity from both extended (I_E) and contracted (I_C) spots by

$$I = \frac{2 \times I_E \times I_C}{(I_E + I_C)}$$

but when the distortions are severe or the spots on both sides are not available, the intensity of extended spots are only measured and corrected as $I = W.\ I_E$.

The intensities of higher layer photographs were measured from extended spots and were corrected for 'W' correction. The curves for constant 'W' in reciprocal space given by Phillips[7] (1956) were used to get the required correction factors for each layer.

(iii) Scale and temperature factor:

The atomic scattering factors are calculated from the electron density distribution of the atoms at rest; but the atoms in a crystal always have a finite amplitude of oscillation at all temperatures; even at absolute zero. The effect of the thermal motion is to make the electrons of each atom sweep out a larger average volume than they would occupy if the atom were at rest, resulting in the rapidly fall off 'f' curves with $\sin\theta/\lambda$ thereby decreasing its scattering strength. Debye[8] (1914) gave the relation

$$f = fo.\ \exp.\ -B\left(\frac{\sin\theta}{\lambda}\right)^2$$

where f is scattering at a temp; fo. is same at rest and B is temperature factor.

To determine preliminary B-value and also to place the corrected intensities on absolute scale Wilson's method[9] (1942) was employed for hko and hol projections. The method is explained: We know that

$\langle|F^2|\rangle = \sum_{n=1}^{N} f_n^2$ i.e. the average value of $|F^2|$ is equal to the sum of the squares of the diffracting powers of the atoms in unit cell. For a unit cell of known contents of atoms, any arbitrary arrangement of atoms would give a set of reflexions with the same average value of intensity (i.e. $|F^2|$) and average observed intensity on absolute scale is given by

$$\langle I\,abs\rangle = \langle|F^2|\rangle = \sum_{n=1}^{N} f_n^2 \qquad \text{and}$$

$$K\langle Iobs\rangle = \langle Iabs\rangle$$

$$K\langle Iobs\rangle = \sum_{n=1}^{N} fo^2 e^{-2B\left(\frac{\sin\theta}{\lambda}\right)^2}$$

taking logarithms of both sides we get

$$\log_e K = \log_e \frac{\sum_{n=1}^{N} fo^2}{\langle Iobs \rangle} - 2\,B\,(\mathrm{Sin}\,\theta/\lambda)^2$$

or

$$\log_e \frac{\sum_{n=1}^{N} fo^2}{\langle Iobs \rangle} = 2\,B\,(\mathrm{Sin}\,\theta/\lambda)^2 + \log_e K$$

thus plot of $\log_e \frac{\sum_{n=1}^{N} fo^2}{\langle Iobs \rangle}$ against $(\mathrm{Sin}\,\theta/\lambda)^2$ will be a straight line whose slope shall be equal to 2B and intercept on Y-axis shall be $\log_e K$.

The reflexions in each projection (hk0) and (h0l) were divided into suitable groups of Sin θ (as shown in table 1 and 2). The mean value of observed intensities $\langle Iobs \rangle$ was calculated for each range counting zero intensities and extinguished reflexions as points present but having zero intensity. For axial reflexions half the value of intensity was taken. $\sum fo^2$ was obtained by

$$\sum_{n=1}^{N} fo^2 = 8\left[(fo\ Na)^2 + 3(fo\ O)^2 + 5(foC)^2\right]$$

McWeeny's[10] (1951) values of atomic scattering factors were used for carbon and oxygen; and for Na^+ that of James and Brindlay[11] (1931) ~~was~~ were used. $\log_e C$ was plotted against $(\mathrm{Sin}\,\theta/\lambda)^2$ for each zone, where C is $\sum_{n=1}^{N} fo^2/\langle Iobs \rangle$. These graphs are shown in figs. 1 a, and b.

The corresponding K and B values are indicated below each table.

(C) Space group determination:

From the diffraction photographs the crystals are orthorhombic and systematic abscences are:

hk0 for h + k = odd; h0l for l odd;

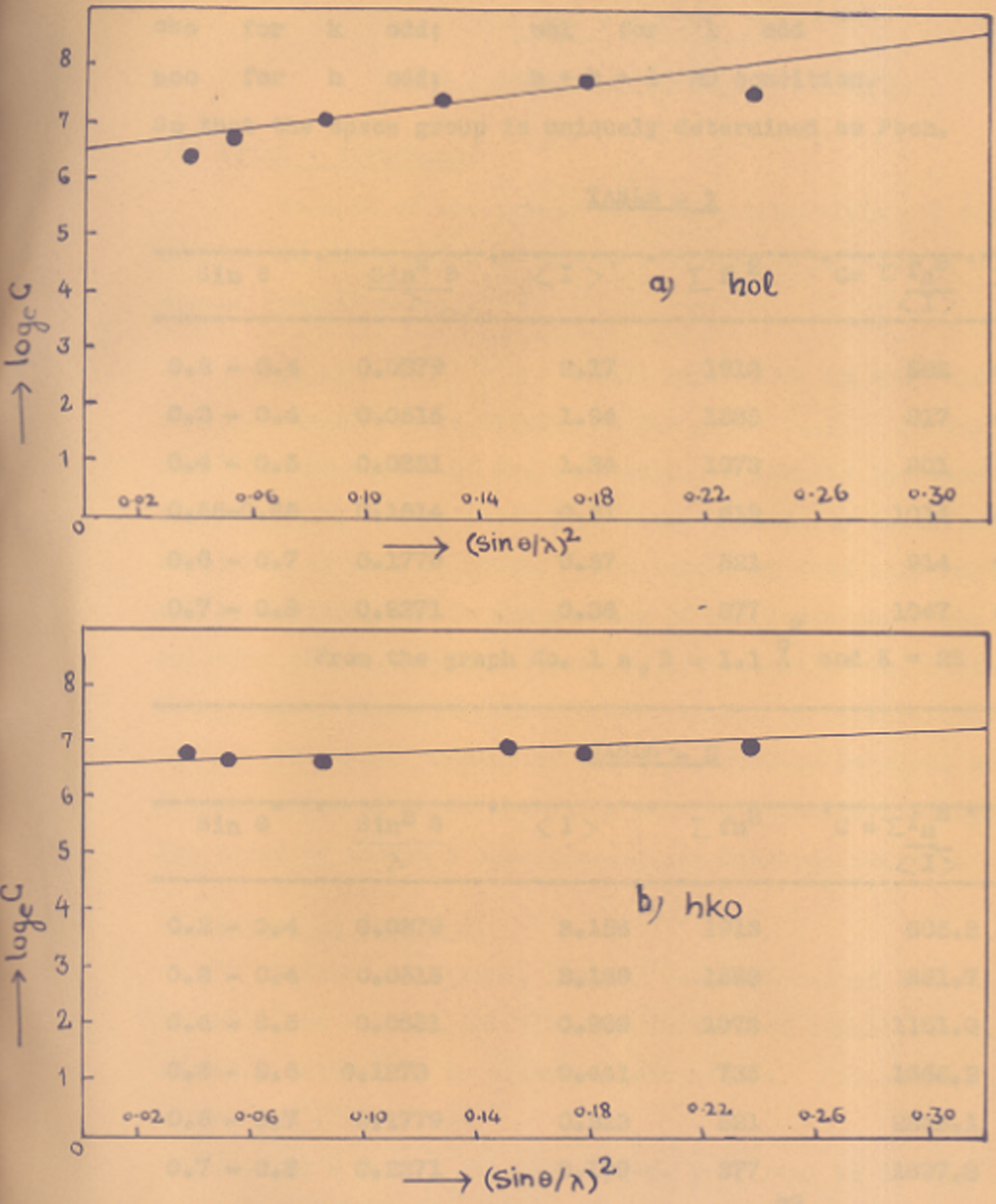


Fig. 1 DETERMINATION OF PRELIMINARY SCALE & TEMPERATURE FACTOR BY WILSON'S METHOD

oko for k odd; ool for l odd

hoo for h odd; h + k + l no condition.

So that the space group is uniquely determined as Pbcn.

TABLE - 1

Sin θ	$\frac{\sin^2\theta}{\lambda}$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.2 - 0.4	0.0379	2.17	1913	882	6.7822
0.3 - 0.4	0.0515	1.94	1585	817	6.7057
0.4 - 0.5	0.0851	1.34	1073	801	6.6859
0.55-0.65	0.1514	0.61	619	1014	6.9216
0.6 - 0.7	0.1779	0.57	521	914	6.8179
0.7 - 0.8	0.2371	0.36	377	1047	6.9537

From the graph No. 1 a, B = 1.1 Å^2 and K = 28

TABLE - 2

Sin θ	$\frac{\sin^2\theta}{\lambda}$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.2 - 0.4	0.0379	3.158	1913	605.8	6.4066
0.3 - 0.4	0.0515	3.129	1583	861.7	6.7589
0.4 - 0.5	0.0851	0.909	1073	1181.0	7.0742
0.5 - 0.6	0.1273	0.441	735	1665.2	7.4176
0.6 - 0.7	0.1779	0.223	521	2332.1	7.7546
0.7 - 0.8	0.2371	0.199	377	1897.3	7.5482

From the graph No. 1 b, B = 3.6 Å^2 and K = 25

C H A P T E R - III

TRIAL - STRUCTURE AND ITS REFINEMENT

(A) Trial - structure:

Because of the triply periodic distribution of electron density in the crystal it can be represented by a three dimensional Fourier series.

$$\rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l=-\infty}^{+\infty} F(hkl) \exp.\left[-2\pi i(hx + ky + lz)\right] \text{ --(1)}$$

where $\rho(x,y,z)$ is the density at the point (x,y,z) in the crystal and V is the volume of the unit cell. F (hkl) is the expression for structure factor which is a complex quantity involving amplitude as well as phase. From intensity data only amplitudes can be derived, and in the absence of knowledge about the relative phases, crystal structure determination which otherwise would appear to be straight forward cannot be carried out.

The whole problem of crystal structure revolves about determination of these phases or some satisfactory trial-structure. The trial of sodium 2 oxo-valerate was fixed as follows:

(i) Patterson function:

Patterson[12] (1934, 1935 a) used squares of the values of $|F(hkl)|^2$ as Fourier coefficients instead of F(hkl), which are directly related to be observed intensities. Patterson defined a function $P(u,v,w)$ as

$$P(u,v,w) = V \int_0^1\int_0^1\int_0^1 \rho(x,y,z)\ \rho(x+u,\ y+v,\ z+w)\ dx\ dy\ dz.....(2)$$

where the $\rho(x,y,z)$ and $\rho(x+u,\ y+v,\ z+w)$ are the electron densities at the points (x,y,z) and $(x+u,\ y+v,\ z+w)$ respectively. Putting the values of $\rho(x,y,z)$ and $\rho(x+u,\ y+v,\ z+w)$ derived from equation (1) in equation (2) and integrating, the following equation is obtained:

$$P(u,v,w) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l=-\infty}^{+\infty} |F(hkl)|^{2} \exp.\left[-2\pi\,(hu+kv+lw)\right] \;......(3)$$

If $|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})|$ the above equation (3) simplifies to

$$P(u,v,w) = \frac{1}{2V} \sum_{h} \sum_{k} \sum_{l=-\infty}^{\infty} |F(hkl)|^{2} \operatorname{Cos} 2\pi(hu+kv+lw) \;.....(4)$$

It means that the product $\rho(x,y,z)$ and $\rho(x+u,\ y+v,\ z+w)$ will be finite only when both points (x,y,z) and $(x+u,\ y+v,\ z+w)$ lie in the region of finite electron density. Thus a peak in the Patterson function implies the presence of two atoms in the structure separated by the distance of the peak from the Patterson origin and oriented in the same direction. The height of the peak depends upon the product of atomic number of two atoms involved.

In a structure of N atoms, there will be N(N-1)/2 independent peaks. If there are many atoms of nearly the same diffracting power, many interactions will be possible and several of them will overlap each other making it difficult to derive the original set of atoms which gave rise to the particular peak. Neverthless, the Patterson synthesis becomes of immense importance when there is a heavy atom and a number of light atoms. Then the peaks due to the interaction between the heavy atoms will stand out clearly from which the coordinates of heavy atom can be derived. The Fourier synthesis calculated using observed amplitudes and phases based upon the calculations of heavy atom position alone will help in deriving the coordinates of other atoms; and the structure can be solved and refined by iterative Fourier synthesis methods.

(ii) The modified Patterson function:

It is conceivable that the Patterson map will be of more use if the peaks are resolved to its greatest extent.

If the crystal consists of spherically symmetric atoms, the values of $|F^2|$ may be multiplied by any function $M(S)$ without effecting its spherically - symmetric peaks centred at the points of the vector set. Naturally, the best modification will be one which makes the central maxima as sharp as possible without introducing any large subsidiary maxima and minima which may obsecure or distort the neighbouring peaks. For this, instead of $|F^2|$ coefficient $|F_M{}^2|$ are used as coefficient where $|F^2{}_M| = M(S)\,|F^2|$ and $M(S)$ is any modifying (or sharpening) function.

Patterson[13] (1935 b) used the following modification to increase the resolution of peaks in case of $Cuso_4$-$5H_2O$ which is

$$M(S) = \left(\frac{1}{\hat{f}}\right)^2 \ \text{exp.}\left[-\ \frac{\Pi^2}{p}.S^2\right]$$

where $\hat{f}$ is unitary scattering factor, taking account of the temperature factor; p is a constant given by Costain's[14] (1941) formula; and $S = \left|2 \sin \theta/\lambda\right|$

Schomaker and Shoemaker suggested (unpublished) the following modification;

$$M(S) = \left(\frac{1}{\hat{f}}\right)^2 \ S^2 \ \text{exp.}\left[-\ \frac{\Pi^2}{p^2}\ S^2\right]$$

This type of modification reduces greatly the influence of low-order terms on the Patterson function, and is of particular importance when they are likely to be in error due to extinction.

In the present case, the sharpening of the Patterson function was affected by multiplying corrected intensities of each reflexion by the square of the length of the corresponding reciprocal lattice vector from the origin. The (001) and (010) sharpened Patterson projections were taken on von Eller Photosommateur.

(iii) von Eller Photosommateur:

von Eller[15] (1955) designed an elegant optical device based on Bragg-Huggins principle. Electron density of any centro-symmetrical projection can be represented by $\rho(XY) = \frac{1}{Ac} \sum_{h} \sum_{k} F(hk) \cos 2\pi(hx+ky)$; where $\cos 2\pi(hx+ky)$ is diagonally fluctuating function which can be represented photographically by variation in blackening of a film.

A vertical slit source of light passing through a specifically designed grating produces a sinusoidal distribution of intensity on the photographic plate which is attached at the centre of rotating disc. A reciprocal lattice drawing is mounted on the disc and by coinciding successively each lattic point with the cross wire on the rotating disc, thereby adjusting the wave length to be impressed on the photographic plate by backward or forward motion of the grating, exposures proportional to $|F|$ or $|F^2|$ are made according to whether Fourier synthesis or Patterson synthesis is required. The phases of the structure factors can be altered by the lateral movement of the grating plate by means of the knob. Thus after all the reflexions are exposed the optical summation of the required series is obtained on photographic plate.

(iv) Sharpened Patterson projections:

A reciprocal lattice section ($a^* b^*$) and ($a^* c^*$) plotted on the scale of 1 r.l.u. = 20 cms for a^* (a being long axis) and 1 r.l.u. = 10 cms for b^* and c^* respectively was put on the disc of Eller's machine and corresponding lattice points (only for observed reflections) were exposed; exposures being proportional to the products of corrected intensities and corresponding S^2. Sharpened Patterson photographs obtained on Eller's machine are shown in figs. 2 and 3.

The equivalent points and the symmetry elements for the space group Pbcn are shown in fig. 4. The eight equivalent points are;

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

origin being at $\bar{1}$.

x and y parameters were obtained for Na-atom from the following peaks marked in the photograph (fig.2).

Peak No.1 was interpreted as due to the interaction between Na(x,y) and Na($\bar{x}$,y) falling at (2x,0).

Peak No.2 was presumed to be due to interaction between Na(x,y) and Na($\bar{x},\bar{y}$) falling at (2x, 2y).

Approximately $X_{Na} = 0.217$ and $Y_{Na} = 0.230$ were obtained from these peaks.

Further, since the unit cell dimensions of sodium 2-oxo valerate are a = 34.09; b = 6.14 and c = 5.97 Å; while those of sodium 2-oxo-caprylate[16] (Tavale, Pant and Biswas, 1964) are similar except that of 'a' which is longer by about 15.5 Å. Assuming the usual bond-lengths and angles this is the expected decrease in 'a' axis of 2oxo valerate for a structure iso-typic with 2-oxo caprylate.

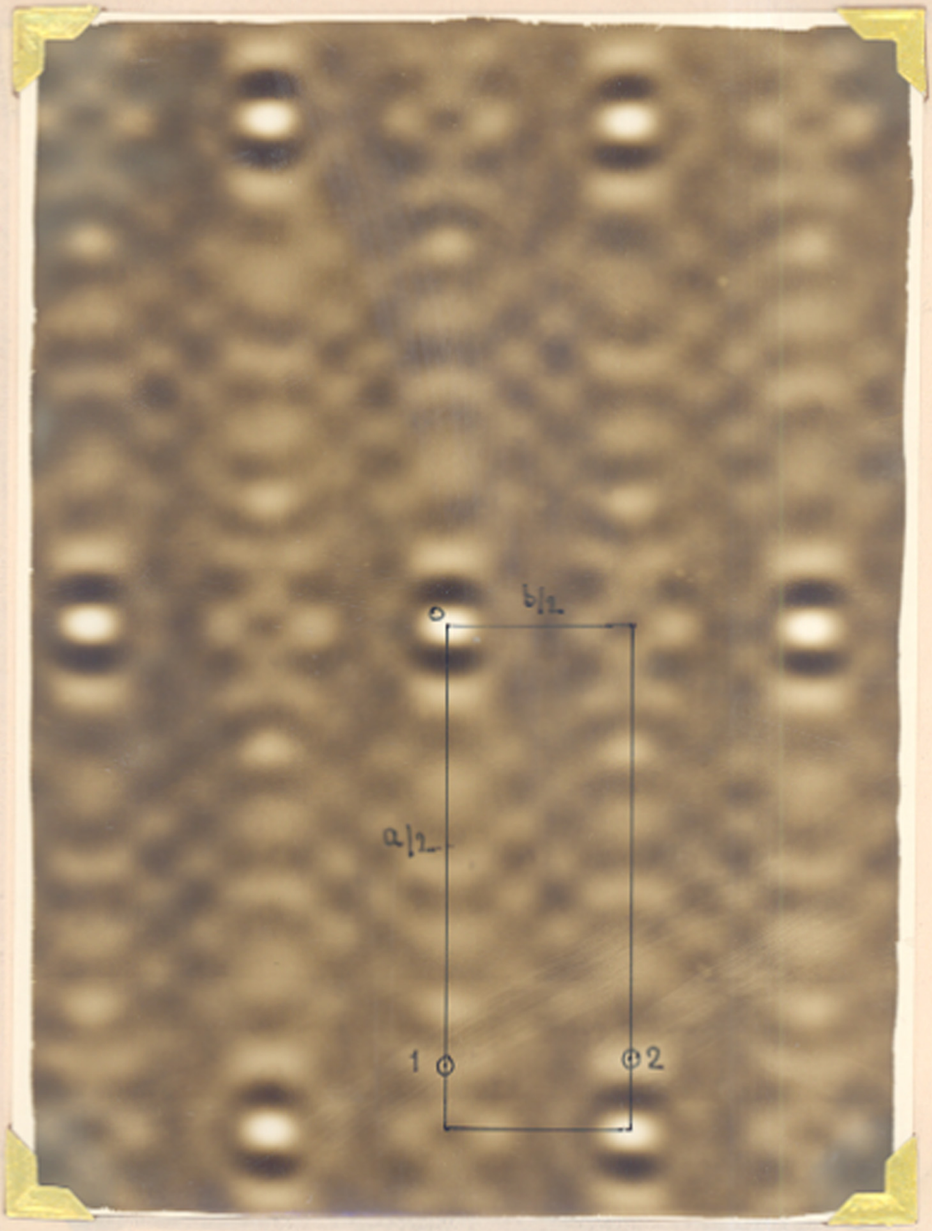


FIGURE 2 : (001) SHARPENED PATTERSON PROJECTION

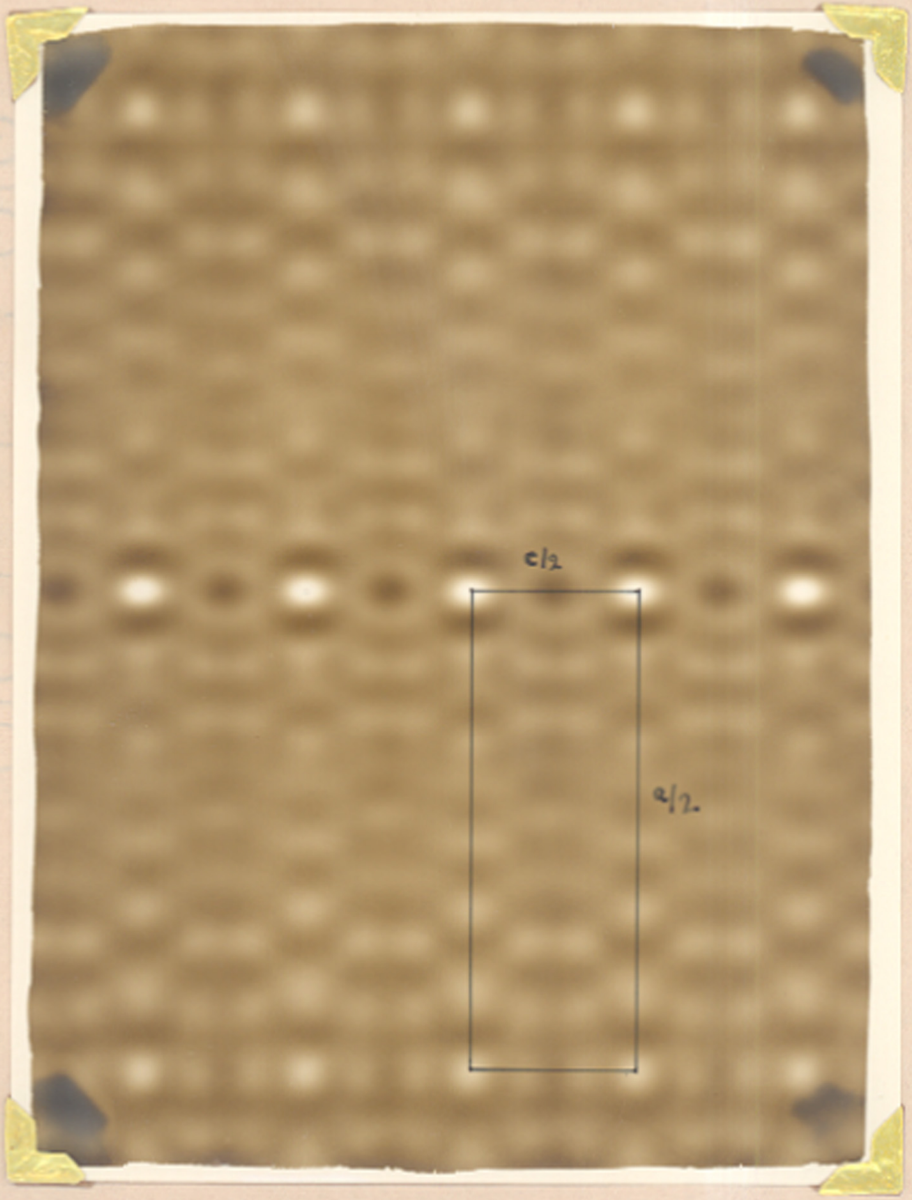


FIGURE 3 : (010) SHARPENED PATTERSON PROJECTION

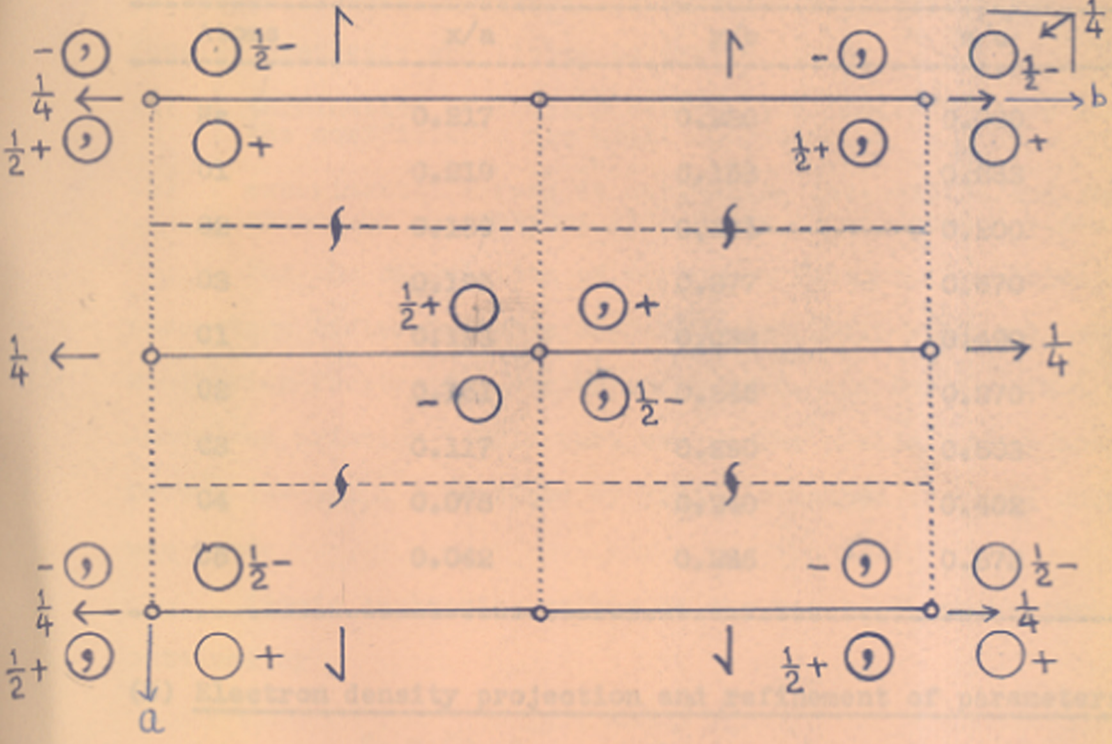


FIG. 4 SPACE GROUP Pbcn

A trial structure on this basis was, therefore, postulated and the trial parameters are listed in table 3.

TABLE - 3

Atoms	x/a	y/b	z/c
Na	0.217	0.230	0.000
O1	0.219	0.158	0.383
O2	0.150	0.161	0.200
O3	0.195	0.377	0.670
C1	0.193	0.238	0.490
C2	0.151	0.245	0.370
C3	0.117	0.290	0.503
C4	0.078	0.240	0.402
C5	0.042	0.285	0.573

(B) Electron density projection and refinement of parameters:

Structure factor and electron density expressions for (hko) projection ~~is~~ are derived which ~~is~~ are

$$F(hko) = \sum_{n=1}^{N} 8f_n \operatorname{Cos} 2\pi hx_n \operatorname{Cos} 2\pi ky_n \; .....(1)$$ and

$$\rho(x,y,0) = \frac{1}{Ac}\Big[F(000) + 2\Big\{\sum_{h=2}^{\infty} F(h00) \operatorname{Cos} 2\pi hx + \sum_{k=2}^{\infty} F(0k0) \operatorname{Cos} 2\pi ky\Big\} + 4\sum_{h=1}^{\infty}\sum_{k=1}^{\infty} F(hk0) \operatorname{Cos} 2\pi hx \operatorname{Cos} 2\pi ky\Big] \; ....(2)$$

(i) Refinement of x and y parameters by Fourier syntheses:

With the trial parameters structure factors are calculated. With calculated signs and observed amplitudes the electron density map is computed. From the map parameters are calculated which are then used for the calculation of phases and thus the process is repeated till there is no change in sign of any structure factor. However, the coordinates derived from Fourier synthesis are liable to errors due to

(a) termination of Fourier series at a finite θ value while the coefficients are still appreciable,

(b) experimental errors in estimating intensities and those caused by absorption, extinction and disperson effects.

For the calculation of structure factors from trial parameters listed in table 3, McWeeny's (1951) values of atomic scattering factors for carbon and oxygen, and for Na^+ that of James and Brindlay (1931) were used. The preliminary temperature factor ($B= 1.1\ \mathring{A}^2$) obtained by Wilson's method (Part I, chapter 1) was used.

Atomic scattering values at the required temperature were obtained by

$$f_n = fo\ e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$$

where fo is atomic scattering factor at zero temperature and B is temperature factor.

After calculating the structure factors with the trial parameters, agreement was seen with observed Fo values. The reliability index 'R' given by

$$R = \frac{\sum \left|\left(|Fo| - |Fc|\right)\right|}{\sum |Fo|}$$

came out to be $\simeq$ 0.22 for observed reflexions excluding 020 and 1800 (020 appeared to suffer from extinction effect). The trial parameters were refined by three successive Fourier syntheses taken on von Eller photosommateur as explained earlier. Everytime the resolution of the peaks were better. Final Fourier reduced 'R' to 0.158. The successive changes in parameters are shown in table 4.

TABLE - 4

Atoms	Trial		I Fourier		II Fourier		III Fourier	
	x	y	x	y	x	y	x	y
Na	0.217	0.230	0.217	0.237	0.217	0.233	0.217	0.233
01	0.219	0.158	0.219	0.162	0.219	0.160	0.219	0.160
02	0.150	0.161	0.150	0.165	0.150	0.165	0.150	0.165
03	0.195	0.377	0.195	0.379	0.195	0.379	0.195	0.379
C1	0.193	0.238	0.193	0.258	0.193	0.258	0.193	0.258
C2	0.151	0.245	0.151	0.240	0.151	0.235	0.151	0.235
C3	0.117	0.290	0.117	0.276	0.115	0.279	0.115	0.296
C4	0.078	0.240	0.078	0.206	0.077	0.208	0.077	0.216
C5	0.042	0.285	0.042	0.270	0.044	0.272	0.044	0.266
	$R \simeq 0.220$		$R \simeq 0.190$		$R \simeq 0.175$		$R \simeq 0.158$	

In all these cases $R \simeq$ factor was calculated excluding 1800, & 020 reflexions (reflexion 1800 showed serious disagreement and therefore was excluded for the present). Further refinement was done by the least squares method.

(ii) The least squares refinement of atomic parameters:

The method of least squares which is free from inherent errors of Fourier synthesis (as mentioned earlier) was first suggested by Hughes[17] (1941). The method is effective when the assumed structure is close to its correct structure.

According to the theory of errors, if measured Fo's follow the normal law, best atomic parameters shall be those which result in minimization of the quantity

$$R_1 = \sum_{u} w_1 (hkl) \left(|Fo (hkl)| - |Fc (hkl)| \right)^2$$

where "w_1" is the weight of particular term to be taken as inversely proportional to the square of the probable error of the respective Fo. "$\sum_{u}$" denotes the summation over all structure factors included in refinement. Fo has the sign of Fc. Shoemaker and collaborator[18] (1950) suggested the minimization of function R_2 which is given as:

$$R_2 = \sum_{u} w_2 (hkl) \left(|Fo (hkl)|^2 - |Fc (hkl)|^2 \right)^2$$

However, in the present case minimization of function R_1 was used.

R_1 shall be influenced by atomic coordinates as well as by temperature factor; however at present we shall see how R_1 varies with changes in atomic coordinates.

The changes in Fc due to change in Δx_n in the x-coordinate of the n^{th} atom is

$$\frac{\partial Fc}{\partial x_n} \Delta x_n.$$

Thus change in Fc due to changes in all the coordinates simultaneously is

$$\Delta Fc = \sum_{n=1}^{N} \left(\frac{\partial Fc}{\partial x_n} \Delta x_n + \frac{\partial Fc}{\partial y_n} \Delta y_n + \frac{\partial Fc}{\partial z_n} \Delta z_n \right) \ldots\ldots (3)$$

The correct Δx_n, Δy_n & Δz_n are those which most nearly equate ΔFc to (Fo - Fc). This implies that as many equations shall be available as many structure factors are included in refinement. Obiviously, the number of this type of equations should be considerably greater than the independent coordinates to be refined.

Multiplying both sides by $W \frac{\partial F_c}{\partial x_n}$ to (3) and putting (Fo-Fc) for ΔFc and summing up for all the terms (reflexions) we get

$$\sum_q W(F_o-F_c)\frac{\partial F_c}{\partial x_n} = \sum_{\textcircled{m}} W\left\{\left(\frac{\partial F_c}{\partial x_n}\right)^2 \Delta x_n + \frac{\partial F_c}{\partial x_n}\cdot\frac{\partial F_c}{\partial y_n}\cdot\Delta y_n + \frac{\partial F_c}{\partial x_n}\cdot\frac{\partial F_c}{\partial z_n}\cdot \Delta z_n + \sum_m \frac{\partial F_c}{\partial x_n}\left(\frac{\partial F_c}{\partial x_m}\Delta x_m + \frac{\partial F_c}{\partial y_m}\Delta y_m + \frac{\partial F_c}{\partial z_m}\Delta z_m\right)\right\} \quad \ldots\ldots(4)$$

where $\sum_m$ denotes sum over all atoms except nth. The next normal equation can be formed by multiplying both sides by $W \frac{\partial F_c}{\partial x_{n+1}}$ and getting equations as earlier. Thus getting as many normal equations as many unknowns are to be solved, one can get Δx_n, Δy_n and Δz_n for each atom. But it would be formidable task because of the labour involved. However, if the atoms are resolved in any particular projection then it can be shown that the quantities such as $\sum_q W \frac{\partial F_c}{\partial x_n}\frac{\partial F_c}{\partial x_m}$ are likely to be comparably smaller than $\sum_q W\left(\frac{\partial F_c}{\partial x_n}\right)^2$ and if the axes are orthogonal or nearly so then $\sum_q W \frac{\partial F_c}{\partial x_n}\cdot\frac{\partial F_c}{\partial y_n}$ are small enough to be neglected and therefore equation (4) reduces to

$$\sum_q W(F_o-F_c)\frac{\partial F_c}{\partial x_n} = \Delta x_n \sum_{\textcircled{m}} W\left(\frac{\partial F_c}{\partial x_n}\right)^2$$

$$\text{or} \qquad \Delta x_n = \frac{\sum_q W(F_o-F_c)\frac{\partial F_c}{\partial x_n}}{\sqrt{\sum_q W\left(\frac{\partial F_c}{\partial x_n}\right)^2}} \quad ------(5)$$

similarly we can derive equations for Δy_n and Δz_n. However, if ith and jth atoms in any projection are not well resolved than the quantities such as $\sum_q \frac{\partial F_c}{\partial x_n}\cdot\frac{\partial F_c}{\partial y_m}$ cannot be neglected compared to $\sum_q\left(\frac{\partial F_c}{\partial x_n}\right)^2$ and so the equations

$$\Delta x_i \sum_q \left(\frac{\partial F_c}{\partial x_i}\right)^2 + \Delta x_j \sum_q \frac{\partial F_c}{\partial x_i} \cdot \frac{\partial F_c}{\partial x_j} = \sum_q (F_o - F_c) \frac{\partial F_c}{\partial x_i}$$ and

$$\Delta x_i \sum_q \frac{\partial F_c}{\partial x_i} \cdot \frac{\partial F_c}{\partial x_j} + \Delta x_j \sum_q \left(\frac{\partial F_c}{\partial x_j}\right)^2 = \sum_q (F_o - F_c) \frac{\partial F_c}{\partial x_j}$$ must

be solved for Δx_i and Δy_i. Similarly equations for Δy_i, Δy_j, Δz_i and Δz_j could be deduced.

Thus after getting corrections, the new coordinates (corrected) are used for Fc calculations and the process is repeated till corrections obtained are negligibly small.

For (hk0) projection the formula is

$$F(hk0) = \sum_{n=1}^{N} 8\, f_n \operatorname{Cos} 2\pi h x_n \operatorname{Cos} 2\pi k y_n$$

differentiating this with respect to x_n, we get

$$\partial Fc / \partial x_n = -\, 8\, f_n\, 2\pi h \operatorname{Sin} 2\pi h x_n \operatorname{Cos} 2\pi k y_n$$

$$\therefore \Delta x_n = \frac{(Fo - Fc)\,(-8\; 2\pi h\, f_n \operatorname{Sin} 2\pi h x_n \operatorname{Cos} 2\pi k y_n)}{(-8\; 2\pi h\, f_n \operatorname{Sin} 2\pi h x_n \operatorname{Cos} 2\pi k y_n)^2}$$

and similarly for Δy_n and Δz_n could be obtained.

First least squares refinement gave the coordinates (xr_1, yr_1) which improved R-factor to 0.142. Second least squares (xr_2, yr_2) refinement, however, spoiled the agreement and consequently the R-factor. It was noted that with xr_1 parameters, h00 type of reflexions showed much better agreement and were thought to be the best. Y-parameters were again refined by least squares and new parameters yr_3 with xr_1 parameters dropped R-factor to 0.124.

After this, it was tried to correct temperature factor and scale factor by Wilson's method, but no significant corrections were obtained. The theory of the method is explained below:

If K_1 is the scaling factor for the present F (hko) and B_1 is the temperature factor used and B_2 is the correct temperature to be applied then

$$K_1 \frac{Fo}{Fc} = e^{-(B_2 - B_1)\left(\frac{\sin\theta}{\lambda}\right)^2}$$

or $K_1 \times C = e^{-\Delta B \left(\frac{\sin\theta}{\lambda}\right)^2}$ where $Fo/Fc = C$; and $B_2 - B_1 = \Delta B$ or $\log_e C = -\Delta B \left(\frac{\sin\theta}{\lambda}\right)^2 + \log_e 1/K_1$

Thus if the graph is drawn between $(\sin\theta/\lambda)^2$ and $\log_e C$. The slope of the straight line shall be $-\Delta B$ and the intercept at the X-axis shall give correction to scale factor. The necessary data are given in table 5 and graph shown in fig.5.

TABLE - 5

$(\sin\theta/\lambda)^2$	ΣFc	ΣFo	$C = \Sigma Fo/\Sigma Fc$	$\log_e C$
0.026	285	305	1.0702	0.0677
0.052	518	507	0.9788	-0.0215
0.085	477	498	1.0440	0.0430
0.127	270	270	1.0000	0.0000
0.178	451	451	1.0000	0.0000
0.236	393	374	0.9517	-0.0496

(iii) The least squares refinement of temperature factor:

Another variable which affects R-factor is temperature factor which as well can be refined to give minimum R-factor. Following exactly as in the case of atomic coordinates refinement

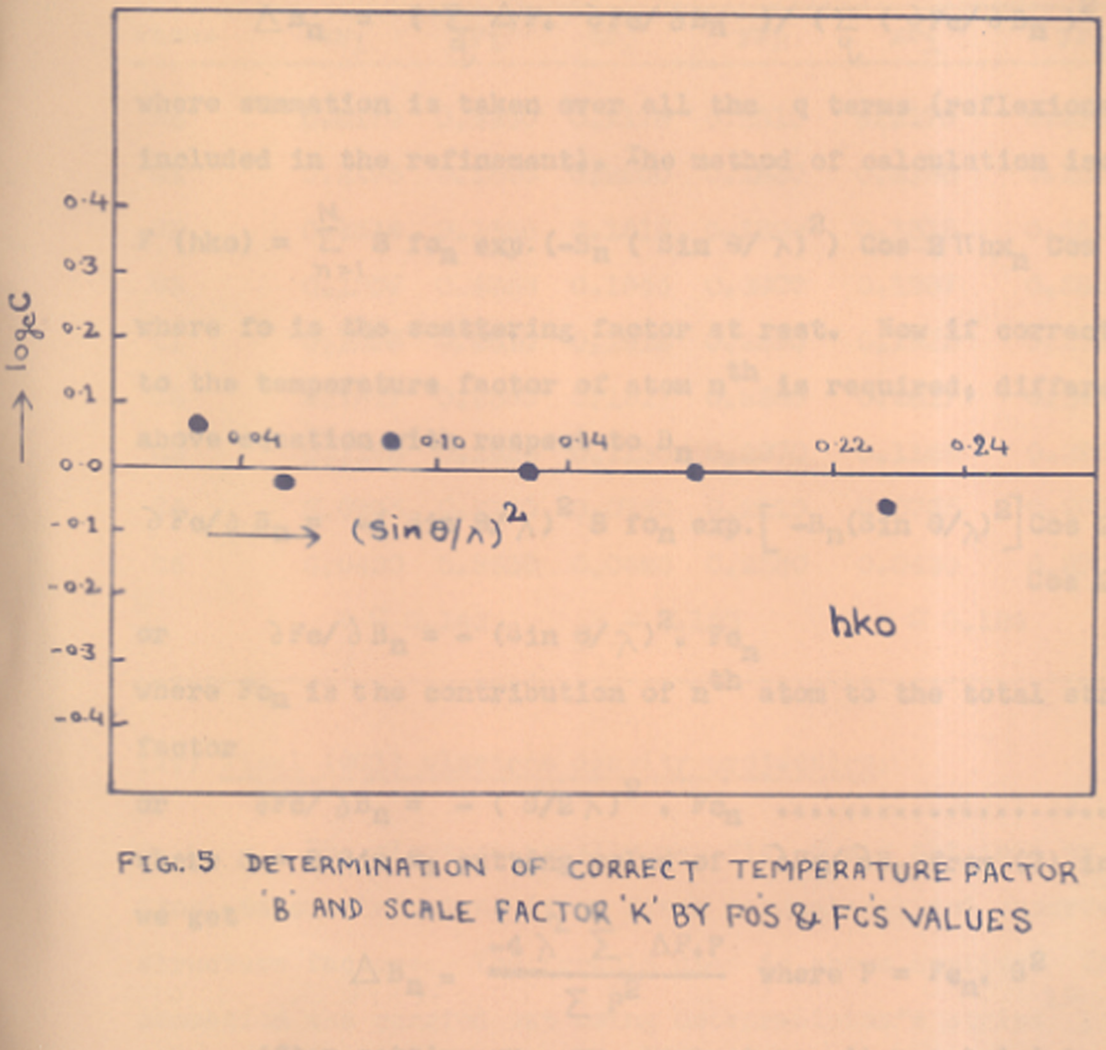


FIG. 5 DETERMINATION OF CORRECT TEMPERATURE FACTOR 'B' AND SCALE FACTOR 'K' BY FOS & FCS VALUES

but instead of varying x,y,z coordinates, now B is varied. The temperature factor correction $\triangle B_n$ for the n^{th} atom is given

$$\triangle B_n = \left(\sum_q \triangle F . \ \partial Fc/\partial B_n \right) / \left(\sum_q (\partial Fc/\partial B_n)^2 \right. \quad \ldots (6)$$

where summation is taken over all the q terms (reflexions included in the refinement). The method of calculation is:

$$F\,(hko) = \sum_{n=1}^{N} 8\ fo_n\ \exp.(-B_n\ (\sin\theta/\lambda)^2)\ \cos 2\pi hx_n\ \cos 2\pi kyn$$

where fo is the scattering factor at rest. Now if correction to the temperature factor of atom n^{th} is required, differentiating above equation with respect to B_n

$$\partial Fc/\partial B_n = -(\sin\theta/\lambda)^2\ 8\ fo_n\ \exp.\left[-B_n(\sin\theta/\lambda)^2\right] \cos 2\pi hx_n \,.\ \cos 2\pi ky_n$$

or $\partial Fc/\partial B_n = -(\sin\theta/\lambda)^2 .\ Fc_n$

where Fc_n is the contribution of n^{th} atom to the total structure factor

or $\partial Fc/\partial B_n = -(S/2\lambda)^2 .\ Fc_n$ ....(7)

where $S = 2 \sin\theta$, putting value of $\partial Fc/\partial B_n$ from (7) in (6) we get

$$\triangle B_n = \frac{-4\lambda^2 \sum \triangle F.P}{\sum P^2} \quad \text{where } P = Fc_n .\ S^2$$

After getting xr_1, yr_3 parameters, it was tried to calculate individual temperature factor as explained above. With the new temperature factors again Fc values were calculated but without any improvement in R-factor.

No further refinement was therefore, attempted for this projection. The changes in the coordinates and corresponding R-factor at various stages are shown in table 6.

FIG. 7: ELECTRON DENSITY PROJECTION ON (010). CONTOURS ARE DRAWN AT INTERVALS OF 1 e/$Å^2$. FIRST FIVE CONTOURS AROUND Na^+, O_1 AND O_3 ATOMS ARE AT 1 e/$Å^2$ INTERVALS AND THEN ALTERNATE CONTOURS ARE DRAWN. 1 e/$Å^2$ CONTOUR IS DASHED.

TABLE - 6

Refinement of x and y parameters by L. S. Method

Atoms	xr_1	yr_1	xr_2	yr_2	xr_1	yr_3
Na	0.2170	0.2330	0.2175	0.2310	0.2170	0.2360
01	0.2195	0.1560	0.2200	0.1550	0.2195	0.1500
02	0.1515	0.1620	0.1515	0.1590	0.1515	0.1590
03	0.1957	0.3850	0.1945	0.3800	0.1957	0.3850
C1	0.1925	0.2610	0.1915	0.2590	0.1925	0.2650
C2	0.1517	0.2380	0.1517	0.2380	0.1517	0.2440
C3	0.1145	0.2930	0.1135	0.2970	0.1145	0.2950
C4	0.0765	0.2130	0.0760	0.2110	0.0765	0.2090
C5	0.0430	0.2630	0.0420	0.2580	0.0430	0.2700
	$R \simeq 0.142$		$R \simeq 0.153$		$R \simeq 0.124$	

(iv) Final (001) electron density projection:

The electron density map fig. 6 (pl. see after p. 32) was obtained by using final calculated signs (from final parameters) and observed structure factors. The formula used is shown earlier. The summation was carried out using Beevers-Lipson's strips^{19}, along one quarter of the a-axis and along half of the b-axis at interval of 1/120th along a and 1/60th along b.

(vi) Refinement of (010) projection:

Structure factor and electron density expressions are;

for h+l = 2n

$$F(hol) = \sum_{n=1}^{N} 8f_n \operatorname{Cos} 2\pi hx_n \operatorname{Cos} 2\pi lz_n$$

for h+l = 2n+1

$$F(hol) = -\sum_{n=1}^{N} 8\, f_n \operatorname{Sin} 2\pi hx_n \operatorname{Sin} 2\pi lz_n \text{ and}$$

$$\rho(xoy) = \frac{1}{A_c}\Big[F(000) + 2\Big\{\sum_{h=2}^{\infty} F(hoo) \operatorname{Cos} 2\pi hx + \sum_{l=1}^{\infty} F(hol) \operatorname{Cos} 2\pi lz\Big\} + 4\Big\{\sum_{h=2,\,l=1}^{\infty}\sum^{\infty}_{h+l=2n} F(hol) \operatorname{Cos} 2\pi hx \operatorname{Cos} 2\pi lz - \sum_{h=2,\,l=1}^{\infty}\sum^{\infty}_{h+l=2n+1} F(hol) \operatorname{Sin} 2\pi hx \operatorname{Sin} 2\pi lz\Big\}\Big]$$

When the refinement of (hko) was in progress, the refinement of this projection was also taken up with x-parameters obtained after third Fourier synthesis and the trial z parameters as shown in table 3. Temperature factor 3.6 Å^2 was used (Part I, chapter 1). R-factor came out to be 0.207. It was tried to refine twice by Fourier syntheses taken on Eller's photosommateur but rather it increased the discrepancies and R-factor. It was, therefore, refined by difference Fourier. The theory is explained below.

(vi) The difference Fourier synthesis:

In this method, Fourier series is summed up using (Fo-Fc) values instead of Fo values as Fourier coefficients. The difference Fourier map free from series termination error, provided the correct f_n values are used, and will be relatively smooth in the region near the atomic positions. The incorrect positioning is indicated when the assumed atomic position lies on a gradient in the difference map. The map also indicates the incorrect temperature parameters defined by $f_n = fo \exp(-B(\operatorname{Sin}\theta/\lambda)^2)$ for isotropically vibrating atom by rasidual electron density or hole at the assumed atomic positions. If the thermal vibration of an atom is anisotropic, but an isotropic scattering factor is assumed for this atom in the calculation of structure factors, the positive electron density in the direction of anisotropy and negative electron density in the direction perpendicular to it is observed with zero electron density at the atomic position. The correction (Δr_n) in atomic position can be calculated by

$$\Delta r_n = (\partial D/\partial r)_n / 2p(\rho_o)_n \quad \text{(Lipson and Cochran, 1953)}^{20}$$

where 'ρ_o' is the observed density at the centre of atom; 'D' is the value of '$\rho_o - \rho_c$' at the distance 'r' from the centre of the atom and 'p' is a constant which is given by

$$\rho = Z\,(p/\pi)^{3/2}\exp.\left[-pr^2\right] \text{ -----(Costain, 1941)}$$

where ρ is the density at a distance r from the centre of the atom and Z is atomic number.

The value of 'p' can be obtained from the slope of the graphs log ρ versus r^2. In practice, p is taken equal to 5.0$\overset{o}{A}^{-2}$. The value of $(\rho_o)_n$ is taken from the corresponding an Fo synthesis.

The z-parameters were refined by a difference Fourier synthesis taken on photosommateur which with the x-parameters shown below gave 'R' factor $\simeq$ 0.194.

	Na	O1	O2	O3	C1	C2	C3	C4	C5
x-parameters	0.217	0.219	0.150	0.195	0.193	0.151	0.115	0.077	0.044
z-parameters	0.000	0.383	0.200	0.670	0.485	0.370	0.503	0.402	0.563

(vii) <u>The 'Least-Squares' refinement:</u>

By this time (hko) projection was refined to 0.124. The final xr_1-parameters with the zr_1-parameters obtained by first least squares refinement gave R-factor $\simeq$ 0.165. zr_2-parameters from second least square cycle with the revised temperature factor of 1.1 Å^2 by Wilson's method dropped R to 0.140. Another least square cycle of z-parameters reduced R to 0.133. Further refinement of this projection was stopped here. Z-parameters at various refinement stages with corresponding R-factor are shown in table 7.

TABLE - 7

Atoms	xr_1	First L.S. zr_1	Second L. S. zr_2	Third L. S. zr_3
Na	0.2170	0.000	0.000	0.000
01	0.2195	0.387	0.393	0.400
02	0.1515	0.190	0.185	0.179
03	0.1957	0.665	0.662	0.661
C1	0.1925	0.488	0.488	0.496
C2	0.1517	0.377	0.371	0.367
C3	0.1145	0.506	0.512	0.517
C4	0.0765	0.392	0.390	0.390
C5	0.0430	0.557	0.549	0.543
		$R \simeq 0.165$	$R \simeq 0.140$	$R \simeq 0.133$

(viii) <u>(010) electron density projection:</u>

At the end of this refinement, electron density map was computed (fig.7) according to the formula already given. The summation was carried out using Beever-Lipson's strips along one quarter of a-axis and half of the c-axis at interval of 1/120th along a and 1/60th along c.

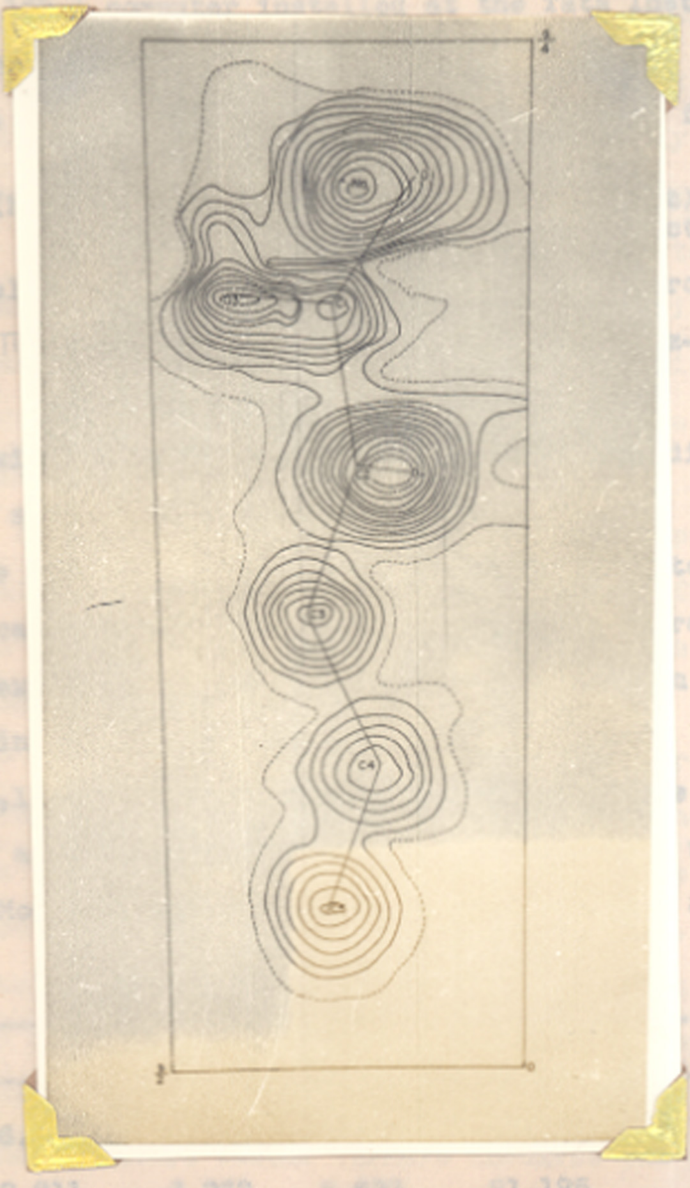


FIG. 6: ELECTRON DENSITY PROJECTED ON (001). CONTOURS ARE DRAWN AT INTERVALS OF 1 $e/\mathring{A}^2$. FIRST FOUR CONTOURS AROUND Na^+ AND O_1 ATOMS ARE AT 1 $e/\mathring{A}^2$ INTERVAL AND THEN ALTERNATE CONTOURS ARE DRAWN.

(C) Three dimensional refinement:

(1) Three dimensional refinement was carried out on CDC-3600, 160-A computer installed at the Tata Institute of Fundamental Research, Bombay.

The formula used for calculating structure factor is

$$Fc(hkl) = \sum_{n=1}^{N} 8(\text{Atomic scattering factor part}) \times (\text{Geometrical structure factor part})$$

Geometrical structure factor part for the space group Pbcn is

$$A = \cos 2\pi(hx+(h+k)/4) \cos 2\pi(ky+1/4) \cos 2\pi(lz-(h+k)/4)$$

and $B = 0$

while atomic scattering part was calculated according to the following scheme.

The scattering factor of each asymmetric atom for each plane is calculated by the following equation at rest.

$$fo = A \exp(-ax^2) + B \exp(-bx^2) + C \text{ where } x = \sin\theta/\lambda$$

and $(\sin\theta/\lambda)^2 = h^2/4a^2 + k^2/4b^2 + l^2/4c^2$

where h,k,l are Miller's indices and a,b and c are axial lengths. Values of analytical constants A,a,B,b and C were used, given by F. H. Moor[21] (1961) and are tabulated in table 8.

TABLE - 8

Atoms	A	a	B	b	C
Na^+	6.298	3.751	1.938	11.842	1.764
O	3.811	6.363	2.633	21.195	1.550
C	1.620	6.785	2.988	28.126	1.380

The scattering factor values, then, are calculated at the required temperature as

$$f = fo \times \exp.\left[-B(\sin\theta/\lambda)^2\right]$$ where 'f' is scattering factor values at the temperature 'B'.

The general scheme of the program is explained below:

It calculates contribution of n^{th} atom and adds to the progressive sum and after every calculation of Fc for each plane, it computes Sin θ; Fo-Fc and prints out h,k,l; Sin θ; Fobs; Fcal; and ΔF(i.e. Fo-Fc). It simultaneously computes partial derivatives of variables being refined and after necessary cross-products of derivatives, it adds to progressive sums. When all the planes have been considered, it calculates corrections to the variables and prints out coordinates being used, shifts to the coordinates and new coordinates to be used for the next cycle.

As already indicated, reflexions of the type $h+k+l = 2n+1$ were of diffuse nature and, therefore, left out of refinement. But it was known that the structure may not refine to the desired accuracy, because of the neglect of nearly half of the reflexions which were of diffuse type. This was the case particularly with z-coordinates, because of the space group Pbcn, the neglect of reflexions $h+k+l = 2n+1$ amounts to weighting the structure by half and supprimposing on its reflection on (001). Although the right structure from the two possibilities of each atom could be derived from bond length consideration, the accuracy of z-parameters had suffered specially for atoms near $z = 0.5$, because the structure factor formula involves the term $\cos 2\pi lz$ which changes very slowly near $z = 0.5$.

It was therefore decided to include all the diffuse reflexions in the three dimensional refinement.

Following the disorder explained in case of sodium 2-oxo caprylate (Pant, L. M., 1964) where the intensity expression when α differs from zero by an amount $\gg 1/n_1$ is given as

$$\mathcal{J}(h+w,\ k,l) = n_2^2\, n_3^2\, A^2\, \mathrm{Sin}^2\, \tfrac{1}{2}\pi w\, (\mathrm{Sin}^2 \pi(h+w)n_1)/(\mathrm{Sin}^2 \pi(h+w))$$

$$+\ n_1\, n_2^2\, n_3^3\, B^2\, \frac{\{(1-2\alpha)\ \mathrm{Cos}^2 \tfrac{1}{2}\pi\omega + \alpha^2\}\{1-(1-2\alpha)^4\}}{1-2(1-2\alpha)^2 \mathrm{Cos}\, 2\pi\omega + (1-2\alpha)^4}$$

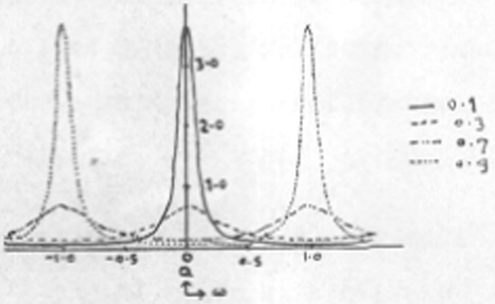
The first term contains the factor $\mathrm{Sin}^2\, \tfrac{1}{2}\pi w$ which implies that when w is even the term vanishes; that means the reflexions with h+k+l = odd do not appear and obviously this term therefore corresponds to sharp reflexions. When h+k+l = even (i.e. w odd) the reflexions appear with the same intensity and sharpness as from ordered crystal.

The second term corresponds to diffuse reflexions in the X-ray photographs which can be written as

$$\mathrm{Id} \propto B^2\, Q$$

where $Q = \dfrac{\{(1-2\alpha)\ \mathrm{Cos}^2 \tfrac{1}{2}\pi\omega + \alpha^2\}\{1-(1-2\alpha)^4\}}{1-2(1-2\alpha)^2 \mathrm{Cos}\, 2\pi\omega + (1-2\alpha)^4}$

The plots of Q against w are shown for α=0.1, 0.3, 0.7, 0.9 respectively. The curves are symmetrical about w = 0 having maxima at w = 0 when $\alpha < 0.5$ and at w = 1 when $\alpha > 0.5$. Which means for $\alpha < 0.5$ the curves have maxima at reciprocal points with h+k+l = odd. Since the diffuse spots in the X-ray photographs show maxima near reciprocal lattice points with h+k+l = odd, obviously α is close to zero or so. This implies that the



structure is closer to ordered structure of space group Pbcn except that intensities of reflexions with h+k+l = odd are reduced owing to diffuseness caused by disorder. It is, therefore, clear that if intensity of diffuse~~d~~ spots are measured at its reciprocal lattice points and scaled separately they would behave as if they were sharp reflexions. Further, though the intensities of these reflexions are decreased but they are reduced proportionately for all the reflexions. Their inclusion in the three dimensional refinement was therefore, expected to give certainly more reliable results.

Intensit~~y~~ies of all the diffuse reflexions w~~as~~ere measured and corrected for Lp and extension-correction, and scaling was applied by calculating structure-factors with the final parameters obtained from projectional refinement. With the x,y,z coordinates obtained from (001) and (010) projection refinement, R-factor after necessary scaling for all the reflexions sharp as well diffuse was 0.1654. Refinement was accomplished with number of 'Least-Squares' cycles and layerwise scaling was frequently applied to sharp and diffuse reflexions separately.

The parameters obtained are listed in the following table 9. R-factor at this stage was 0.120 for only observed reflexions.

(ii) <u>Standard-deviations</u>:

The agreement between calculated and observed structure factors given by the reliability index was taken as a measure of the accuracy of the results. Proper assessment of the accuracy of the final results is however, the determination of the standard deviation of each result i.e. standard-deviation of

TABLE - 9

Atoms	x/a	y/b	z/c	B in $Å^2$
Na	0.2167	0.2368	-0.0025	1.77
O1	0.2195	0.1519	0.3968	1.72
O2	0.1508	0.1596	0.1759	2.20
O3	0.1934	0.3836	0.6550	1.92
C1	0.1913	0.2600	0.4890	1.99
C2	0.1515	0.2316	0.3661	2.01
C3	0.1155	0.3015	0.5022	2.03
C4	0.0784	0.2020	0.3927	2.72
C5	0.0411	0.2799	0.5270	3.72

coordinates, bond-lengths and bond-angles in case of structure determination.

In the refinement by least-squares method, the problem is complicated because of the way of proper treatment of unobserved reflexions i.e. reflexions which $0 \leqslant F^2 \leqslant F^2$ min. In the present case, the unobserved reflexions were rather as many as observed reflexions, and therefore it was felt necessary to include them in the refinement so as to get reliable estimates of error, which is one of the most useful feature of the least-squares procedure. Therefore, all the unobserved reflexions were included taking their intensity as $\mu \simeq$ I min/3 (Walter C. Hamilton, 1955)[22] and refinement was carried out with few cycles. R-factor at the start was 0.1880 which remained steady at 0.1843. R-factor for only observed reflexions is, however, 0.1230. The final parameters along with their standard deviations are listed in table 10.

In three dimensional synthesis of a centro-symmetric structure, the standard deviation $\sigma(x_n)$ of an atomic coordinate of x_n is given by

$$\sigma(x_n) = (K/\sqrt{2}\,Z_n)\,(\pi/2p)^{5/4}\,\Big(\frac{1}{V}\sum_{n=1}^{N} Z_n^2\Big)^{\frac{1}{2}}$$ - (Lipson & Cochran, 1953)[23]

In the equation $K = (\Sigma \Delta F)/|Fo|$, which is the R-factor at the end of refinement; p is constant given by Costain's equation, and has been taken as 5.0 Å^{-2}. Z_n is the atomic number of the atom in question and 'V' is the volume of unit cell. The standard deviations are listed along with the final parameters in table 10.

The standard deviations in bond lengths were calculated by the relation

$$\sigma^2(d_{12}) = \sigma^2(x_1) + \sigma^2(x_2)$$

where $\sigma(x_1)$ and $\sigma(x_2)$ are the deviations in the atomic coordinates of the atom 1 and 2 respectively.

For estimation of standard-deviations in bond-angles, Darlow's (1960)[24] method was employed. With isotropic standard deviation for each atom the standard deviation of a bond-angle θ, subtended by the bonds from atoms 1 and 3 at the atom 2 is given by

$$\sigma^2(\theta) = \sigma^2(r_1)/l_1^2 + l_3^2\,\sigma^2(r_2)/l_1^2\,l_2^2 + \sigma^2(r_3)/l_2^2$$

where $\sigma(r_1)$, $\sigma(r_2)$ and $\sigma(r_3)$ are the deviations of coordinates of atoms 1, 2 and 3 respectively and l_1, l_2 and l_3 are the distances between atoms 1 and 2, 2 and 3 and 3 and 1 respectively. The standard deviations in bond-angles and bond lengths are given in table 12, along with bond angles and bond-lengths.

TABLE - 10

FINAL ATOMIC PARAMETERS

Atoms	x	y	z	B in Å^2
Na	0.2166 ± 0.0002	0.2366 ± 0.0008	- 0.0010 ± 0.0008	1.62
O1	0.2193 ± 0.0002	0.1516 ± 0.0011	0.3962 ± 0.0011	1.24
O2	0.1507 ± 0.0002	0.1601 ± 0.0011	0.1774 ± 0.0011	2.03
O3	0.1931 ± 0.0002	0.3837 ± 0.0011	0.6599 ± 0.0011	1.57
C1	0.1915 ± 0.0003	0.2576 ± 0.0014	0.4866 ± 0.0014	1.60
C2	0.1513 ± 0.0003	0.2272 ± 0.0014	0.3649 ± 0.0014	2.01
C3	0.1157 ± 0.0003	0.3000 ± 0.0014	0.5014 ± 0.0014	1.53
C4	0.0782 ± 0.0003	0.2062 ± 0.0014	0.3935 ± 0.0014	2.30
C5	0.0410 ± 0.0003	0.2770 ± 0.0014	0.5341 ± 0.0014	4.08

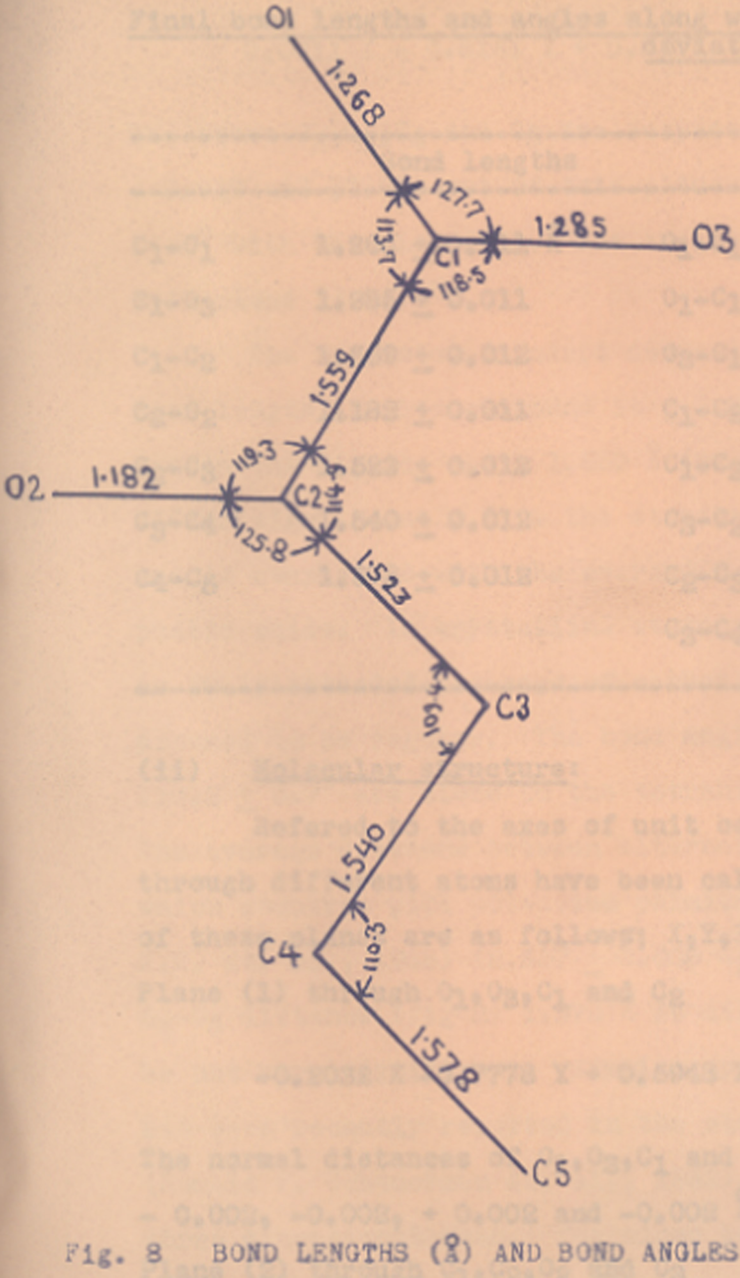


Fig. 8 BOND LENGTHS (Å) AND BOND ANGLES (°) IN α-KETO VALERATE GROUP.

CHAPTER - IV

RESULTS AND DISCUSSION

(1) The final atomic coordinates in Å listed below in table 11 were used for the calculations of intramolecular and intermolecular bond distances and angles. Bond distances were calculated using the following formula:

$$d^2 = (x_2-x_1)^2 + (y_2-y_1)^2 + (z_2-z_1)^2$$

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

Using the same coordinates, bond angles were calculated with the following formula:

$$\mathrm{Cos}\ \widehat{r_1\ r_2}\ r_3 = (\ r_1^2 + r_2^2 - r_3^2\ ) / \ 2\ r_1\ r_2$$

where r_1, r_2 and r_3 are the distances between the atoms 1 and 2, 2 and 3 and 3 and 1 respectively. The bond-lengths and bond-angles in α-keto valerate group are shown in fig. 8 and tabulated in table 12.

TABLE - 11

Atoms	X	Y	Z
Na	7.3839	1.4527	-0.0059
01	7.4759	0.9308	2.3415
02	5.1374	0.9830	1.0484
03	6.5828	2.3559	3.9000
C1	6.5282	1.5817	2.8758
C2	5.1578	1.3950	2.1566
C3	3.9442	1.8420	2.9633
C4	2.6658	1.2661	2.3256
C5	1.3977	1.7008	3.1565

TABLE - 12

Final bond lengths and angles along with their estimated standard deviations

Bond lengths		Bond angles	
C_1-O_1	1.268 ± 0.011 Å	O_1-C_1-O_3	127.7 ± 0.8°
C_1-O_3	1.285 ± 0.011	O_1-C_1-C_2	113.7 ± 0.8
C_1-C_2	1.559 ± 0.012	O_3-C_1-C_2	118.5 ± 0.8
C_2-O_2	1.182 ± 0.011	C_1-C_2-C_3	114.9 ± 0.7
C_2-C_3	1.523 ± 0.012	C_1-C_2-O_2	119.3 ± 0.8
C_3-C_4	1.540 ± 0.012	C_3-C_2-O_2	125.8 ± 0.8
C_4-C_5	1.578 ± 0.012	C_2-C_3-C_4	109.4 ± 0.7
		C_3-C_4-C_5	110.3 ± 0.7

(ii) Molecular structure:

Refered to the axes of unit cell, the mean planes through different atoms have been calculated. The equations of these planes are as follows; X,Y,Z are expressed in Å units.

Plane (1) through O_1,O_3,C_1 and C_2

$$-0.2032\,X - 0.7778\,Y + 0.5948\,Z + 0.8483 = 0$$

The normal distances of O_1,O_3,C_1 and C_2 from this plane are - 0.002, -0.002, + 0.002 and -0.002 Å respectively.

Plane (2) through C_1,C_2,O_2 and C_3

$$0.0809\,X + 0.9273\,Y - 0.3655\,Z - 0.9332 = 0$$

The atoms C_1,C_2,O_2 and C_3 are respectively + 0.011, -0.011, + 0.011 and + 0.011 Å away from this plane. It makes an angle of 17.2 degrees with the plane (1).

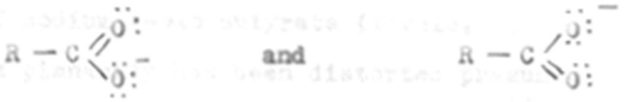
Plane (3) through C_2, C_3, C_4 and C_5

$$0.0811\,X - 0.8151\,Y + 0.5737\,Z - 0.5286 = 0$$

The atoms C_2, C_3, C_4 and C_5 are respectively - 0.010, - 0.010, - 0.010 and +0.010 out of this plane. It makes an angle of 16.5° with the plane (1). The angle between plane (2) and this plane is 16.5°.

The estimated standard deviation of the measured C-C bond length in this compound is ± 0.012 Å. The bond length C-C in the zig-zag chain 1.550 Å (average value) do not differ significantly from the standard C-C distance of 1.545 Å and is comparable with the average C-C values of many n-aliphatic acids. In crystalline state such chains usually occur as fully extended zig-zags of carbon atoms and are generally assumed to be regular. The bond angles C-C-C 109.4 ± 0.7° and 110.3 ± 0.7° are close to the tetrahedral values of 109.48°. The average distance between alternate carbon atoms is 2.552 Å which compares with potassium palmitate[25] (form-B) (Dumbleton, J.H. et. al., 1965) (2.557 ± 0.005 Å). The rather unnatural C_4-C_5 distance (fig 8) 1.578 Å is disturbing but is felt to be not very significant. Similar type of unnatural bond (1.57 Å) has been recently reported in the structure of valeric acid[26] (Ronald F. Scheuerman et. al., 1962), which has been refined by three dimensional data. The minor bond lengths variation can be attributed partially to the presence of neglected hydrogens. The hydrogens contribution form nearly 10% to the total electrons of the molecule. The inclusion of hydrogens normally show marked effect on the parameters of carbon atoms and tend to improve C-C distances as have been demonstrated in dodecanedioic acid[27], pimelic acid[28] and sebacic acid[29] (Housty and Hospital, 1966). An attempt, of course in vain, to locate hydrogens in case of sodium 2-oxo heptylate (Part III, chapter 2) did not encourage to do so in this compound. The thermal vibration parameters show that the atoms near the ionic layers have smaller vibration amplitudes than those at the further end of the molecule. This effect is not unexpected since the movement of these atoms is restrained by the heavy atom Na. The atoms C_2, C_3, C_4 and C_5 are in plane with the maximum deviation of 0.01 Å on either side of the plane.

The mean plane passing through carboxylic group and corresponding deviation of atoms suggest that it is planar. In carboxylic acids such as propionic acid[30] (Frederick, J. et. al., 1962), butyric acid [31] (Frederick, J. et. al., 1962 a) and valeric acid, the two C-O distances have been of different lengths. The difference has been interpreted by pauling (1960)[32] on the basis of the difference in single-double bond character of the two bonds. The predicted confuguration of carboxylate in ion (Pauling, 1960) is that with the angle of O-C-O = 125.27° and equal distances of C-O (1.27 Å). The results $O_1-C_1-O_3 = 127.7°$ and $C_1-O_1 = 1.268 \pm 0.011$ Å and $C_1-O_3 = 1.285 \pm 0.011$ Å are in favour of almost purely ionic form of the carboxylate group in the present compound. An elegent illustration has been provided by the structure of sodium and lithium dihydrogen citrate[33] (Glusker, J. P., et. al., 1965) in which both ionised and unionised carboxylic groups are present in the same molecule. It has been shown that it is the central x carboxylic group which is ionised (C-O = 1.253 and 1.252 Å) in the crystalline form; because the hydrogens located have been found to be attatched to the end carboxylic oxygens (C-O = 1.203, 1.321 Å and 1.216, 1.313 Å). The two similar C-O distances in the present case suggest resonance between two C-O bonds in the carboxylate group



However, many recent investigations favour the view that the two C-O distances approach each other when the environment of the two oxygens are identical or in those structures which exist in zwitterion form. To exemplify this point, the following table 13 shall suffice.

TABLE - 13

Compounds	C-O (Å)	C-O (Å)	References
Mono pyridine copper (II) acetate (orthorhombic form)	1.248 1.236	1.250 1.250	(Hanic, F. et. al., 1964)[34]
Monopyridine copper (II) acetate (monoclinic form)	1.247 1.247	1.231 1.231	(Barclay & Kennard, 1961)[35]
α -glycine	1.261	1.265	(Marsh, 1958)[36]
Dl -serine	1.268	1.261	(Shoemaker et. al., 1953)[37]
β -alanine	1.292	1.287	(Jose, P., et. al., 1964)[38]

The angles O_1-C_1-O_3, O_1-C_1-C_2 and O_3-C_1-C_2 are 127.7°, 113.7° and 118.5° respectively are regular with respect to the values obtained in other carboxylates.

127.3°, 115.0°, 118.1° (Barclay and Kennard, 1961)
127.8°, 115.7°, 116.4° (Hanic, F. et. al., 1964)
127.0°, 115.6°, 117.4° (Jose, P. et. al., 1964)

The atoms C_1, C_2, C_3 and O_2 are in plane with the maximum deviation of 0.011 Å. This is a striking difference from the structure of sodium 2-oxo butyrate (Tavale, S. S. et. al., 1963)[39] where the ~~xx~~ planarity has been distorted presumably due to enolization of the compound in the crystalline state. The observed C_2-O_2 distance of 1.182 ± 0.011 Å may be significantly shorter than the usual C = O distance of 1.23 ± 0.01 Å (International Tables for Crystallography, Vol. III, 1962). Similar short bond has been observed in tri-ketoindane (Bolton, W., 1964)[40], anhydrous barbituric acid (Bolton, W., 1963)[41] and tetra chlorobenzoquinone (Chu. S. C., et. al., 1963)[42] where the values for C = O have been reported as 1.187° Å, 1.189 Å and 1.191 Å respectively.

(iii) Crystal structure:

The projections of the crystal down the c and b axes are shown in figs. 9 and 10 respectively. There are six short bonds between Na (x, y, z) and the neighbouring oxygens. These distances are

Na - O1 (x, y, z)	2.406 Å
Na - O_1 (x, $\bar{y}$, z-½)	2.462
Na - O_1 (½-x, ½-y, z-½)	2.370
Na - O_2 (x, y, z)	2.526
Na - O_3 (x, 1-y, z-½)	2.642
Na - O_3 (x, y, z-1)	2.340

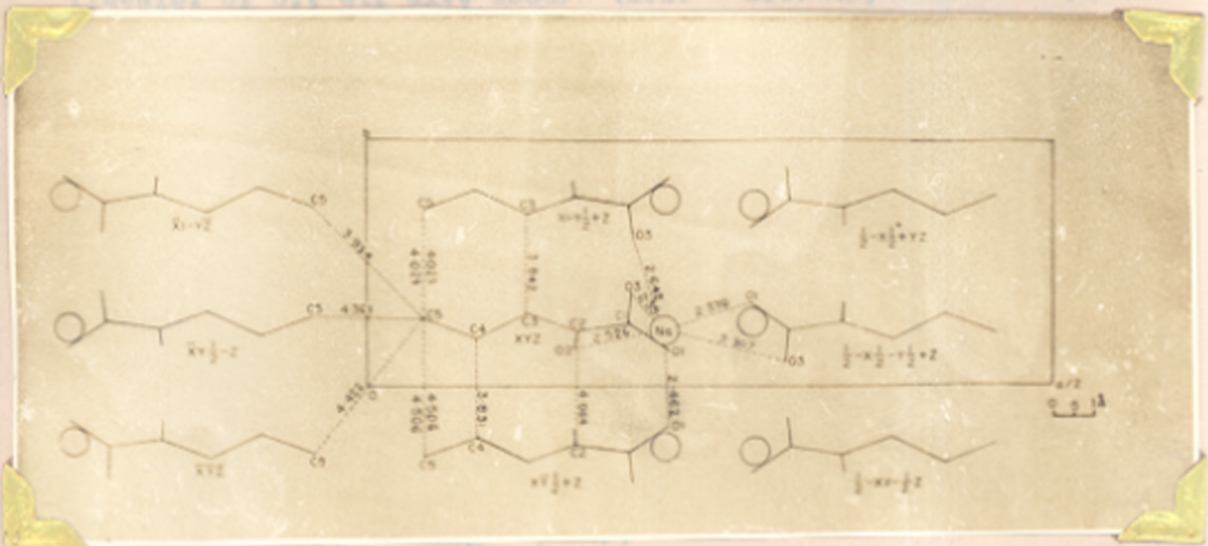


FIGURE 9: STRUCTURE PROJECTED ON (001)

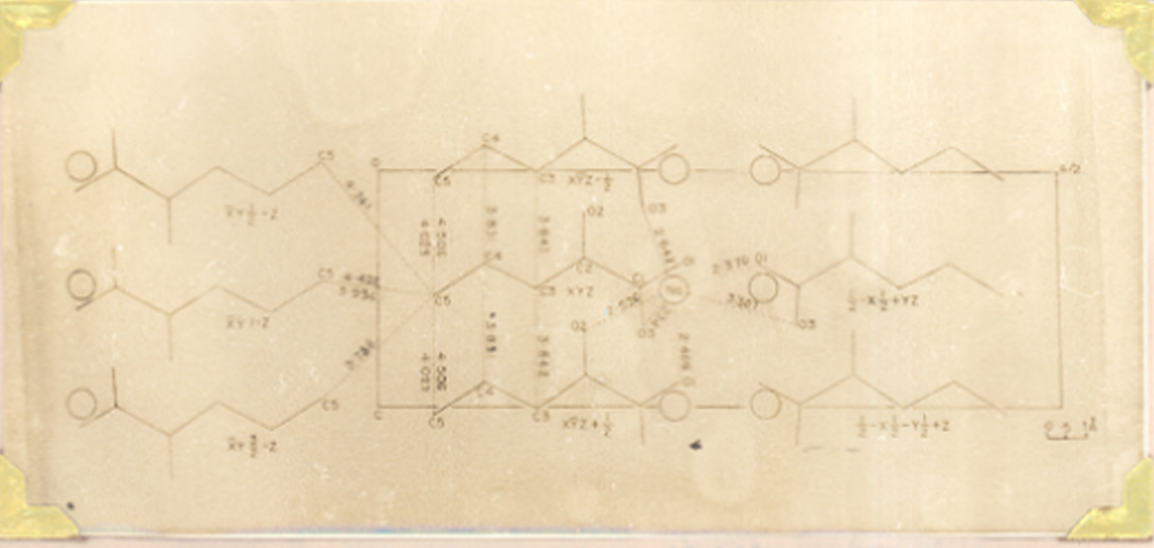


FIGURE 10: STRUCTURE PROJECTED ON (010)

These Na-O distances compare with sodium 2-oxo caprylate (Tavale, S. S., et. al., 1964)[42] (2.37 - 2.67 Å), sodium tropolonate (Sasada and Nitta, 1956;[44] Shiono, 1961)[45] (2.37-2.61 Å) and those given in International tables for crystallography (1960) (2.22 - 2.78 Å). Other significant distances are as follows:

$C_5\ (x, y, z) - C_5\ (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.506 Å
$C_5\ (x, y, z) - C_5\ (x, y, \frac{1}{2}-z)$	4.369
$C_5\ (x, y, z) - C_5\ (x, y, \frac{3}{2}-z)$	3.786
$C_5\ (x, y, z) - C_5\ (\bar{x}, \bar{y}, 1-z)$	4.422
$C_5\ (x, y, z) - C_5\ (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.029
$C_5\ (x, y, z) - C_5\ (\bar{x}, 1-y, 1-z)$	3.934
$C_1\ (x, y, z) - C_1\ (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.329
$C_2\ (x, y, z) - C_2\ (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.064
$C_2\ (x, y, z) - C_2\ (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.467
$C_3\ (x, y, z) - C_3\ (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.722
$C_3\ (x, y, z) - C_3\ (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	3.842
$C_4\ (x, y, z) - C_4\ (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	3.891
$C_4\ (x, y, z) - C_4\ (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2})$	4.663

The short Na - Na contact distances are

Na (x, y, z) - Na $(\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.733 Å
Na (x, y, z) - Na $(\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2})$	3.733
Na (x, y, z) - Na $(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3.830
Na (x, y, z) - Na $(\frac{1}{2}-x, y-\frac{1}{2}, z)$	3.830

The strong Na-O bonds tie the molecules into infinite layers parallel to (100) planes. Any one layer of molecules is linked with the neighbouring layers tightly on one side by Na-O bonds and loosely on other by van der Waals bonds. Similar arrangement has been observed in sodium 2-oxo caprylate (Tavale, Pant and Biswas, 1964)[46], potassium caprate (Vand, Lomer and Lang, 1949)[47] and potassium caproate (Lomer, 1952)[48].

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PART-II: CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM 2-OXO CAPROATE

CHAPTER - IV

CRYSTAL DATA AND EXPERIMENTAL DETAILS

(A) Sodium 2-oxo caproate ($C_6H_9O_3Na$) prepared as sodium 2-oxo valerate is considerably soluble in water. The crystals were grown from water-isopropyl alcohol as very thin flakes perpendicular to a-axis. The preliminary X-ray work placed it in orthorhombic system.

After accurately setting the crystal, rotation photographs about 'b' and 'c' axes were taken respectively and axial lengths 'b' and 'c' were derived from these photographs; while 'a' was determined from high angle reflexions in zero layer Weissenberg photograph. Thickness of the black wrapper was taken into consideration while determining the unit cell dimensions which are as follow;

$a = 39.46$ Å $b = 6.11$ Å $c = 5.94$ Å

The calculated and observed density values are 1.43 and 1.42 gm cm^{-3} respectively. The number of molecules per unit cell is deduced as Z = 8. The coefficient of linear absorption calculated for Cu$K\alpha$ radiation is 16.0 cm^{-1}.

(B) **Collection of data and determination of space group:**

The crystal used for intensity data was roughly of 1.5 x 0.7 mm^2 area. Equi-inclination Weissenberg photographs were taken from zero to fourth layer with 'c' as oscillation axis employing multiple film technique, while only zero layer was taken along 'b' axis. All data were collected with Cu$K\alpha$ radiations. It is seen from zero and higher layers photograph that reflexions with $h+k+l$ = even and $k+l$ = even are sharp while those with $h+k+l$ = even and $k+l$ = odd are diffuse suggesting that the type of disorder in these crystals may be of different nature from that observed in case of sodium 2-oxo valerate. The systematic presences are as follow:

h k l	h+k+l = 2n
h k o	h+k = 2n
h o l	h = 2n, l = 2n
o k l	k = 2n, l = 2n

The conditions limiting to these possible reflemions correspond to space groups Ibam or Iba2, the later being non-centro, symmetric.

(C) Estimation of intensities and data processing:

The intensity values of all the reflexions except diffuse were estimated visually using the intensity scale prepared from the same crystal. These intensities were corrected for Lp factor and spot extension effect in the way as has been described in Part I, (chapter 1). The correction for absorption was neglected. An arbitrary scale factor of 25 was applied in the beginning and temperature factor 2.5 $Å^2$ was used to start with. McWeeny's (1951) values of atomic scattering factors were used for C and O; and for Na^+ those of James and Brindley's (1931) were ~~was~~ used.

CHAPTER - VI

TRIAL STRUCTURE AND ITS REFINEMENT

(i) Comparing the unit cell dimensions of sodium 2-oxo caproate with those of sodium 2-oxo valerate, it is found that there is an increase of approximate 5 Å in the axial length of 'a' while 'b' and 'c' remain ~~comparable~~ equal within experimental errors. Assuming the usual bond lengths and angles this is the expected increase in axis a. It suggested that the packing of molecules in the crystalline state is similar except that the symmetry relations between the neighbouring layers are different in the two cases, giving rise to different limiting reflexions in the case of sodium 2-oxo caproate. It was, therefore, not difficult to postulate a suitable trial structure on the basis of above guiding lines. The following table 13 contains the trial parameters.

TABLE - 13

Atoms	X/a	Y/b	Z/c
Na	0.220	0.235	0.000
O1	0.224	0.154	0.392
O2	0.165	0.158	0.176
O3	0.201	0.373	0.652
C1	0.199	0.248	0.479
C2	0.165	0.233	0.362
C3	0.134	0.297	0.497
C4	0.100	0.213	0.379
C5	0.067	0.299	0.520
C6	0.036	0.220	0.370

It may be recalled that up to this stage space group was undecided, however, first calculations were made with these trial parameters considering the space group to be Ibam, a centro-symmetric space group. Structure factors were calculated for h0l projection, but there were certain serious discrepancies. Before ruling out the space group Ibam in preference to Iba2 on the basis of this disappointing agreement, a consideration to the validity of fair trial structure had to be given. Since the structure is isotypic with that of sodium 2-oxo valerate, it was thought that the trial structure may not be very unreasonable. Therefore, in expectation for the better agreement, space group Iba2 was considered. Though there were still minor discrepancies, neverthless, the comparison was quite encouraging and followed the required trend i.e. large calculated structure factor for large observed structure factor while small for small observed values. Therefore space group Iba2 was chosen for further refinement of the parameters.

(ii) Structure factor expressions are as follow for Iba2 space group:

$$A = 8 \mathrm{Cos}^2 2\pi((h+k+l)/4) \mathrm{Cos}\, 2\pi(hx+l/4) \mathrm{Cos}\, 2\pi(ky-l/4) \mathrm{Cos}\, 2\pi lz$$

$$B = 8 \mathrm{Cos}^2 2\pi((h+k+l)/4) \mathrm{Cos}\, 2\pi(hx+l/4) \mathrm{Cos}\, 2\pi(ky-l/4) \mathrm{Sin}\, 2\pi lz$$

and $\mathrm{Tan}\, \alpha = B/A$

The corresponding expressions for respective projections were deduced for the calculation of structure factors.

(iii) Refinement of (001) projection:

With the trial parameters, the reliability factor 'R' (defined earlier, Part I, Chapter 2) came out $\simeq 0.226$ after scaling of Fo values comparing them with Fc values. It was noted that axial reflexions (h00) were agreeing satisfactorily, therefore, y-parameters were only refined with "Least squares" method. The new y-parameters were used with x-parameters to compute structure factors. This dropped R-factor to 0.191. Then both x and y-parameters were refined with another cycle of least squares which brought down R to 0.137. Another cycle of least squares was performed for the refinement of only x-parameters reducing R to 0.103 after scaling. Further refinement of this projection was not attempted.

(iv) Refinement of (010) projection:

A program was written to refine h0l projection on CDC-3600 computer. In the first 5 "Least squares" cycles only z-parameters were shifted for optimum agreement of Fo and Fc values, and later on in further 5 cycles both x and z parameters were refined. All the calculated shifts were damped by multiplying them with partial shift factor of 0.70 except individual isotropic temperature factors which were kept constant as shown in table 14 for smooth refinement. This projection was thus refined to $\simeq$0.15. The final x and z parameters obtained from this projection and y-parameters from hk0 projection are listed below in table 14. It may be mentioned that x-parameters obtained from this projection were more trustable, obviously, because of absence of any diffuse reflexion in it according to the conditions of diffuse reflexionsalready given.

TABLE - 14

Atoms	X/a	Y/b	Z/c	B in Å^2
Na	0.2217	0.2220	0.0048	2.5
01	0.2231	0.1400	0.3702	2.5
02	0.1630	0.1480	0.1916	3.0
03	0.2038	0.3900	0.6573	3.0
C1	0.2033	0.2420	0.4721	3.0
C2	0.1654	0.2200	0.3623	3.0
C3	0.1341	0.2920	0.4665	3.0
C4	0.1025	0.2150	0.3595	3.0
C5	0.0687	0.2960	0.5186	3.0
C6	0.0355	0.2190	0.3881	3.5

(v) Three dimensional refinement:

For three dimensional refinement all the observed reflexions except diffuse were included along with unobserved reflexions at their minimum observable value. The scaling was done layer-wise by comparing them with their calculated structure factor values. The formulae used for the calculation of structure factors are already given. The parameters used to start with are given in table 14, which gave $R \simeq 0.20$.

All the four parameters (x_j, y_j, z_j and B_j) were refined simultaneously by the method of "Least squares" in the computer. All atomic shifts were multiplied by 0.70 and individual isotropic temperature factor by 0.20 for smoothness of refinement. R-factor dropped to $\simeq$ 0.15 in about eleven cycles. At this stage again scaling was done layerwise. Further refinement brought down R-factor to 0.1134, thereafter R remained unimpaired. The final atomic and thermal parameters are listed in table 15.

TABLE - 15

Atoms	X/a	Y/b	Z/c	B in Å^2
Na	0.2215	0.2205	-0.0060	3.17
O1	0.2230	0.1560	0.3830	2.22
O2	0.1639	0.1588	0.1682	3.64
O3	0.2014	0.3784	0.6521	2.62
C1	0.2017	0.2729	0.4856	2.48
C2	0.1653	0.2254	0.3511	3.19
C3	0.1344	0.3091	0.4906	3.63
C4	0.1022	0.2103	0.3721	3.99
C5	0.0708	0.3159	0.5202	4.65
C6	0.0375	0.1965	0.4088	4.96

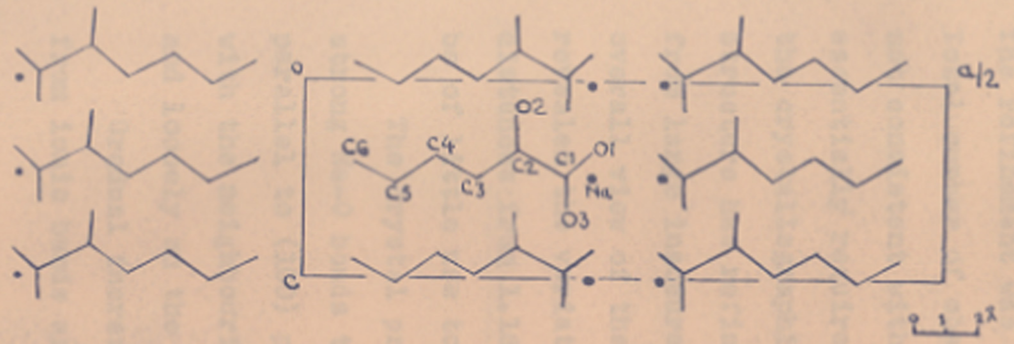

Fig. 11 STRUCTURE PROJECTED ON (O10).

CHAPTER - VII

RESULTS AND DISCUSSION

As already pointed out that the structure is disordered. The refinement was carried out using only sharp reflexions. Total number of observed reflexions are only 155 , certainly not consistent with the "Least squares" motivation which essentially requires large number of observations compared to the crystallographic variables to be refined. Though the structure has refined to R $\simeq$ 0.1134 still it seems to suffer from large inaccuracies, nevertheless, it gave satisfactory overall view of the crystal structure. Bond-lengths calculation revealed the variation of C-C bond from 1.55 to 1.65 Å and C-O distances from 1.16 to 1.26 Å. It was, therefore, thought to be of little use to calculate other close distances etc.

The crystal projected on (010) is shown (fig. 11). The strong Na-O bonds tie the molecules into infinite layers parallel to (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.

Gradual increase of thermal parameters of the atoms away from ionic bonds are also consistent as expected.

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PART-III: CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM 2-OXO HEPTYLATE

CHAPTER - VIII

CRYSTAL DATA AND EXPERIMENTAL DETAILS

(A) Sodium 2-oxo heptylate ($C_7H_{11}O_3Na$) prepared as usual was crystallised from water-butanol mixture which grew perpendicular to a-axis as thin flakes. The preliminary X-ray data showed it to belong to the orthorhombic system.

A suitable crystal was accurately set by double oscillation method. Axial lengths a, b and c were determined from high angle reflexions in zero layer Weissenberg photographs. Due allowance for the thickness of wrapper was made. The values are

$a = 44.18$ Å $\qquad b = 6.08$ Å $\qquad c = 5.91$ Å

The calculated and observed density values are 1.39 and 1.37 gm cm $^{-3}$ respectively. The number of molecules per unit cell is deduced as $Z = 8$. The coefficient of linear absorption for CuK_{α} radiations is 14.6 cm^{-1}.

(B) Data collection and space group determination :

Equi-inclination Weissenberg photographs were taken from zero to fourth layers with 'c' as oscillation axis using multiple film technique, with the crystal of roughly 2.0 x 0.4 mm^2 area. For collecting h0l photograph, crystal of 1.0 x 0.6 mm^2 area was used. Nearly thirty per cent of the theoretically possible reflexions were recorded. Reflexions with h+k+l = odd were found to be diffuse while h+k+l = even were sharp as in case of sodium 2-oxo valerate exhibiting similar type of disorder. The systematic presences are

h k l no condition; h k 0 for h+k = even

h 0 l for l = even; h 0 0 for h= even
0 k 0 for k = even; 0 0 l for l = even

so that the space group is uniquely determined as Pbcn.

(C) Data processing:

The intensities of all the reflexions were measured visually using the relative intensity scale prepared from the same crystal. In higher layer photographs, intensities were measured from extended spots. All the visually estimated intensities were corrected for usual Lp and spot extension effects.

To determine preliminary B-factor and also to place the corrected intensities on absolute scale, Wilson's method was made use of. The method is explained in Part I (chapter I). The necessary data to determine B and K factors are given in table 16, and the plot of ~~kmgs~~ $\log_e C$ versus $(\sin \theta/\lambda)^2$ for hko projection is shown in fig. 12. The corresponding B and K values are 3.6 Å^2 and 21 respectively. The same values were used for h0l projection to start with.

TABLE -16

$\sin \theta$	$(\sin \theta/\lambda)^2$	$\langle I \rangle$	$\sum f_n^2$	$C = \sum f_n^2/\langle I \rangle$	$\log_e C$
0.2 - 0.3	0.0263	5.097	2686	526.98	6.2672
0.3 - 0.4	0.0515	2.269	1738	765.98	6.6412
0.4 - 0.5	0.0851	2.403	1772	487.72	6.1897
0.5 - 0.6	0.1271	0.545	805	1477.06	7.2979
0.6 - 0.7	0.1779	0.562	562	1000.00	6.9078

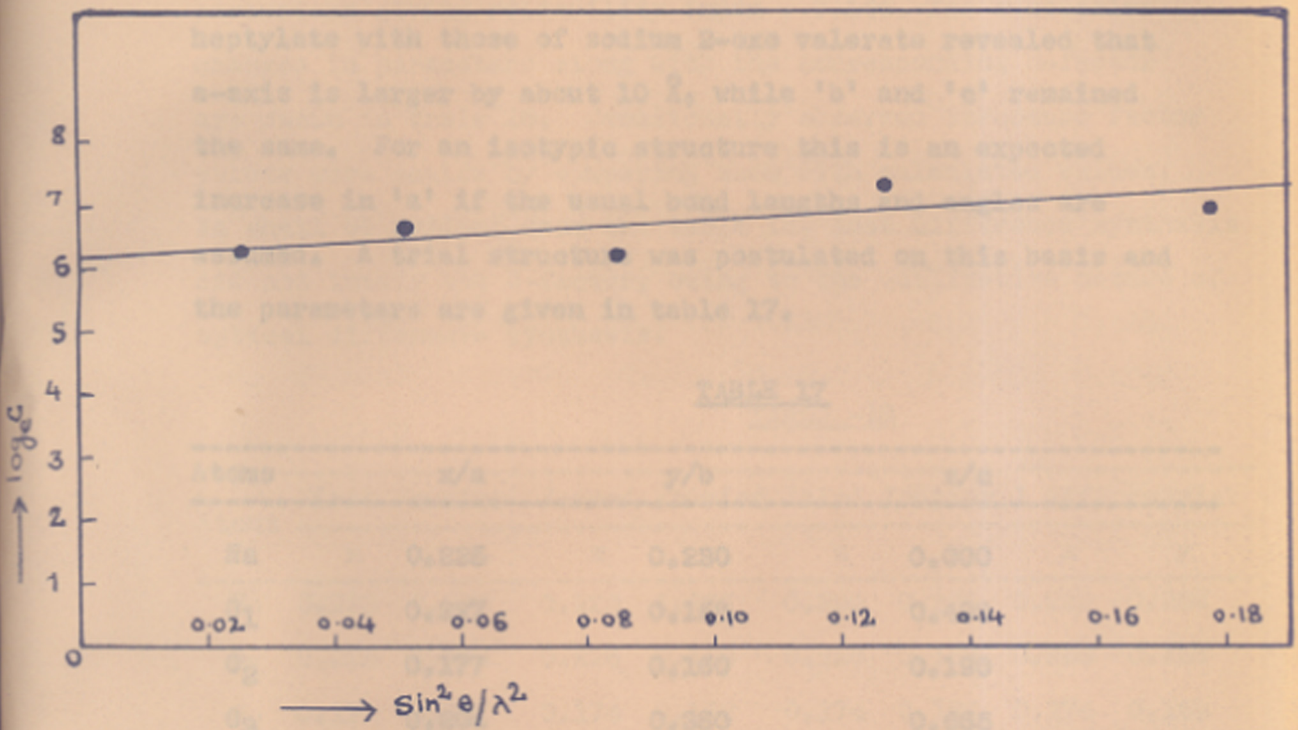

FIG. 12 DETERMINATION OF PRELIMINARY SCALE & TEMPERATURE FACTOR BY WILSON'S METHOD

CHAPTER - IX

TRIAL STRUCTURE AND REFINEMENT

(i) Comparison of unit cell dimensions of sodium 2-oxo heptylate with those of sodium 2-oxo valerate revealed that a-axis is larger by about 10 Å, while 'b' and 'c' remained the same. For an isotypic structure this is an expected increase in 'a' if the usual bond lengths and angles are assumed. A trial structure was postulated on this basis and the parameters are given in table 17.

TABLE 17

Atoms	x/a	y/b	z/c
Na	0.225	0.230	0.000
O_1	0.227	0.158	0.400
O_2	0.177	0.160	0.190
O_3	0.204	0.380	0.665
C_1	0.202	0.240	0.490
C_2	0.175	0.260	0.380
C_3	0.147	0.280	0.520
C_4	0.120	0.210	0.400
C_5	0.094	0.290	0.520
C_6	0.057	0.220	0.410
C_7	0.032	0.280	0.530

(ii) Refinement of (001) projection:

Structure factor and electron density expressions are already given in Part I (chapter 2). The trial parameters x and y were refind successively by Fourier syntheses (thrice taken on Eller's photosommateur) and difference Fourier syntheses (twice taken on Eller's photosommateur) which finally gave parameters giving reliability index $\simeq 0.166$. The successive changes in parameters along with the corresponding R-factor are shown in table 18. Occasionally observed structure factor values were scaled by comparing them with calculated values. As shall be evident from the table 18, last difference synthesis did not impair the R-factor, owing to the qualitative nature of optical difference synthesis.

TABLE -18

Atoms	First Fourier		Second Fourier		Third Fourier		I dif. Fourier	
	x	y	x	y	x	y	x	y
Na	0.223	0.236	0.225	0.236	0.225	0.236	0.225	0.236
O_1	0.225	0.158	0.226	0.158	0.226	0.158	0.226	0.158
O_2	0.173	0.167	0.174	0.162	0.174	0.162	0.174	0.162
O_3	0.203	0.372	0.204	0.360	0.207	0.362	0.207	0.362
C_1	0.201	0.247	0.203	0.240	0.203	0.240	0.203	0.240
C_2	0.172	0.223	0.173	0.240	0.173	0.240	0.173	0.240 ∠[illegible]
C_3	0.146	0.309	0.149	0.300	0.146	0.299	0.145	0.297
C_4	0.116	0.232	0.116	0.225	0.117	0.218	0.117	0.218
C_5	0.089	0.292	0.087	0.294	0.093	0.292	0.091	0.292
C_6	0.059	0.201	0.062	0.195	0.060	0.200	0.060	0.203
C_7	0.033	0.284	0.033	0.280	0.032	0.275	0.032	0.272
	$R \simeq 0.29$		$R \simeq 0.24$		$R \simeq 0.22$ after scaling $\simeq 0.18$		$R \simeq 0.166$	

TABLE - 18 (continued)

Atoms	II dif. Fourier		I Least squares		II Least squares	
	x	y	x	y	x	y
Na	0.2250	0.2360	0.2250	0.2340	0.2254	0.2360
O_1	0.2260	0.1580	0.2260	0.1540	0.2259	0.1540
O_2	0.1740	0.1620	0.1730	0.1590	0.1734	0.1590
O_3	0.2070	0.3620	0.2070	0.3600	0.2064	0.3570
C_1	0.2030	0.2400	0.2040	0.2380	0.2041	0.2390
C_2	0.1730	0.2400	0.1720	0.2360	0.1727	0.2330
C_3	0.1460	0.2990	0.1450	0.2920	0.1455	0.2940
C_4	0.1170	0.2180	0.1180	0.2190	0.1182	0.2150
C_5	0.0910	0.2920	0.0890	0.2940	0.0891	0.2980
C_6	0.0610	0.2060	0.0600	0.2060	0.0596	0.2000
C_7	0.0300	0.2690	0.0330	0.2760	0.0338	0.2760
	$R \cong 0.167$		$R \cong 0.164$ after scaling etc., $R \cong 0.132$		$R \cong 0.178$	

After second difference synthesis, further refinement was done by "Least squares". First least squares refinement improved agreement insignificantly. Second least squares rather spoiled the R-factor to 0.178.

At this stage 'B' factor was tried to correct with Fo and Fc values by Wilson's method. The principle of the method is discussed in Part I (chapter 2). The necessary data are given in table 19 and graph plotted of $\log_e C$ (where $C = \sum|Fc| / \sum|Fo|$) versus $(\sin \theta/\lambda)^2$ (fig. 13 b) gave revised B factor as 2.5 $Å^2$.

The calculation of structure factor values using the parameters obtained after first least squares and revised temperature factor 2.5 Å^2 dropped R-factor to 0.132. Further refinement of this projection was stopped here.

(iii) Refinement of (010) projection:

The final x parameters obtained from hk0 projection were used with trial z-parameters. z-parameters were refined by four Fourier syntheses (taken on Eller's photosommateur) which dropped R-factor from 0.286 to 0.252. Further refinement was done by two difference syntheses, which finally gave R-factor 0.221 after scaling. At this stage, temperature factor was revised by Wilson's method and new B-factor 2.5 Å^2 was used thereafter. The data used and plot of graph is shown in table 20, and fig. 13a respectively. First least squares gave R-factor 0.171. Second cycle of refinement of z-parameters dropped R to 0.156, which on rescaling came down to 0.132. Further refinement was stopped here. The table 21 shows the z-parameters during the stages of refinement.

TABLE - 19

Sin θ	$(\sin\theta/\lambda)^2$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert F_o\rvert$	$C = \Sigma\lvert F_o\rvert / \Sigma\lvert F_c\rvert$	$\log_e C$
0.2 - 0.3	0.026	402	385	0.9577	- 0.0433
0.3 - 0.4	0.052	577	531	0.9203	- 0.0831
0.4 - 0.5	0.085	479	505	1.0543	0.0529
0.5 - 0.6	0.127	248	286	1.1532	0.1400
0.6 - 0.7	0.178	298	333	1.1174	0.1109
0.7 - 0.8	0.236	184	240	1.3043	0.2656

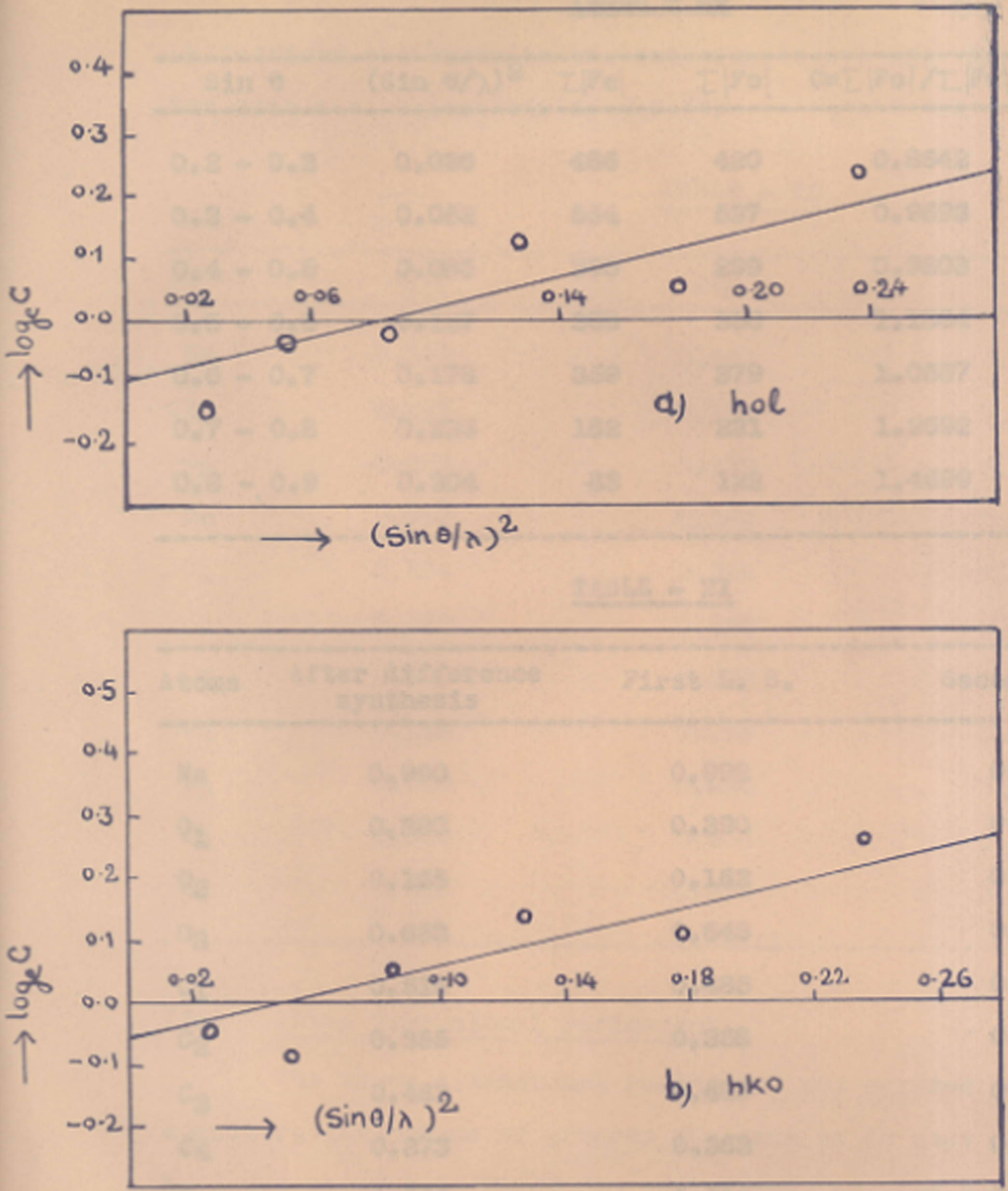

FIG. 13 DETERMINATION OF CORRECT TEMPERATURE FACTOR 'B' AND SCALE FACTOR 'K' FROM FO'S AND FC'S VALUES

TABLE - 20

Sin θ	$(\text{Sin }\theta/\lambda)^2$	$\Sigma\|Fc\|$	$\Sigma\|Fo\|$	$C=\Sigma\|Fo\|/\Sigma\|Fc\|$	$\log_e C$
0.2 - 0.3	0.026	486	420	0.8642	-0.1460
0.3 - 0.4	0.052	554	537	0.9693	-0.0312
0.4 - 0.5	0.085	305	299	0.9803	-0.0199
0.5 - 0.6	0.127	308	350	1.1364	0.1274
0.6 - 0.7	0.178	359	379	1.0557	0.0545
0.7 - 0.8	0.236	182	231	1.2692	0.2383
0.8 - 0.9	0.304	83	122	1.4699	0.3853

TABLE - 21

Atoms	After difference synthesis	First L. S.	Second L. S.
Na	0.990	0.992	0.9915
O_1	0.390	0.390	0.3900
O_2	0.165	0.163	0.1610
O_3	0.653	0.648	0.6425
C_1	0.515	0.485	0.4780
C_2	0.355	0.358	0.3470
C_3	0.483	0.489	0.4900
C_4	0.373	0.363	0.3675
C_5	0.505	0.518	0.5145
C_6	0.405	0.410	0.4000
C_7	0.505	0.522	0.5270

The final atomic parameters obtained from hk0 and h0l projections are listedin the following table 22. The B-factor for both the projections is 2.5 Å^2.

TABLE - 22

Atoms	x/a	y/b	z/c
Na	0.225	0.234	0.992
O1	0.226	0.154	0.390
O_2	0.173	0.159	0.163
O_3	0.207	0.360	0.648
C_1	0.204	0.238	0.485
C_2	0.172	0.236	0.358
C_3	0.145	0.292	0.489
C_4	0.118	0.219	0.363
C_5	0.089	0.294	0.518
C_6	0.060	0.206	0.410
C_7	0.033	0.276	0.522

(iv) Three dimensional refinement:

The three dimensional refinement was carried out in computer, the scheme of program was same as in case of sodium ~~tm~~ 2-oxo valerate. First few cycles were carried out including only sharp and diffuse reflexions. Later on all unobserved reflexions at its $I_{min.}/3$ were also included. Scaling was frequently applied layerwise to sharp and diffuse reflexions separately. The final parameters are given in table 23, along with their estimated standard deviations. The final R-factor for all observed as well as unobserved reflexions ~~was~~ is 0.1890, while for observed reflexions only it is 0.1134.

TABLE - 23

Atoms	x/a	y/b	z/c	B in Å^2
Na	0.2244 ± 0.0001	0.2357 ± 0.0008	-0.0140 ± 0.0008	2.39
O_1	0.2265 ± 0.0002	0.1523 ± 0.0011	0.3796 ± 0.0011	2.21
O_2	0.1732 ± 0.0002	0.1571 ± 0.0011	0.1633 ± 0.0011	2.59
O_3	0.2062 ± 0.0002	0.3803 ± 0.0011	0.6372 ± 0.0011	2.24
C_1	0.2046 ± 0.0002	0.2542 ± 0.0015	0.4670 ± 0.0015	2.01
C_2	0.1737 ± 0.0002	0.2345 ± 0.0015	0.3475 ± 0.0015	3.39
C_3	0.1469 ± 0.0002	0.3018 ± 0.0015	0.4823 ± 0.0015	2.72
C_4	0.1179 ± 0.0002	0.2132 ± 0.0015	0.3646 ± 0.0015	2.79
C_5	0.0894 ± 0.0002	0.2972 ± 0.0015	0.5012 ± 0.0015	3.12
C_6	0.0600 ± 0.0002	0.1975 ± 0.0015	0.3982 ± 0.0015	3.39
C_7	0.0318 ± 0.0002	0.2762 ± 0.0015	0.5377 ± 0.0015	5.41

It may be mentioned that after three dimensional refinement excluding unobserved reflexions, an attempt was made to locate hydrogen positions with difference Fourier synthesis (taken on Eller's photosommateur) fig. 14. The peaks at the expected hydrogen positions are clearly seen. To confirm it, difference Fourier was computed, however, at no place positive electron density of more than 0.5 $e/\text{Å}^2$ was observed. Because of this uncertainty in their positions, they were not included in the refinement.

(v) Standard deviations:

The standard deviations (σ) of atomic coordinates, bond lengths and angles were estimated in the way as has been described in Part I (chapter 2), assuming K=0.1890 and p=6.0 Å^{-2}. The deviations in the coordinates are listed in table 23 along with th

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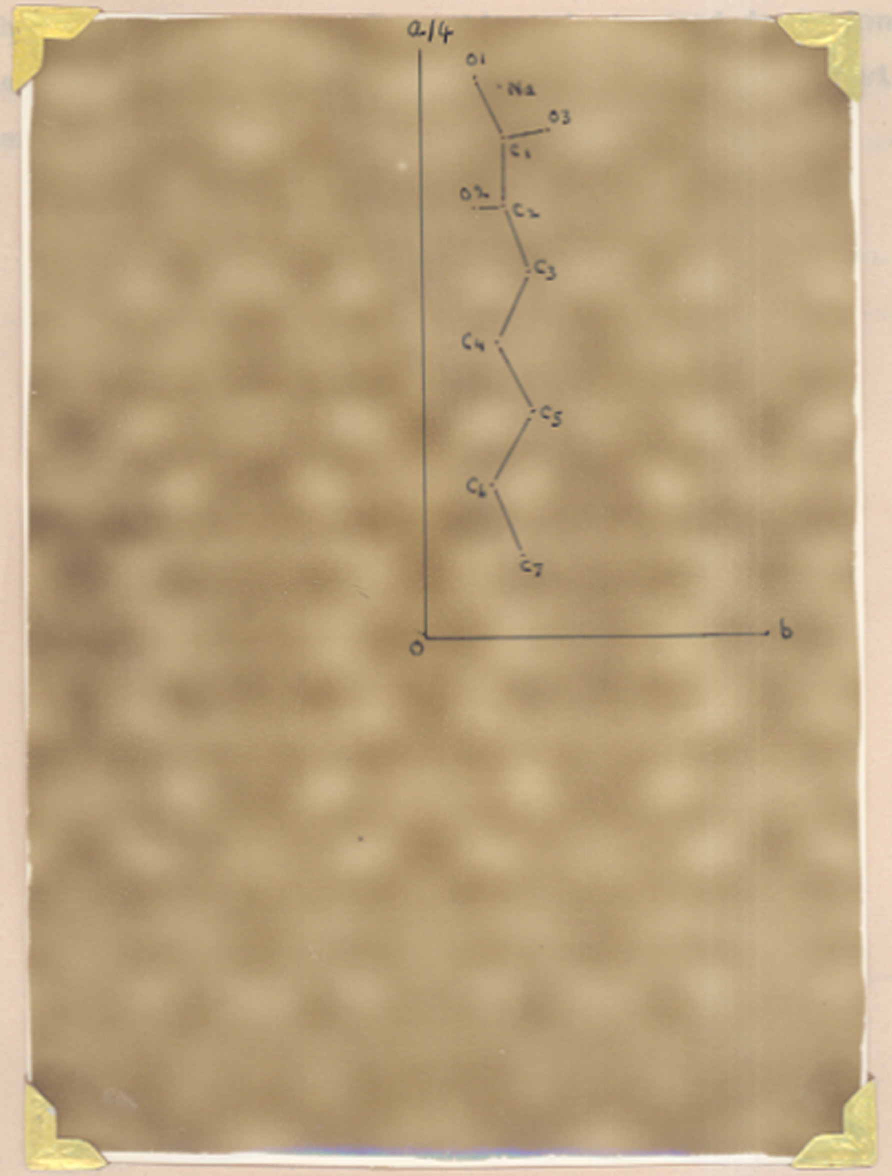

FIGURE 14: (001) DIFFERENCE FOURIER PROJECTION

lengths and angles were estimated in the way as has been described in Part I (chapter 2), assuming $K=0.1890$ and $p=5.0$ Å^{-2}. The deviations in the coordinates are listed in table 23 along with the final parameters. The estimated standard deviations in bond-lengths and bond-angles are listed in table 25 along with bond lengths and angles.

CHAPTER - X

RESULTS AND DISCUSSION

(i) The final atomic coordinates in Å listed below in table 25 were used for the calculation of intermolecular and intramolecular distances and angles. The bond lengths and angles calculated in 2-oxo heptylate group are shown in fig. 15 and listed in table 25.

TABLE - 24

Atoms	X	Y	Z
Na	9.9140	1.4331	-0.0827
O_1	10.0068	0.9260	2.2434
O_2	7.6520	0.9552	0.9652
O_3	9.1099	2.3122	3.7659
C_1	9.0392	1.5455	2.7600
C_2	7.6741	1.4258	2.0537
C_3	6.4900	1.8349	2.8507
C_4	5.1912	1.2963	2.1550
C_5	3.9502	1.8070	2.9621
C_6	2.6508	1.2008	2.3534
C_7	1.4049	1.6794	3.1778

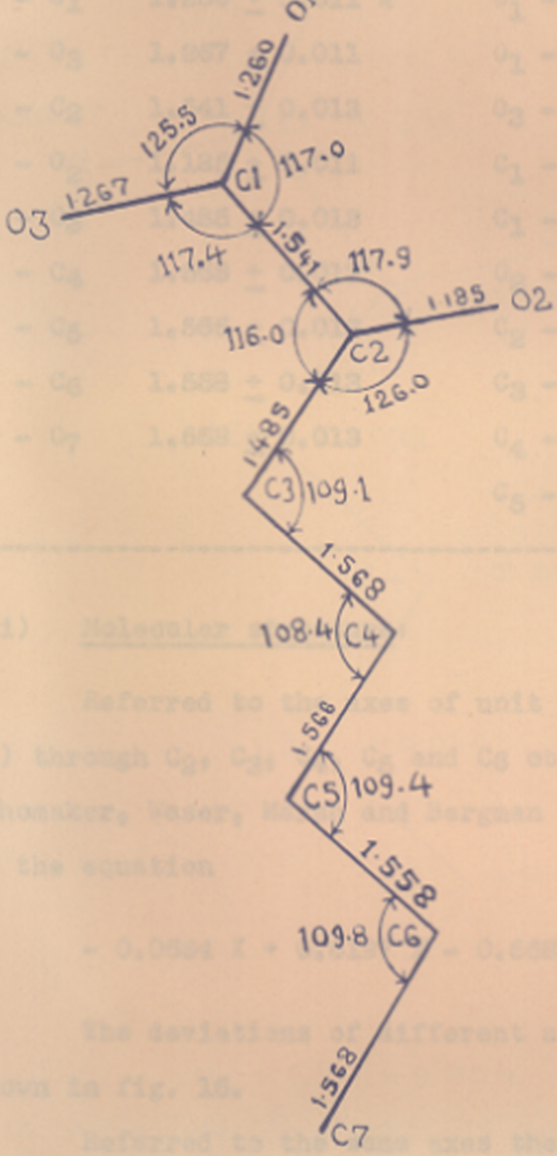

Fig. 15 BOND LENGTHS (Å) AND BOND ANGLES (°) IN α-KETO HEPTYLATE GROUP.

TABLE -25

Bond lengths		Bond angles	
$C_1 - O_1$	1.260 ± 0.011 Å	$O_1 - C_1 - O_3$	125.5 ± 0.8°
$C_1 - O_3$	1.267 ± 0.011	$O_1 - C_1 - C_2$	117.0 ± 0.8
$C_1 - C_2$	1.541 ± 0.013	$O_3 - C_1 - C_2$	117.4 ± 0.8
$C_2 - O_2$	1.185 ± 0.011	$C_1 - C_2 - O_2$	117.9 ± 0.8
$C_2 - C_3$	1.485 ± 0.013	$C_1 - C_2 - C_3$	116.0 ± 0.7
$C_3 - C_4$	1.568 ± 0.013	$O_2 - C_2 - C_3$	126.0 ± 0.8
$C_4 - C_5$	1.566 ± 0.013	$C_2 - C_3 - C_4$	109.1 ± 0.7
$C_5 - C_6$	1.558 ± 0.013	$C_3 - C_4 - C_5$	108.4 ± 0.7
$C_6 - C_7$	1.568 ± 0.013	$C_4 - C_5 - C_6$	109.4 ± 0.7
		$C_5 - C_6 - C_7$	109.8 ± 0.7

(ii) Molecular structure:

Referred to the axes of unit cell, the least square plane (1) through C_2, C_3, C_4, C_5 and C_6 obtained by the method of schomaker, Waser, Marsh and Bergman (1959)[1] can be represented by the equation

$$- 0.0684\,X + 0.8197\,Y - 0.5687\,Z + 0.5224 = 0$$

The deviations of different atoms from this plane are shown in fig. 16.

Referred to the same axes the mean planes through different atoms have been calculated.

Plane (2) through O_1, O_3, C_1 and C_2

$$- 0.2151\,X - 0.7817\,Y + 0.5851\,Z + 1.5635 = 0$$

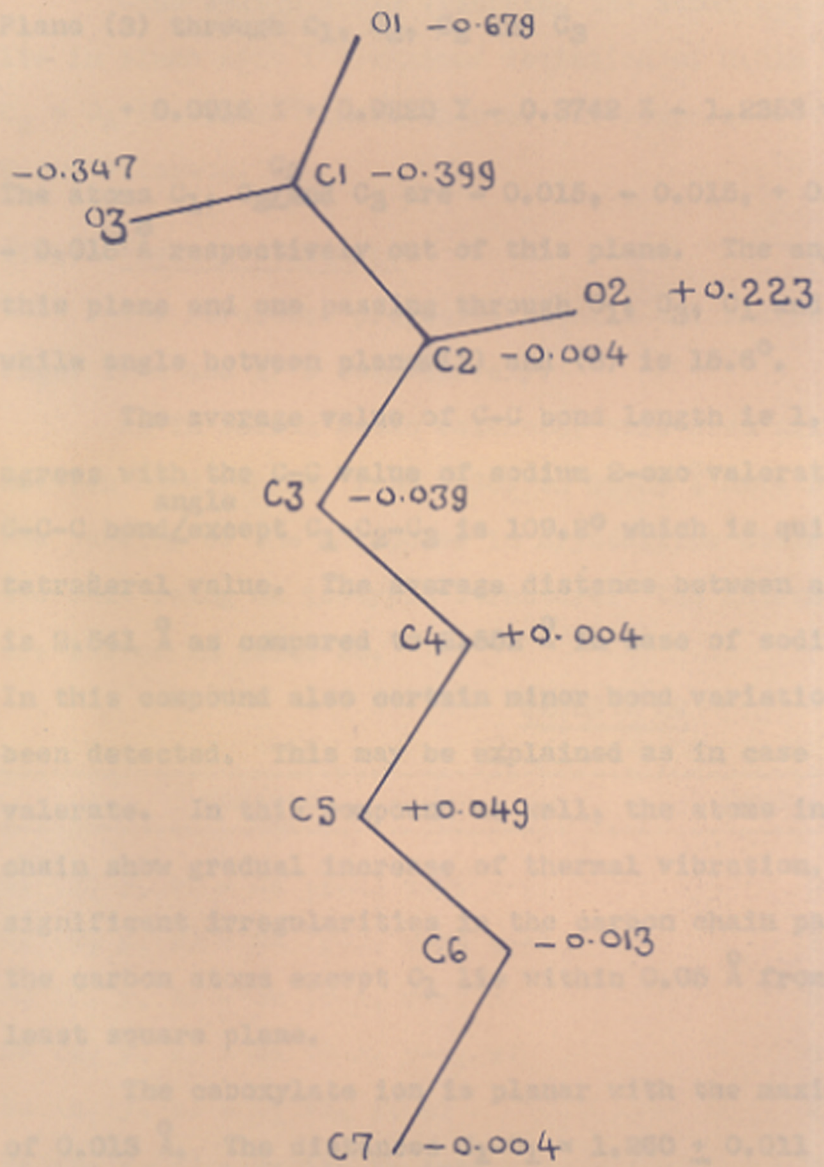

Fig. 16 DEVIATIONS (Å) OF ATOMS IN α-KETO HEPTYLATE GROUP FROM THE LEAST SQUARE PLANE THROUGH CARBONS-CHAIN (C_2 to C_7)

The normal distances of O_1, O_3, C_1 and C_2 from this plane are -0.013, -0.013, -0.013 and $+0.013$ Å respectively. This plane makes an angle of 16.5° with the least square plane (1)

Plane (3) through C_1, O_2, C_2 and C_3

$$+0.0915\ X + 0.9220\ Y - 0.3742\ Z - 1.2353 = 0$$

The atoms C_1, O_2 C_2 and C_3 are -0.015, -0.015, $+0.015$ and -0.015 Å respectively out of this plane. The angle between this plane and one passing through O_1, O_3, C_1 and C_2 is 16.3°, while angle between planes (1) and (3) is 15.6°.

The average value of C-C bond length is 1.547 Å which agrees with the C-C value of sodium 2-oxo valerate. The average C-C-C bond angle except C_1-C_2-C_3 is 109.2° which is quite close to tetraheral value. The average distance between alternate carbon is 2.541 Å as compared to 2.552 Å in case of sodium 2-oxo valerate. In this compound also certain minor bond variations in C-C have been detected. This may be explained as in case of sodium 2-oxo valerate. In this compound as well, the atoms in the end of chain show gradual increase of thermal vibration. There is no significant irregularities in the carbon chain packing. All the carbon atoms except C_1 lie within 0.05 Å from their best least square plane.

The caboxylate ion is planar with the maximum deviation of 0.013 Å. The distances C_1-O_1 = 1.260 ± 0.011 Å and C_1-O_3 = 1.267 ± 0.011 Å are equal as expected, and are comparable with those of sodium 2-oxo valerate. The angles O_1-C_1-O_3 = 125.5°; O_1-C_1-C_2 = 117.0° and O_3-C_1-C_2 = 117.4° are comparable with the values normally observed in carboxylate group.

125.5, 117.4, 117.1°	(Marsh, 1958)[2]
124.3, 117.4, 118.3°	(Freeman, Snow, Nitta and Tomita, 1964)[3]

Like sodium 2-oxo valerate, the atoms C_1, C_2, C_3 and O_2 lie in plane with the maximum deviation of 0.015 Å. The distance $C_2 = O_2$ is 1.185 Å again shorter but compares with that in sodium 2-oxo valerate.

(iii) Crystal structure:

The structure projected along c and b axes are shown in figs. 17-a and 17-b respectively.

As in sodium 2-oxo valerate, here also six short bonds between Na-O ranging from 2.359 to 2.626 Å have been found. The packing of the molecules in crystalline state is essentially the same being an isotypic structure. The intermolecular distances are listed in table 26.

TABLE - 26

Contact	Bond length in Å
Na (x, y, z) - Na $(\frac{1}{2}-x, \frac{1}{2}-y, z+\frac{1}{2})$	3.726
Na (x, y, z) - Na $(\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2})$	3.726
Na (x, y, z) - Na $(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3.790
Na (x, y, z) - Na $(\frac{1}{2}-x, y-\frac{1}{2}, z)$	3.790
Na (x, y, z) - O_1 (x, y, z)	2.382
Na (x, y, z) - O_1 $(x, \bar{y}, z-\frac{1}{2})$	2.443
Na (x, y, z) - O_1 $(\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2})$	2.359
Na (x, y, z) - O_2 (x, y, z)	2.539
Na (x, y, z) - O_3 $(x, 1-y, z-\frac{1}{2})$	2.626
Na (x, y, z) - O_3 $(x, y, z-1)$	2.381
C7 (x, y, z) - C_7 $(x, \bar{y}, \frac{1}{2}+z$ or $z-\frac{1}{2})$	4.473

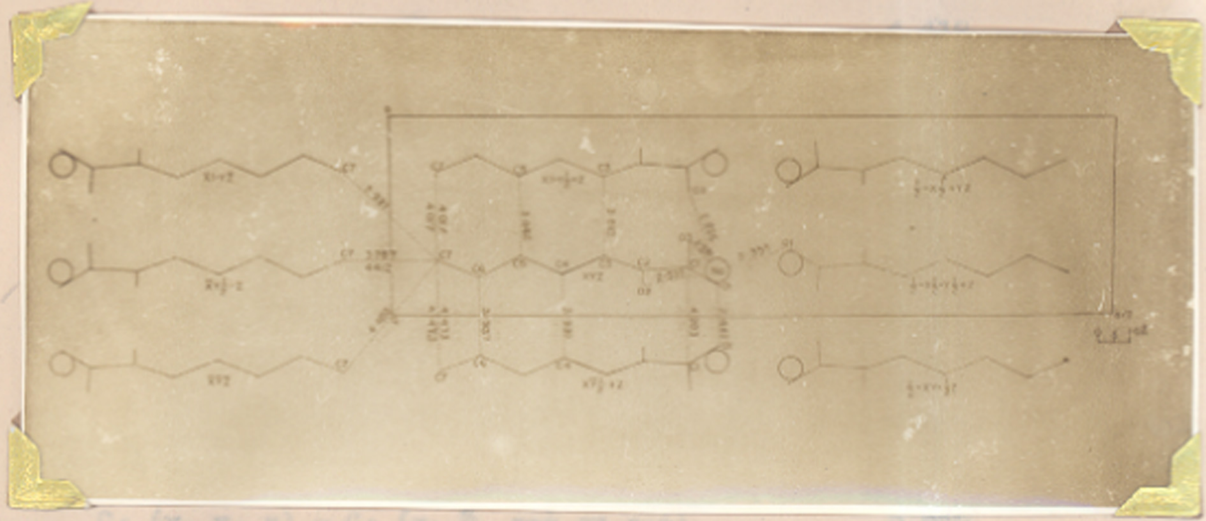

FIGURE 17-a: STRUCTURE PROJECTED ON (001).

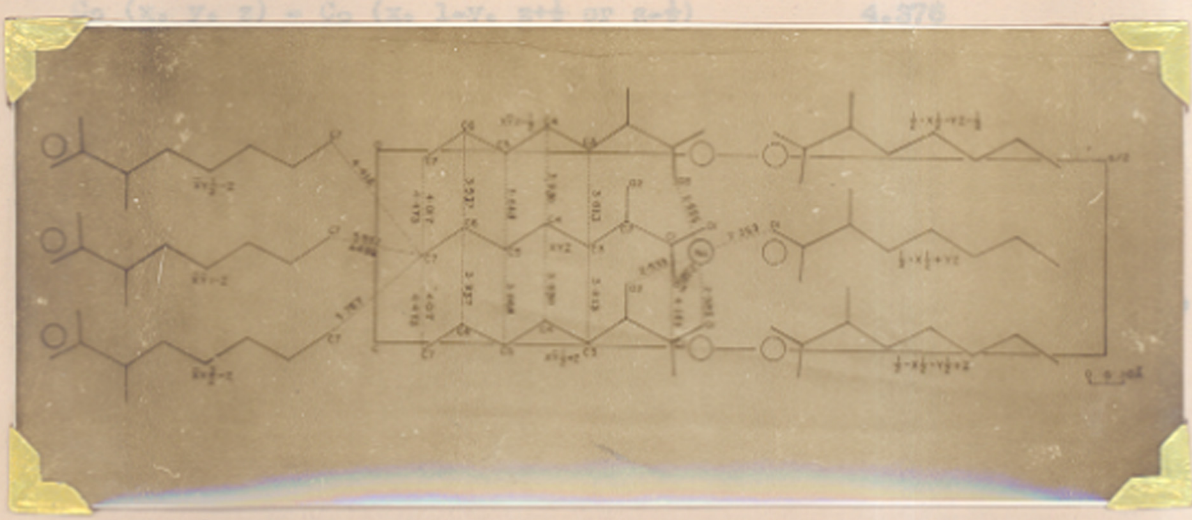

FIGURE 17-b: STRUCTURE PROJECTED ON (010).

TABLE - 26 (continued)

C_7 (x, y, z) - C_7 ($\bar{x}$, y, $\frac{1}{2}$-z)	4.412
C_7 (x, y, z) - C_7 ($\bar{x}$, y, $\frac{3}{2}$ - z)	3.767
C_7 (x, y, z) - C_7 ($\bar{x}$, $\bar{y}$, 1-z)	4.402
C_7 (x, y, z) - C_7 (x, 1-y, $\frac{1}{2}$ + z or z-$\frac{1}{2}$)	4.017
C_7 (x, y, z) - C_7 ($\bar{x}$, 1-y, 1-z)	3.937
C_6 (x, y, z) - C_6 (x, $\bar{y}$, $\frac{1}{2}$+z or z-$\frac{1}{2}$)	3.937
C_6 (x, y, z) - C_6 (x, 1-y, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.718
C_5 (x, y, z) - C_5 (x, $\bar{y}$, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.668
C_5 (x, y, z) - C_5 (x, 1-y, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	3.848
C_4 (x, y, z) - C_4 (x, $\bar{y}$, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	3.930
C_4 (x, y, z) - C_4 (x, 1-y, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.671
C_3 (x, y, z) - C_3 (x, $\bar{y}$, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.712
C_3 (x, y, z) - C_3 (x, 1-y, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	3.813
C_2 (x, y, z) - C_2 (x, $\bar{y}$, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.106
C_2 (x, y, z) - C_2 (x, 1-y, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.376
C_1 (x, y, z) - C_1 (x, $\bar{y}$, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.276
C_1 (x, y, z) - C_1 (x, 1-y, z+$\frac{1}{2}$ or z-$\frac{1}{2}$)	4.203

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1. Schomaker, V., Waser, J., Marsh, R. E. and Bergman, G. (1959), Acta Cryst., 12, 600.

2. Marsh, R. E., (1958) Acta Cryst., 11, 654.

3. Freeman, H. C., Snow, M. R., Nitta, I. and Tomita, K. (1964), Acta Cryst., 17, 1463.

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PART-IV: CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM PYRUVATE

CHAPTER - XI

CRYSTAL DATA AND EXPERIMENTAL DETAILS

Sodium pyruvate ($C_3H_3O_3Na$) prepared as usual was crystallised from aqueous solution as thin plates. The preliminary X-ray data confirmed it to belong to the monoclinic system.

A suitable crystal was accurately set by double oscillation method. Zero layer Weissenberg photographs were taken (without inner wrapper) around 'b' and 'c' as oscillation axes respectively for the purpose of determining the unit cell dimensions which are as follows:

$a = 22.12$ Å (22.25 Å)
$b = 5.27$ Å (5.31 Å)
$c = 3.68$ Å (3.71 Å)
$= 98.2^\circ$ (98.2°)

The values in brackets are those reported by Tavale, Pant and Biswas (1961)[1].

Equi-inclination Weissenberg photographs were taken from zero to fourth layer with 'b' as oscillation axis using multiple film technique. The crystal used for collecting the data was roughly of 2.0×0.8 mm^2 area. It may be mentioned that there was no diffuse reflexion in the data of this compound and, therefore, do not suffer from any disorder.

From the systematic absences the space group $P\,2_1/a$ was confirmed.

The intensities of all the reflexions were estimated visually by the relative intensity scale prepared from the same crystal. Absorption correction was neglected.

The usual Lp and spot extension corrections were applied and scale factors were calculated for each layer as follows

$$K = \sum |Fc| / \sum |\sqrt{Ic}|$$

The structure factors were calculated using the final parameters reported by Tavale, et. al. (1961) which are listed in table 27. Isotropic temperature factor for each atom was taken as 2.1 Å to start with.

TABLE - 27

Atoms	x/a	y/b	z/c	B in $Å^2$
Na	0.1989	0.1802	0.1638	2.1
O_1	0.2035	0.4887	0.6491	2.1
O_2	0.1004	0.4100	0.1617	2.1
O_3	0.1707	0.8843	0.7144	2.1
C_1	0.1657	0.6608	0.5854	2.1
C_2	0.1024	0.5803	0.3685	2.1
C_3	0.0523	0.7722	0.3882	2.1

CHAPTER - XII

REFINEMENT

The reliability index for all the observed reflexions (622) was $\simeq$ 0.1748. The three dimensional refinement by least squares method was carried out in computer. In the first two cycles, each layer was scaled by comparing them with calculated structure factors as $K = \sum |Fc| / \sum |Fo|$. In the further three cycles only overall scaling was applied. R-factor had dropped to 0.1435 and then it remained steady. The final atomic and thermal parameters are listed in table 28.

TABLE - 28

Atoms	x/a	y/b	z/c	B in Å
Na	0.1993 ± 0.0002	0.1801 ± 0.0008	0.1658 ± 0.0012	2.13
O_1	0.2041 ± 0.0003	0.4882 ± 0.0011	0.6494 ± 0.0016	2.29
O_2	0.0993 ± 0.0003	0.4043 ± 0.0011	0.1706 ± 0.0016	2.48
O_3	0.1707 ± 0.0003	0.8833 ± 0.0011	0.7104 ± 0.0016	2.83
C_1	0.1653 ± 0.0004	0.6618 ± 0.0015	0.5920 ± 0.0022	1.36
C_2	0.1039 ± 0.0004	0.5888 ± 0.0015	0.3636 ± 0.0022	1.71
C_3	0.0509 ± 0.0004	0.7755 ± 0.0015	0.3753 ± 0.0022	2.70

Standard deviations:

The standard deviations (σ) of atomic coordinates, bond lengths and angles were calculated as described in Part I (chapter 2) assuming $K = 0.1435$ and $p = 5.0$ Å^{-2}. The e.s.d. in coordinates are listed in table 28 and those of bond lengths and angles in table 29 along with the final coordinates, bond lengths and angles respectively.

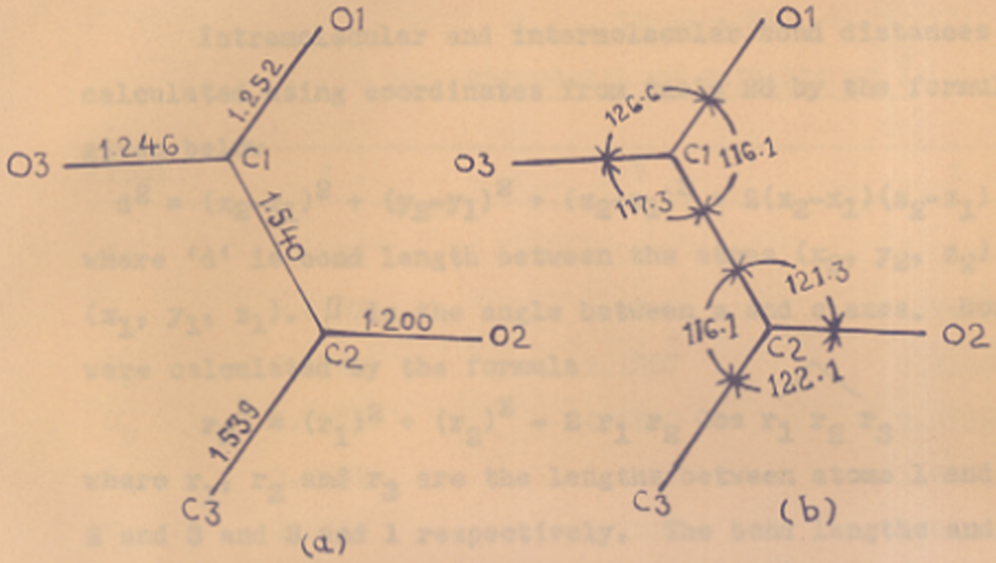

Fig. 18 BOND LENGTHS (Å) AND BOND ANGLES (°) IN PYRUVATE GROUP.

CHAPTER - XIII

RESULTS AND DISCUSSION

(i) Bond distances and angles:

Intramolecular and intermolecular bond distances were calculated using coordinates from table 28 by the formula given below

$$d^2 = (x_2-x_1)^2 + (y_2-y_1)^2 + (z_2-z_1)^2 + 2(x_2-x_1)(z_2-z_1)\ \mathrm{Cos}\ \beta$$

where 'd' is bond length between the atoms (x_2, y_2, z_2) and (x_1, y_1, z_1). β is the angle between a and c axes. Bond angles were calculated by the formula

$$r_3^{\,2} = (r_1)^2 + (r_2)^2 - 2\, r_1\, r_2\ \mathrm{Cos}\ \widehat{r_1\, r_2\, r_3}$$

where r_1, r_2 and r_3 are the lengths between atoms 1 and 2, 2 and 3 and 3 and 1 respectively. The bond lengths and angles calculated in pyruvate group are shown in figs. 18 a, b and are listed in table 29 along with their e.s.d.

TABLE - 29

Bond lengths in Å		Bond angles in degrees	
C_1-O_1	1.252 ± 0.011 (1.242)	$O_1-C_1-O_3$	126.6 ± 0.8 (126.3)
C_1-O_3	1.246 ± 0.011 (1.278)	$O_1-C_1-C_2$	116.1 ± 0.7 (115.4)
C_1-C_2	1.540 ± 0.011 (1.579)	$O_3-C_1-C_2$	117.3 ± 0.7 (117.8)
C_2-O_2	1.200 ± 0.011 (1.183)	$C_1-C_2-O_2$	121.3 ± 0.7 (119.1)
C_2-C_3	1.539 ± 0.011 (1.518)	$C_1-C_2-C_3$	116.1 ± 0.7 (113.7)
		$O_2-C_2-C_3$	122.1 ± 0.7 (125.8)

The values reported by Tavale, et. al. (1961) are given in brackets for comparison.

(ii) Molecular structure:

The orthogonal coordinates X, Y, Z of the atoms in sodium pyruvate were calculated by the formulae.

$$X = x \sin\beta \quad ; \quad Y = y \quad ; \quad Z = z + x \cos\beta$$

and are listed in table 30.

TABLE - 30

ORTHOGONAL COORDINATES IN Å

Atoms	X	Y	Z
Na	4.3635	0.9491	-0.0186
O_1	4.4687	2.5728	1.7460
O_2	2.1741	2.1307	0.3146
O_3	3.7374	4.6550	2.0759
C_1	3.6191	3.4877	1.6572
C_2	2.2749	3.1030	1.0103
C_3	1.1144	4.0869	1.2205

The equation of the plane through O_1, O_3, C_2 and C_1 can be represented as

$$-0.3641\,X - 0.2691\,Y + 0.8915\,Z + 0.7708 = 0$$

where X, Y and Z are expressed in Å units and referred to the orthogonal coordinates (table 30). The atoms O_1, O_3, C_2 and C_1 are + 0.008, + 0.008, + 0.008 and - 0.008 Å respectively out of this plane.

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

$$-0.2659\,X - 0.5199\,Y + 0.8117\,Z + 1.4144 = 0$$

The normal distances of the atoms O_2, C_1, C_2 and C_3 are - 0.016, -0.016, + 0.016 and - 0.016 Å respectively from this plane. These two planes make an angle of 16.2°.

All bond lengths and angles found in pyruvate group (figs. 18 a, b) are normal. The central C_1-C_2 bond length 1.540 ± 0.011 Å is close to single C-C bond length (1.545 Å) and suggests that there is no appreciable degree of conjugation accross this bond. However, the possibility of the free rotation of the two planes O_1-O_3-C_1-C_2 and C_1-C_2-C_3-O_2 can not be ruled out, the fact that the two planes make an angle of 16.2° and displacement of O_1 and O_3 from the plane passing through C_1-C_2-O_2-C_3 is + 0.306 and - 0.315 Å (i.e. in opposite direction) supports the rotation of two planes around the central C_1-C_2 bond.

The distances C_1-O_1 = 1.252 ± 0.011 Å and C_1-O_3 = 1.246 ± 0.011 Å are of equal lengths and suggest the existence of carboxylate group in ionic form as found in sodium 2-oxo valerate and sodium 2-oxo heptylate.

(iii) <u>Crystal structure:</u>

There are six short bonds between Na(x, y, z) and the neighbouring oxygens;

Na - O_1 (x, y, z)	2.400 ± 0.007 Å
Na - O_1 (x, y, z-1)	2.513
Na - O_1 ($\frac{1}{2}$-x, y-$\frac{1}{2}$, 1-z)	2.374
Na - O_2 (x, y, z)	2.510
Na - O_3 (x, y-1, z)	2.688
Na - O_3 (x, y-1, z-1)	2.375

There are van der Waals bonds between the methyl carbons C_3 and keto group oxygens O_2, and between carbons and carbons of the neighbouring molecules. The more significant are as follows:

C_3 ($\bar{x}$, 1-y, $\bar{z}$) - O_2 (x, y, z-1) 4.038 ± 0.010 Å

C_3 ($\bar{x}$, 1-y, $\bar{z}$) - O_2 (x, y, z)	3.751 ± 0.010 Å
C_3 (x, 1-y, z) - O_2 (x, y, z)	3.579 ± 0.010
C_3 (x, y, z-1) - O_2 (x, y, z)	3.556 ± 0.010
C_3 ($\bar{x}$, 1-y, $\bar{z}$) - C_3 (x, y, z)	4.499 ± 0.011
C_3 ($\bar{x}$, 1-y, $\bar{z}$) - C_3 (x, y, z-1)	3.864 ± 0.011
C_3 ($\bar{x}$, 1-y, $\bar{z}$) - C_3 (x, y-1, z)	4.066 ± 0.011
C_3 ($\bar{x}$, 1-y, $\overset{6}{z}$) - C_3 (x, y-1, z-1)	3.479 ± 0.011

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

Na (x, y, z) - Na ($\frac{1}{2}$-x, $\frac{1}{2}$+y, $\bar{z}$)	3.773 ± 0.007 Å
- Na ($\frac{1}{2}$-x, y-$\frac{1}{2}$, $\bar{z}$)	3.773 ± 0.007
- Na (x, y, z-1)	3.680 ± 0.007
- Na (x, y, z+1)	3.680 ± 0.007

The packing of molecules in all the compounds are similar.

REFERENCES

1) Javale, S.S., Pant, L.M. and Biswas, A.B. (1961) Acta Cryst., 14, 1281

APPENDIX

OBSERVED AND CALCULATED STRUCTURE FACTORS

SODIUM 2-OXO VALERATE

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
8	0	0	81.6	-82.1	20	2	0*	7.0	9.2
10	0	0	46.1	42.8	22	2	0*	7.5	4.2
12	0	0	114.3	-108.3	24	2	0*	8.1	-4.8
14	0	0	107.6	106.9	26	2	0	37.5	-26.4
16	0	0	98.9	-89.7	28	2	0	43.2	-33.6
18	0	0	18.3	13.1	30	2	0	54.7	56.1
20	0	0*	5.9	9.3	32	2	0	23.1	-27.1
22	0	0*	7.0	-4.7	34	2	0	18.3	17.3
24	0	0	16.3	- 19.3	1	3	0	14.4	-17.9
26	0	0	66.3	62.3	3	3	0	32.7	42.0
28	0	0	35.5	32.7	5	3	0	16.3	-19.3
30	0	0	74.9	-79.6	7	3	0*	6.0	11.9
32	0	0	35.5	48.8	9	3	0	10.6	-7.3
34	0	0	33.6	-35.8	11	3	0	+47.1	50.1
36	0	0	17.3	20.5	13	3	0	88.4	-101.7
38	0	0	17.3	-15.0	15	3	0	12.5	11.4
40	0	0*	6.4	-1 .6	17	3	0	41.3	44.1
42	0	0	21.1	22.5	19	3	0	25.0	-28.3
3	1	0	10.6	-14.1	21	3	0	22.1	23.4
5	1	0	9.6	-8.7	23	3	0	18.3	-19.7
7	1	0*	3.8	7.5	25	3	0	27.9	28.1
9	1	0	9.6	8.9	27	3	0	27.9	-26.2
11	1	0	58.6	-56.3	29	3	0*	8.6	10.1
13	1	0	98.9	91.6	31	3	0*	8.1	9.7
15	1	0	25.9	-23.9	33	3	0	13.5	-15.1
17	1	0	43.2	-25.6	35	3	0	12.5	15.3
19	1	0	36.5	28.0	0	4	0	32.7	29.3
21	1	0	38.4	-26.8	2	4	0*	7.0	1.7
23	1	0	20.2	22.0	4	4	0*	7.0	10.7
25	1	0	25.0	-22.7	6	4	0	16.3	-18.1
27	1	0	18.3	16.4	8	4	0*	7.5	-1.9
2	2	0	60.5	69.3	10	4	0*	7.5	3.5
4	2	0*	4.6	1.1	12	4	0	20.2	-18.5
6	2	0*	4.6	4.0	14	4	0	13.5	12.3
8	2	0	23.1	23.9	16	4	0	21.1	-20.6
10	2	0*	5.4	-9.7	18	4	0	18.3	16.2
12	2	0	57.6	60.1	20	4	0*	8.6	-12.7
14	2	0	61.5	-66.1	22	4	0*	8.6	- 1.2
16	2	0	65.3	68.9	24	4	0	16.3	17.7
18	2	0	35.5	-27.5	26	4	0*	8.6	-5.4
					28	4	0	18.3	18.7

* indicates unobserved reflexion.

020 appeared to suffer from extinction and therefore was not included in the refinement.

h	k	l	|Fo|	Fc
3	5	0	26.9	-28.0
5	5	0	26.9	26.0
7	5	0	26.9	-22.5
9	5	0*	8.6	-5.3
11	5	0*	8.6	-4.7
13	5	0	31.7	28.7
15	5	0*	8.6	15.5
17	5	0	31.7	-27.6
0	6	0	22.1	-15.5
2	6	0	19.2	14.4
4	6	0*	8.6	-16.0
6	6	0*	8.6	-2.8
8	6	0	20.2	19.7
10	6	0	20.2	-18.3
12	6	0	18.3	14.2
3	1	1	53.9	58.9
4	1	1	35.6	33.0
5	1	1	23.5	20.3
6	1	1	14.0	10.7
7	1	1	34.3	-31.5
8	1	1	24.4	22.4
9	1	1	13.7	13.0
10	1	1	27.2	-35.1
11	1	1	39.2	45.2
12	1	1	72.1	62.5
13	1	1	107.6	-94.0
14	1	1	47.7	-47.8
15	1	1*	6.5	13.6
16	1	1	18.7	-13.0
17	1	1	41.1	36.4
18	1	1	37.5	31.0
19	1	1	17.7	-25.5
20	1	1	54.4	-49.9
21	1	1	16.6	14.5
22	1	1	30.0	30.5
23	1	1*	8.4	3.6
24	1	1	59.0	-55.8
25	1	1*	8.9	7.0
26	1	1	20.7	17.7
27	1	1	25.5	-28.0
28	1	1	33.7	32.9
29	1	1*	9.5	13.3
30	1	1*	7.9	-8.4
31	1	1	16.6	16.0
32	1	1	20.7	17.8
33	1	1*	9.5	-16.2
34	1	1	20.2	-20.7
1	2	1	25.3	-21.1
2	2	1	49.0	58.0
3	2	1	18.7	-18.4
4	2	1	13.7	11.8
5	2	1	36.5	37.4
6	2	1	34.3	-32.7
7	2	1	30.0	-25.9
8	2	1	27.5	26.8
9	2	1*	4.9	-4.3
10	2	1*	6.0	-1.4
11	2	1	22.5	-20.4
12	2	1*	6.5	8.9
13	2	1*	5.4	-6.5
14	2	1	37.3	-34.9
15	2	1	46.9	37.5
16	2	1	17.7	19.6
17	2	1	15.0	-15.9
18	2	1	18.6	15.7
19	2	1	25.3	25.8
20	2	1	17.7	-19.1
21	2	1	23.4	-23.3
22	2	1*	8.4	2.1
23	2	1*	7.4	2.0
24	2	1	19.6	20.4
25	2	1	18.7	16.0
26	2	1	27.5	-27.8
27	2	1	19.7	-16.7
1	3	1	18.6	17.3
2	3	1	20.7	-20.3
3	3	1	27.5	-28.8
4	3	1	46.9	-54.8
5	3	1*	6.5	11.6
6	3	1	47.7	53.5
7	3	1*	6.5	-5.8
8	3	1	58.1	-67.3
9	3	1	11.7	-13.1
10	3	1	42.2	44.3
11	3	1	18.6	21.4
12	3	1	28.1	-28.7
13	3	1*	7.8	-5.6
14	3	1	15.0	13.6
15	3	1	17.7	18.1
16	3	1	15.0	11.0
17	3	1	18.6	-10.5
18	3	1	18.7	-17.0
19	3	1*	8.9	-10.1
20	3	1	36.5	37.5
21	3	1*	8.9	14.3
22	3	1	33.7	-33.5
23	3	1	16.6	-19.9
24	3	1	45.0	47.0
25	3	1*	9.5	11.6
26	3	1	21.5	-21.1

h	k	l	|Fo|	Fc
27	3	1*	9.5	6.0
28	3	1	18.2	-10.7
29	3	1*	9.5	-10.2
30	3	1*	7.9	-4.8
31	3	1*	8.9	4.0
32	3	1*	7.4	-3.3
33	3	1*	8.4	-3.7
34	3	1*	6.8	11.7
35	3	1*	7.8	0.3
36	3	1*	15.9	-15.9
37	3	1*	6.5	2.5
38	3	1	16.9	15.1
0	4	1	28.4	36.1
1	4	1*	6.3	10.3
2	4	1*	7.8	-6.6
3	4	1*	6.3	7.0
4	4	1	13.7	-13.3
5	4	1	11.2	- 9.0
6	4	1*	8.4	4.0
7	4	1*	6.8	-1.8
8	4	1*	8.4	4.2
9	4	1	14.0	16.1
10	4	1	18.6	-19.6
11	4	1	15.9	21.5
12	4	1*	8.9	7.7
13	4	1*	7.4	-5.1
14	4	1	23.5	24.9
15	4	1	19.7	-18.2
16	4	1	22.6	-24.3
17	4	1	15.0	-13.7
4	5	1	18.7	23.5
5	5	1*	9.5	2.8
6	5	1	36.5	-36.7
7	5	1*	9.5	1.7
8	5	1	49.7	54.3
9	5	1*	9.5	6.6
10	5	1	32.8	-38.9
11	5	1	19.6	-19.3
12	5	1	20.7	20.2
13	5	1	16.6	16.8
14	5	1*	7.9	-9.6
15	5	1*	9.5	-8.7
16	5	1*	7.9	0.5
17	5	1*	9.5	-5.0
18	5	1*	7.9	7.4
19	5	1*	9.5	11.3
20	5	1	34.7	-31.6
21	5	1*	9.5	-8.0
22	5	1	43.1	37.0
23	5	1*	8.9	8.2
24	5	1	43.1	-34.3
0	6	1	19.6	7.0
1	6	1	15.0	-12.7
2	6	1*	9.5	-14.7
3	6	1*	7.9	8.4
4	6	1*	9.5	7.8
5	6	1*	7.9	-10.9
6	6	1*	9.5	6.4
7	6	1*	7.9	9.8
8	6	1*	9.5	-6.2
9	6	1*	7.9	-6.2
10	6	1*	8.9	12.0
11	6	1	23.4	-24.5
12	6	1*	8.9	-10.6
13	6	1	15.9	13.1
14	6	1*	8.9	-3.1
15	6	1*	7.4	2.8
16	6	1*	8.4	5.5
17	6	1	20.7	22.9
18	6	1*	8.4	-1.2
19	6	1	20.7	-19.3
0	0	2	115.7	124.3
1	0	2*	6.0	15.1
2	0	2	39.6	-41.5
3	0	2*	6.0	-2.4
4	0	2	61.2	59.4
5	0	2	53.8	46.5
6	0	2	59.3	-57.0
7	0	2	55.7	-55.9
8	0	2	12.2	-15.0
9	0	2	10.6	- 9.0
10	0	2	70.6	64.8
11	0	2	17.3	-16.9
12	0	2	96.9	-91.4
13	0	2	13.5	-19.5
14	0	2	12.2	13.8
15	0	2	74.9	60.2
16	0	2	35.7	-29.3
17	0	2	31.7	-30.8
18	0	2	56.5	53.1
19	0	2	55.7	50.9
20	0	2	47.3	-44.9
21	0	2	31.7	-30.7
22	0	2	14.1	8.9
23	0	2	13.5	-10.9
24	0	2	27.3	26.3
25	0	2*	10.2	14.6
26	0	2 *	10.2	-8.1
27	0	2	18.3	-17.5

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
28	0	2	32.7	30.7	21	2	2*	9.4	3.3
29	0	2	25.0	24.1	22	2	2*	8.7	-5.2
30	0	2	30.1	-32.6	23	2	2*	10.0	3.4
31	0	2*	9.4	-11.1	24	2	2	17.7	-13.0
32	0	2	18.8	19.0	25	2	2*	10.0	9.4
33	0	2*	8.6	2.3	26	2	2*	8.8	-2.6
34	0	2	27.3	-22.2	27	2	2	23.3	-20.7
35	0	2*	8.4	-9.4	29	2	2*	10.0	-9.4
36	0	2	20.4	17.3	30	2	2	27.0	27.8
38	0	2	15.1	-5.3	31	2	2*	9.4	7.6
40	0	2	19.8	-20.6	32	2	2	20.5	-19.2
1	1	2	19.6	-11.2	33	2	2*	9.4	-2.4
2	1	2	28.4	22.5	34	2	2	27.0	20.7
3	1	2*	4.7	-0.3	35	2	2*	8.2	7.8
4	1	2	31.1	-29.5	36	2	2	14.0	-15.1
5	1	2	28.9	24.9	1	3	2	15.9	19.2
6	1	2	47.6	55.6	2	3	2	19.2	-17.6
7	1	2	36.3	-33.3	3	3	2*	6.6	-6.2
8	1	2	44.9	-45.1	4	3	2	25.0	11.8
9.	1	2	15.9	12.3	5	3	2	26.1	-27.7
10	1	2*	6.2	4.8	6	3	2	47.6	-48.5
11	1	2	15.4	8.9	7	3	2	39.1	41.8
12	1	2	20.2	15.3	8	3	2	44.9	47.2
13	1	2*	6.1	-3.9	8	3	2	20.5	-17.3
14	1	2	16.5	-17.0	10	3	2*	8.2	- 9.0
15	1	2	13.1	8.4	11	3	2*	7.7	-4.9
16	1	2	15.6	7.9	13	3	2*	7.7	-9.5
0	2	2	99.1	-112.1	14	3	2*	8.7	-4.7
1	2	2	28.4	-33.3	15	3	2*	8.3	-7.2
2	2	2	50.3	49.3	16	3	2*	9.4	-5.9
3	2	2*	6.2	-0.8	17	3	2*	8.3	4.1
4	2	2	42.8	-40.7	18	3	2*	9.2	-7.0
5	2	2*	6.9	-0.7	19	3	2*	9.2	5.0
6	2	2	18.6	23.7	20	3	2*	10.0	0.2
7	2	2*	6.9	5.0	21	3	2*	8.8	8.7
8	2	2	21.4	24.1	22	3	2	20.2	20.1
9	2	2	20.2	22.4	23	3	2	21.4	-20.2
10	2	2	53.1	-51.6	24	3	2*	10.0	-8.5
11	2	2*	7.5	9.8	25	3	2	21.4	16.6
12	2	2	66.2	70.2	0	4	2	58.7	71.4
13	2	2*	7.5	6.4	1	4	2*	9.4	22.6
14	2	2	18.6	-15.7	2	4	2	39.1	-39.2
15	2	2	24.8	-25.6	3	4	2*	9.4	12.7
16	2	2	26.1	20.5	4	4	2*	8.3	16.7
17	2	2*	8.7	-7.7	5	4	2	32,9	-33.5
18	2	2	30.7	-28.6	6	4	2*	8.3	5.3
19	2	2*	8.7	-3.9	7	4	2	27.5	22.6
20	2	2	21.4	22.2	8	4	2	23.3	-21.5

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
9	4	2*	9.4	-9.4	25	5	2	18.6	-15.1
10	4	2	25.2	23.3	0	6	2	24.2	-27.5
11	4	2*	10.0	-14.3	1	6	2*	9.4	4.0
12	4	2	32.7	-34.3	2	6	2	21.4	19.8
13	4	2*	10.4	7.2	3	6	2*	9.4	-12.2
14	4	2	19.6	16.8	5	6	2	22.0	19.4
15	4	2*	10.0	-1.5	6	6	2*	8.3	-5.0
16	4	2	17.7	-13.7	7	6	2*	9.4	-4.2
17	4	2	33.9	27.2	8	6	2	13.1	10.1
18	4	2*	8.8	3.7	9	6	2	15.6	-12.9
19	4	2	28.4	-31.4	10	6	2	12.5	-5.0
20	4	2*	8.8	1.9	11	6	2	19.2	16.2
21	4	2	24.8	21.6	12	6	2	14.0	11.7
22	4	2*	8.8	1.6	1	1	3	16.3	-12.6
23	4	2*	10.0	1.5	2	1	3*	5.9	2.2
24	4	2*	8.3	-1.4	3	1	3	24.0	23.7
25	4	2	22.9	-24.2	4	1	3	57.1	49.8
26	4	2*	8.3	8.4	5	1	3*	6.8	-5.5
27	4	2	20.2	20.9	6	1	3	79.5	-71.1
28	4	2*	7.7	9.2	7	1	3	19.2	30.0
29	4	2*	8.2	-3.0	8	1	3	88.8	76.0
30	4	2	22.4	-18.4	9	1	3	16.3	-18.0
31	4	2*	6.9	-2.0	10	1	3	27.1	-24.0
32	4	2	20.5	16.3	11	1	3*	8.1	2.9
33	4	2*	6.2	-3.2	12	1	3	36.5	36.5
34	4	2	15.9	-14.3	13	1	3	23.1	-34.9
1	5	2*	9.9	-12.9	14	1	3	20.6	-22.6
2	5	2*	10.0	3.0	15	1	3*	8.7	-5.0
3	5	2*	8.8	6.3	16	1	3	24.4	-29.5
4	5	2	19.2	20.4	17	1	3*	10.0	8.4
5	5	2*	8.8	9.4	18	1	3	17.8	16.8
6	5	2*	10.0	-7.9	19	1	3*	10.0	1.8
7	5	2	17.7	-15.2	20	1	3	29.0	-28.2
8	5	2*	10.0	0.8	21	1	3	17.3	17.4
9	5	2*	8.8	5.8	22	1	3	38.3	38.0
10	5	2*	10.0	-1.3	23	1	3*	10.9	-7.8
11	5	2*	8.8	-5.1	24	1	3	39.3	-40.9
12	5	2	19.6	-16.4	25	1	3*	10.9	7.7
13	5	2	20.5	23.0	26	1	3	21.5	20.9
14	5	2	22.0	16.2	27	1	3	18.3	-15.8
15	5	2*	8.8	-0.4	0	2	3	36.5	-38.9
17	5	2*	8.3	-8.9	1	2	3	19.7	13.2
18	5	2*	9.4	-1.8	2	2	3	21.1	19.5
19	5	2*	8.3	3.0	3	2	3*	7.0	-5.7
20	5	2*	9.4	4.7	4	2	3	18.3	-18.5
21	5	2*	8.3	-9.5	5	2	3	38.3	-35.0
22	5	2*	8.7	-14.3	6	2	3	16.3	15.9
23	5	2	19.6	16.8	7	2	3	36.5	35.0
24	5	2*	8.2	0.9					

h	k	l	|Fo|	Fc
8	2	3	14.4	10.4
9	2	3*	8.2	-6.9
10	2	3	15.4	-13.3
11	2	3	18.7	-15.0
12	2	3	15.4	13.0
13	2	3*	8.7	7.7
14	2	3	22.1	-18.3
15	2	3*	9.3	-3.7
16	2	3	17.3	14.9
17	2	3	23.4	26.5
18	2	3*	9.6	-9.0
19	2	3	30.0	-38.0
20	2	3*	10.9	15.0
21	2	3	21.5	20.5
22	2	3*	10.9	-7.2
23	2	3	19.2	13.6
24	2	3*	10.9	-1.9
25	2	3	21.5	-18.9
2	3	3*	8.7	-2.9
3	3	3	21.1	-12.6
4	3	3*	8.7	-8.2
5	3	3*	9.3	-5.7
6	3	3*	8.7	3.1
7	3	3*	10.0	2.9
8	3	3	19.7	-20.0
9	3	3*	10.0	-10.3
10	3	3	28.0	27.6
11	3	3*	10.0	15.3
12	3	3	56.1	-59.7
13	3	3*	10.0	7.7
14	3	3	43.0	45.7
15	3	3*	10.9	10.7
16	3	3*	10.2	12.3
17	3	3*	10.9	-6.7
18	3	3	25.3	-27.6
19	3	3*	10.9	-8.0
20	3	3	28.0	37.9
21	3	3*	10.9	5.4
22	3	3	28.0	-34.2
23	3	3*	10.9	-13.5
24	3	3	25.3	31.2
25	3	3*	10.2	7.9
26	3	3	19.7	-18.1
27	3	3*	10.3	3.2
28	3	3*	9.3	-2.9
29	3	3*	10.0	-5.1
30	3	3*	8.7	12.5
31	3	3*	8.7	-1.7
32	3	3	21.5	-20.8
33	3	3*	8.1	-0.9
343	3	3	19.7	16.7
0	4	3	21.1	21.6
1	4	3	20.6	24.4
2	4	3*	10.9	-1.9
3	4	3*	10.3	-1.6
4	4	3*	10.9	4.8
5	4	3	15.4	14.4
6	4	3*	10.9	-12.2
7	4	3*	10.2	-7.3
8	4	3*	10.9	-4.9
9	4	3*	10.2	-12.9
10	4	3*	10.9	1.1
11	4	3	25.3	25.8
12	4	3		
1	5	3*	10.9	-1.3
2	5	3*	10.2	-12.0
4	5	3*	10.9	9.6
5	5	3*	10.9	9.3
6	5	3*	10.2	8.0
7	5	3	20.2	-15.8
8	5	3*	10.2	0.2
9	5	3	20.2	16.1
10	5	3	18.7	-17.3
11	5	3*	10.9	-13.2
12	5	3	35.5	35.4
13	5	3*	10.9	2.5
14	5	3	29.0	-25.1
15	5	3*	10.2	-6.5
16	5	3*	9.6	-7.6
17	5	3*	10.0	3.1
18	5	3	23.4	22.2
19	5	3*	10.0	5.4
20	5	3	28.0	-24.2
21	5	3*	9.3	-11.4
22	5	3	18.7	12.0
23	5	3	18.3	16.6
0	6	3*	10.0	-2.7
1	6	3	27.1	-30.0
1	0	4	48.0	49.5
2	0	4*	8.8	-8.3
3	0	4*	9.4	-16.4
4	0	4	24.5	20.7
5	0	4	14.4	-19.0
6	0	4	16.9	-14.0
7	0	4*	9.7	10.9
8	0	4*	8.6	10.4
9	0	4	14.4	-20.0
10	0	4	28.2	26.8
11	0	4*	10.0	-0.5
12	0	4	44.3	-46.7

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
13	0	4	13.5	-11.8	11	2	4*	8.1	5.0
14	0	4	15.1	-16.6	12	2	4	39.4	49.7
15	0	4	24.0	22.2	13	2	4*	8.6	2.4
16	0	4*	10.1	0.9	14	2	4*	7.4	4.9
17	0	4*	10.8	10.2	15	2	4*	8.6	-12.2
18	0	4	31.0	31.3	16	2	4*	7.4	0.6
19	0	4*	10.8	-8.5	17	2	4*	8.8	-5.0
20	0	4	16.0	-13.2	18	2	4	17.3	-21.5
25	0	4	19.2	-19.9	19	2	4*	8.8	-2.7
1	1	4	10.6	-7.7	20	2	4	13.5	9.4
2	1	4	10.5	7.1	1	3	4	15.4	19.4
3	1	4*	5.1	0.4	2	3	4	16.6	-16.5
4	1	4*	6.0	3.3	3	3	4	10.6	-9.7
5	1	4	14.4	10.2	4	3	3*	8.6	1.9
6	1	4*	6.4	-8.0	5	3	4	14.4	-12.2
7	1	4*	5.6	-1.4	6	3	4*	8.6	2.9
8	1	4*	6.4	6.0	7	3	4*	7.7	0.7
9	1	4*	6.0	-8.3	8	3	4*	8.6	-6.0
10	1	4*	7.0	9.5	9	3	4*	7.4	7.7
11	1	4	15.4	15.8	10	3	4*	8.6	-8.8
12	1	4	18.3	-22.8	11	3	4	16.3	-13.2
13	1	4	14.4	-16.1	12	3	4	23.6	24.3
14	1	4	14.9	17.5	13	3	4	13.5	12.3
15	1	4	12.5	9.7	14.	3	4	17.5	-17.2
16	1	4*	7.5	-0.7	15	3	4*	7.6	-7.1
17	1	4*	7.4	-0.5	16	3	4*	8.8	-3.0
18	1	4	14.9	-10.3	17	3	4*	7.6	0.7
19	1	4*	7.6	-7.3	18	3	4*	8.8	13.5
20	1	4*	8.8	8.9	19	3	4*	7.6	5.0
21	1	4	14.4	13.0	20	3	4*	8.8	-7.1
0	2	4	34.6	-38.2	21	3	4*	7.6	-12.4
2	2	4	31.7	32.4	22	3	4*	8.8	5.6
3	2	4*	7.0	3.8	23	3	4*	7.4	1.8
4	2	4	29.8	-27.8	24	3	4*	8.6	-2.0
5	2	4*	7.5	6.3	25	3	4*	8.9	3.6
6	2	4	13.5	6.4	26	3	4*	8.1	8.5
7	2	4*	7.5	4.0	27	3	4	20.9	17.1
8	2	4	15.4	7.4	28	3	4*	7.0	-11.3
9	2	4*	8.0	8.1	29	3	4	15.4	--9.1
10	2	4	35.5	-37.6	0	4	4	36.5	51.2

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
1	4	4*	8.8	-19.6	13	5	4	11.5	9.9
2	4	4	34.6	-43.4	0	6	4	20.2	-22.5
3	4	4*	8.8	4.2	1	6	4*	6.4	6.9
4	4	4	26.9	29.7	2	6	4	20.2	20.9
5	4	4*	8.8	5.7	3	6	4*	6.4	1.9
6	4	4*	7.6	-2.9	4	6	4	18.3	-18.6
7	4	4*	8.8	-10.3	5	6	4*	6.4	-3.5
8	4	4	19.2	-17.3	6	6	4*	5.6	5.6
9	4	4*	8.8	-4.1	7	6	4*	6.4	-0.5
10	4	4	33.6	33.9	8	6	4	11.5	8.3
11	4	4*	8.8	-1.6	9	6	4*	6.4	10.4
12	4	4	36.5	-39.2	10	6	4	15.4	-12.2
13	4	4*	8.8	7.3	11	6	4*	6.0	-6.9
14	4	4	16.3	12.6	12	6	4	15.4	15.3
15	4	4	11.5	-6.5	0.	0	6	38.6	60.3
16	4	4	13.5	-9.4	1	0	6*	10.8	-13.4
17	4	4	13.5	6.1	2	0	6	35.7	-30.3
18	4	4	14.4	13.0	3	0	6*	10.8	-9.5
19	4	4*	8.6	8.2	4	0	6*	10.1	-6.1
20	4	4	13.5	-8.3	5	0	6*	10.5	-3.0
1	5	4	16.3	-18.2	6	0	6	24.5	19.5
2	5	4*	8.6	9.9	7	0	6*	10.5	3.1
3	5	4	16.3	11.2	8	0	6	11.3	-6.5
4	5	4*	8.6	-2.8	9	0	6	10.6	-13.8
5	5	4*	6.7	9.3	10	0	6	9.4	13.4
6	5	4*	8.6	7.2	11	0	6	14.4	13.0
7	5	4*	7.4	-4.4	12	0	6	25.5	-23.6
8	5	4*	8.6	-0.8	13	0	6*	9.7	8.6
9	5	4*	7.4	6.1	14	0	6*	9.1	3.5
10	5	4*	6.9	-3.4	15	0	6	24.0	-23.6
11	5	4	11.5	-9.2	16	0	6*	8.8	-0.6
12	5	4*	8.1	2.6	17	0	6	15.4	17.6

SODIUM 2-OXO CAPROATE

h	k	l	|Fc|	|Fo|	α in °
12	0	0	81.0	91.0	118.0
14	0	0	87.5	87.9	0.0
16	0	0	130.6	135.5	180.0
18	0	0	84.5	83.8	0.0
20	0	0	43.3	54.8	180.0
22	0	0*	8.5	10.2	180.0
24	0	0	19.2	13.4	0.0
26	0	0*	4.3	12.1	0.0
28	0	0*	5.1	12.8	180.0
30	0	0	53.6	56.9	0.0
32	0	0*	5.9	13.9	0.0
34	0	0	58.4	64.1	180.0
36	0	0	38.5	31.0	0.0
38	0	0	32.1	27.9	180.0
40	0	0	19.6	18.6	0.0
42	0	0	17.0	14.5	180.0
2	2	0	81.6	63.7	0.0
4	2	0*	9.8	7.7	180.0
6	2	0*	10.0	8.0	0.0
8	2	0	19.2	17.1	0.0
10	2	0*	6.1	8.8	180.0
12	2	0	33.2	29.6	0.0
14	2	0	39.9	37.5	180.0
16	2	0	75.7	80.8	0.0
18	2	0	57.9	60.3	180.8
20	2	0	38.0	41.0	0.0
22	2	0	11.6	14.8	180.0
24	2	0*	2.5	12.5	180.0
26	2	0*	1.1	13.5	0.0
28	2	0*	7.3	13.6	180.0
30	2	0	22.8	20.5	180.0
32	2	0*	10.8	14.3	180.0
34	2	0	39.5	38.7	0.0
36	2	0	23.1	19.3	180.0
38	2	0	16.8	15.9	0.0
8	1	1	44.3	40.8	279.7
10	1	1	14.2	12.2	158.0
12	1	1	40.9	35.7	21.7
14	1	1	101.7	103.7	230.3
16	1	1	86.8	93.7	55.7
18	1	1	20.3	29.4	129.3
20	1	1	36.9	43.6	224.2
22	1	1	34.7	39.4	51.3
24	1	1	42.1	45.1	196.0
26	1	1	25.7	23.6	8.0
28	1	1	44.3	45.1	179.8
30	1	1	32.6	29.4	22.5
32	1	1	34.3	40.0	309.2
34	1	1*	6.7	16.6	153.3
36	1	1*	14.7	16.6	50.0
38	1	1	21.5	20.8	220.2
2	3	1	34.7	27.2	125.8
4	3	1	32.5	29.4	209.2
6	3	1	39.7	33.6	17.5
8	3	1	48.8	48.6	182.8
10	3	1	41.2	44.3	352.5
12	3	1	39.3	38.2	149.3
14	3	1	21.8	17.9	335.8
18	3	1	18.2	13.6	283.0
20	3	1	11.3	14.3	25.6
22	3	1	15.6	15.7	160.9
24	3	1	27.9	29.4	335.9
26	3	1	28.3	28.6	152.8
28	3	1	33.3	37.2	334.4
30	3	1	19.4	22.2	163.9
32	3	1	8.9	15.1	117.3
2	5	1*	3.9	15.5	121.7
4	5	1*	5.1	15.5	287.7
6	5	1	18.8	24.3	173.4
8	5	1	26.8	24.3	2.8
10	5	1	28.3	24.3	167.6
12	5	1	27.1	24.3	330.6
14	5	1*	17.2	16.4	117.6
16	5	1*	11.4	16.6	279.4
18	5	1*	7.9	16.6	158.7
20	5	1*	4.0	16.4	64.0
24	5	1	18.1	20.2	336.3
26	5	1	23.4	22.8	343.6
28	5	1	18.8	22.8	153.8
0	0	2	130.5	131.5	335.1
2	0	2	39.3	34.2	199.5
4	0	2	52.3	40.8	336.8
6	0	2	86.6	81.5	217.4
8	0	2	50.6	42.1	279.2
10	0	2	18.2	13.2	36.6

h	k	l	|Fe|	|Fo|	∡ in °	h	k	l	|Fc|	|Fo|	∡ in °
12	0	2	79.3	84.2	165.2	22	1	3	14.9	14.9	27.4
14	0	2	82.3	101.2	014.4	24	1	3	32.5	29.8	193.6
16	0	2	56.5	57.9	108.3	26	1	3	33.5	29.8	13.2
18	0	2	43.6	47.3	277.5	28	1	3	29.9	29.8	184.8
20	0	2	57.6	60.5	143.7	30	1	3	20.7	17.9	7.1
22	0	2	64.6	67.1	305.1	32	1	3	14.7	14.9	241.3
24	0	2	34.6	36.8	127.9	2	3	3*	11.9	15.6	75.5
26	0	2*	3.6	9.2	315.0	4	3	3*	1.0	15.3	199.6
28	0	2	33.9	31.6	316.5	6	3	3*	2.9	16.1	164,6
30	0	2*	9.5	9.7	123.7	8	3	3*	6.5	15.8	116.3
32	0	2	23.2	18.4	306.5	10	3	3*	11.8	16.3	348.0
34	0	2	30.8	31.6	135.7	12	3	3	24.7	26.8	148.4
36	0	2*	13.6	9.7	317.8	14	3	3	45.2	47.7	353.2
38	0	2	16.3	17.1	153.9	16	3	3	39.9	38.7	179.9
0	2	2	109.7	93.2	147.3	18	3	3*	10.5	17.7	283.6
2	2	2	48.3	51.4	347.9	20	3	3*	14.6	18.0	354.2
4	2	2	39.1	38.1	174.2	22	3	3	19.3	20.9	170.2
6	2	2	35.2	31.4	348.1	24	3	3	24.8	25.3	344.7
8	2	2*	5.0	16.4	37.6	26	3	3	23.3	25.3	162.3
10	2	2	23.2	25.7	153.9	28	3	3	19.9	20.9	334.6
12	2	2	58.3	53.2	344.6	2	5	3*	8.9	17.5	185.0
14	2	2	57.4	58.0	192.9	4	5	3*	2.6	17.5	248.4
16	2	2	34.3	31.4	305.0	6	5	3*	12.0	17.5	29.9
18	2	2	16.6	18.1	114.7	8	5	3*	15.4	17.5	207.7
20	2	2	25.0	25.7	1.6	10	5	3*	13.9	17.5	57.5
22	2	2	20.1	26.6	154.5	12	5	3	14.3	20.9	320.1
0	4	2	51.2	59.9	324.5	14	5	3	20.5	28.6	161.9
2	4	2	36.0	33.3	164.9	16	5	3	15.9	23.1	341.7
4	4	2*	24.3	19.3	38.1	0	0	4	42.7	44.7	261.1
6	4	2	23.5	19.0	266.8	2	0	4	25.6	22.4	101.5
8	4	2	22.8	23.8	114.0	4	0	4	15.4	15.9	315.3
10	4	2	18.8	23.8	331.2	6	0	4	26.9	21.0	218.4
12	4	2	22.3	24.7	191.7	8	0	4*	12.9	8.6	44.2
14	4	2	21.4	24.7	25.1	10	0	4*	4.8	8.8	241.7
2	1	3	24.2	29.8	264.8	12	0	4	28.3	23.7	135.4
4	1	3	36.8	38.7	1.2	14	0	4	42.2	35.5	335.7
6	1	3	58.7	61.0	192.3	16	0	4	23.5	18.4	43.3
8	1	3	73.9	74.4	1.2	18	0	4	11.6	15.8	183.8
10	1	3	66.4	70.0	203.8	20	0	4	22.0	21.0	195.1
12	1	3	14.0	16.3	353.4	22	0	4	13.8	18.4	11.2
14	1	3	38.0	44.7	199.7	24	0	4*	13.9	10.0	233.6
16	1	3	39.8	40.2	31.8	26	0	4*	5.0	9.8	212.6
18	1	3	25.2	17.9	34.9	28	0	4	12.5	15.8	35.3
20	1	3	17.8	13.4	161.6	30	0	4	15.2	17.1	215.9

h	k	l	|Fc|	|Fo|	α in °	h	k	l	|Fc|	|Fo|	α in °
0	2	4	24.1	27.4	149.8	10	4	4	15.8	13.8	358.8
2	2	4	27.3	24.9	347.8	12	4	4	23.9	19.2	168.3
4	2	4	22.3	22.4	161.6	14	4	4	23.0	19.2	357.4
6	2	4	14.1	11.2	11.1	0	0	6	42.2	34.2	13.1
8	2	4*	2.5	11.7	40.4	2	0	6	29.0	25.0	174.9
10	2	4*	11.5	12.3	185.2	4	0	6*	2.3	9.7	241.7
12	2	4	30.3	27.4	337.7	6	0	6*	10.3	9.5	312.9
14	2	4	39.2	31.2	178.7	8	0	6	9.8	15.8	166.5
0	4	4	33.5	35.5	19.4	10	0	6	9.1	15.8	328.6
2	4	4	33.7	32.6	192.7	12	0	6	11.1	17.1	113.2
4	4	4	23.7	19.5	351.1	14	0	6	18.5	17.1	347.2
6	4	4	10.7	13.8	124.1	16	0	6*	13.2	8.6	232.8
8	4	4	8.7	13.8	220.9	18	0	6	17.2	15.8	61.1

SODIUM 2-OXO HEPTYLATE

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
8	0	0	75.2	-87.5	16	2	0	65.0	62.6
10	0	0	31.5	40.4	18	2	0	64.0	-62.4
12	0	0	71.1	-71.7	20	2	0	69.1	67.4
14	0	0	57.9	51.0	22	2	0	41.7	-38.0
16	0	0	115.9	-112.4	24	2	0	22.4	23.5
18	0	0	105.7	105.9	26	2	0*	7.0	-5.6
20	0	0	97.6	-97.3	28	2	0*	7.2	3.7
22	0	0	41.7	40.0	30	2	0*	7.4	1.4
24	0	0	20.9	-9.9	32	2	0*	7.4	-4.2
26	0	0	17.3	-15.7	34	2	0	39.6	-34.2
28	0	0*	6.6	-1.5	36	2	0	24.4	-26.0
30	0	0	16.3	13.6	38	2	0	48.8	51.3
32	0	0	17.5	-20.0	40	2	0	25.4	-29.8
34	0	0	80.3	70.5	42	2	0	26.4	26.6
36	0	0	27.4	23.7	1	3	0	13.2	-12.0
38	0	0	78.3	-70.1	3	3	0	30.5	31.4
40	0	0	42.7	48.3	5	3	0	32.5	-30.1
42.	0	0	49.8	-46.5	7.	3	0	20.3	24.9
44	0	0	27.4	26.9	9	3	0*	5.6	2.6
46	0	0	24.4	-21.3	11	3	0	18.3	20.3
9	1	0	17.3	-18.9	13	3	0	29.5	-23.6
11	1	0	14.2	-11.6	15	3	0	53.9	49.0
13	1	0	28.5	30.8	17	3	0	88.4	-111.5
15	1	0	53.9	-58.4	19	3	0	25.4	17.2
17	1	0	101.6	99.3	21	3	0	31.5	32.5
19	1	0	29.5	-29.0	23	3	0	24.4	-23.7
21	1	0	23.4	-14.2	25	3	0	36.6	33.7
23	1	0	17.3	20.3	27	3	0	18.3	-16.6
25	1	0	34.6	-31.3	29	3	0	19.3	17.3
27	1	0	22.4	21.1	31	3	0	19.3	-21.9
29	1	0	23.4	-19.7	33	3	0	28.5	26.0
31	1	0	24.4	20.6	35	3	0	29.5	-23.3
33	1	0	25.4	-20.4	0	4	0	37.6	35.1
35	1	0	18.3	15.5	2	4	0*	6.6	2.9
2	2	0	58.9	78.9	4	4	0*	7.2	3.6
4	2	0	17.3	-17.8	6	4	0*	7.2	-16.5
6	2	0	13.2	16.5	8	4	0*	7.0	14.4
8	2	0	21.3	20.6	10	4	0*	7.0	-4.6
10	2	0*	4.8	-2.0	12	4	0*	7.2	-11.8
12	2	0	28.5	28.6	14	4	0*	7.2	3.3
14	2	0	18.3	-18.6	16	4	0	17.3	-16.0

020 appeared to suffer from extinction and therefore was neglected.

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
18	4	0	13.2	10.6	42	1	1	17.3	-18.9
20	4	0	18.9	-18.2	43	1	1	11.1	11.9
22	4	0	13.5	12.7	44	1	1	14.2	15.1
1	5	0*	7.7	5.3	0.	2	1	125.0	-117.6
3	5	0	18.3	-17.3	1	2	1	35.6	-38.4
5	5	0	24.4	22.6	2	2	1	63.0	65.0
7	5	0	23.4	-28.2	3	2	1*	3.2	-1.8
9	5	0	18.3	15.2	4	2	1	18.3	-18.2
11	5	0*	7.9	-13.6	5	2	1	28.5	33.8
13	5	0*	7.9	- 8.5	6	2	1	11.2	-12.2
15	5	0*	7.9	7.2	7	2	1	31.5	-36.3
17	5	0	31.5	34.2	8	2	1	40.7	36.6
19	5	0*	8.1	13.1	9	2	1	23.4	24.6
21	5	0	25.4	-26.8	10	2	1	20.3	-18.6
6	1	1	21.3	21.7	11	2	1	13.2	-14.9
7	1	1	9.2	-10.1	12	2	1	11.2	12.6
8	1	1	17.3	15.8	13	2	1	16.3	-13.0
9	1	1	46.8	42.2	14	2	1*	7.5	-0.3
10	1	1*	9.2	-2.0	15	2	1	35.6	-30.5
11	1	1	11.2	-16.1	16	2	1*	7.5	7.0
12	1	1	14.7	35.0	17	2	1*	4.3	-1.0
13	1	1*	6.5	-13.2	18	2	1	42.7	-39.2
14	1	1	43.7	-48.1	19	2	1	50.8	41.1
15	1	1	42.7	47.1	20	2	1	29.5	28.2
16	1	1	85.4	17.1	21	2	1*	4.6	-6.0
17	1	1	113.8	-97.2	22	2	1*	8.9	1.4
18	1	1	74.2	-60.1	23	2	1	23.4	23.1
19	1	1	13.2	16.7	24	2	1*	9.5	-12.5
20	1	1*	9.2	-0.9	25	2	1	26.4	-27.6
21	1	1	26.4	24.7	26	2	1*	9.8	18.1
22	1	1	25.4	22.7	27	2	1	23.4	19.5
23	1	1	13.2	-23.1	28	2	1*	10.0	-2.4
24	1	1	55.9	-46.0	29	2	1	13.2	-9.8
25	1	1	29.5	24.4	30	2	1*	10.6	-12.0
26	1	1	39.6	37.7	31	2	1*	5.6	-7.6
27	1	1*	9.5	-3.3	33	2	1	16.3	18.2
28	1	1	50.8	-46.1	34	2	1	18.3	-23.7
29	1	1*	9.8	2.4	35	2	1	18.3	-16.8
30	1	1	24.4	24.5	1	3	1	20.3	20.0
31	1	1*	10.0	5.5	2	3	1	25.4	-35.8
32	1	1	55.9	-53.7	3	3	1	31.5	-29.1
33	1	1*	10.2	3.9	4	3	1	25.4	-39.8
34	1	1	21.3	17.2	5	3	1*	8.1	8.6
35	1	1	31.5	-30.6	6	3	1	33.5	38.0
36	1	1	43.7	36.0	7	3	1*	8.1	-9.6
37	1	1	13.9	19.9	8	3	1	49.8	-64.3
38	1	1*	5.7	-3.7	9	3	1*	8.1	-0.1
39	1	1*	11.1	7.0	10	3	1	47.8	53.3
40	1	1	17.3	14.9	11	3	1*	8.6	9.6
41	1	1*	11.1	-12.1	12	3	1	48.8	-54.6

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
13	3	1	20.3	-22.0	6	5	1	20.3	-20.2
14	3	1	27.4	31.9	7	5	1*	10.8	-2.5
15	3	1	31.5	23.1	8	5	1	33.5	38.3
16	3	1	22.4	-21.8	9	5	1*	10.8	-1.7
17	3	1*	8.9	-1.0	10	5	1	35.6	-38.5
18	3	1	12.2	14.3	11	5	1*	10.8	-6.6
19	3	1	15.2	18.3	12	5	1	35.6	42.6
20	3	1	12.2	6.9	13	5	1*	10.8	16.3
21	3	1	15.2	-15.0	14	5	1	22.4	-24.5
22	3	1	8.9	-8.4	15	5	1*	10.8	-20.1
23	3	1*	10.0	-3.2	16	5	1	13.2	11.0
24	3	1	25.4	25.4	17	5	1*	11.1	15.0
25	3	1*	10.0	10.5	18	5	1*	5.8	-6.2
26	3	1	25.4	-26.2	19	5	1*	11.1	-10.4
27	3	1*	10.6	-17.1	20	5	1*	5.8	2 .1
28	3	1	35.6	35.6	21	5	1*	11.1	1.7
29	3	1*	10.8	14.3	22	5	1*	5.8	-2.9
30	3	1	27.4	-26.9	23	5	1*	11.1	7.9
31	3	1*	10.8	-18.5	24	5	1	20.3	-14.2
32	3	1	40.7	38.1	25	5	1*	11.1	-12.3
33	3	1	11.1	11.4	26	5	1	27.4	21.8
34	3	1*	17.3	-15.8	28	5	1	26.4	-29.3
35	3	1	11.1	6.9	27	5	1*	10.8	9.2
36	3	1	18.3	-13.4	29	5	1*	10.6	-7.2
0	4	1	40.7	37.8	30	5	1	25.4	27.6
1	4	1	18.3	16.7	0	6	1*	11.1	5.1
2	4	1*	9.5	-8.2	1	6	1*	5.8	-9.3
3	4	1*	5.0	2.3	2	6	1*	11.1	-15.2
4	4	1*	9.5	-5.0	3	6	1*	5.8	5.4
5.	4	1*	5.0	-11.4	4	6	1*	11.1	10.9
6	4	1*	9.5	3.4	5	6	1*	5.8	-7.4
7	4	1*	5.1	5.5	6	6	1*	11.1	1.8
8	4	1*	9.3	-7.9	7	6	1*	5.8	9.9
9	4	1*	5.1	3.1	8	6	1*	11.1	-4-4
10	4	1*	9.8	-5.8	9	6	1*	5.8	-9.5
11	4	1*	5.1	-4.7	10	6	1*	10.8	6.6
12	4	1*	9.8	6.0	11	6	1*	5.7	4.4
13	4	1*	5.3	16.3	12	6	1*	10.8	-3.3
14	4	1	15.2	-14.2	13	6	1*	5.7	-3.0
15	4	1	22.4	29.8	14	6	1*	10.8	9.8
16	4	1*	10.0	7.5	15	6	1	19.3	-23.8
17	4	1*	5.6	-7.7	16	6	1*	10.8	-10.7
18	4	1	15.2	24.7	17	6	1*	5.6	10.5
19	4	1	20.3	-23.7	18	6	1*	10.6	-3.2
20	4	1	18.3	-22.8	19	6	1*	5.6	7.1
1	5	1*	10.8	1.5	20	6	1*	10.0	3.3
2	5	1*	5.7	4.7	21	6	1	16.3	18.3
3	5	1*	10.8	-2.3	22	6	1*	9.8	1.8
4	5	1*	5.7	9.6	23	6	1	15.2	-17.4
5	5	1*	10.8~~6~~	6.5	0	0	2	143.3	145.2

h	k	l	|Fo|	Fc
1	0	2	31.5	46.3
2	0	2	27.4	-30.3
3	0	2	18.3	16.0
4	0	2	49.8	50.7
5	0	2	36.6	38.0
6	0	2	65.0	-65.2
7	0	2	70.1	-71.2
8	0	2	28.5	21.7
9	0	2	40.7	36.7
10	0	2*	5.4	1.8
11	0	2	22.4	24.5
12	0	2	48.8	-48.0
13	0	2	36.6	-36.4
14	0	2	76.2	75.3
15	0	2*	6.5	-10.4
16	0	2	91.5	-91.3
17	0	2	23.4	-24.1
18	0	2*	7.6	-5.8
19	0	2	68.1	67.2
20	0	2*	7.6	-5.6
21	0	2	21.3	-21.4
22	0	2	43.7	36.8
23	0	2	50.8	54.4
24	0	2	40.7	-40.7
25	0	2	48.8	-50.4
26	0	2	33.5	29.8
27	0	2	37.6	36.2
28	0	2	13.2	-15.4
29	0	2*	8.6	-7.5
30	0	2*	8.1	-5.5
31	0	2	27.4	-26.7
32	0	2	30.5	25.9
33	0	2*	9.3	10.9
34	0	2*	8.5	3.7
35	0	2*	9.5	-11.9
36	0	2	23.4	21.2
37	0	2	35.6	30.0
38	0	2	28.5	-26.6
39	0	2*	9.5	-16.0
40	0	2*	8.7	15.0
41	0	2*	9.5	5.6
42	0	2	20.3	-21.6
43	0	2*	9.5	-9.8
44	0	2	18.3	17.3
45	0	2*	10.4	6.6
46	0	2	18.3	-13.4
6	1	2	53.9	47.5
7	1	2	22.4	-17.7
8	1	2	71.1	-57.4
9	1	2	22.4	17.5
10	1	2	55.9	50.8
11	1	2	18.3	-15.4
12	1	2	20.3	-25.5
13	1	2*	4.3	-1.4
14	1	2	12.2	-13.4
15	1	2	15.2	10.9
16	1	2	14.2	16.4
17	1	2*	5.0	5.6
18	1	2*	7.9	-15.4
19	1	2*	5.2	6.4
20	1	2	20.3	15.3
0	2	2	98.6	-113.3
1	2	2	62.0	-57.9
2	2	2	40.7	40.7
3	2	2*	7.9	1.8
4	2	2	42.7	-44.4
5	2	2*	7.9	-6.6
6	2	2	36.8	40.6
7	2	2*	7.9	14.5
8	2	2*	4.6	-7.9
9	2	2*	7.9	8.4
10	2	2	11.7	-8.4
11	2	2*	7.9	-6.4
12	2	2	38.6	37.3
13	2	2	24.4	30.2
14	2	2	58.9	-54.0
15	2	2*	8.4	7.3
16	2	2	73.2	68.4
17	2	2*	8.7	11.5
18	2	2*	5.4	-4.7
19	2	2	32.5	-34.8
20	2	2	15.2	11.0
21	2	2*	9.3	-6.0
22	2	2	27.4	-26.8
23	2	2*	9.6	-6.8
24	2	2	26.4	25.3
25	2	2*	9.8	5.0
26	2	2	21.3	-17.6
27	2	2*	10.3	- 7.0
28	2	2*	6.3	9.7
29	2	2*	10.6	2.2
30	2	2*	6.5	0.9
31	2	2*	10.6	6.4
32	2	2	20.3	-14.8
33	2	2*	10.9	11.9
34	2	2*	6.7	-5.4
35	2	2*	10.9	-7.8
36	2	2	20.3	-15.9
37	2	2*	10.9	-13.4
38	2	2	22.4	22.5

h	k	l	|Fo|	Fc
0	6	2	21.3	-20.2
1	6	2*	10.3	-4.9
2	6	2	19.3	19.1
3	2	2*	10.3	-1.7
4	6	2	19.3	-16.7
1	1	3	27.4	-19.1
2	1	3*	3.6	3.0
3	1	3	23.4	21.0
4	1	3	44.7	35.9
5	1	3*	6.6	10.4
6	1	3	52.9	-46.3
7	1	3*	6.6	7.8
8	1	3	87.4	79.1
9	1	3*	6.6	6.4
10	1	3	81.3	-75.5
11	1	3*	7.1	8.7
12	1	3	61.0	55.0
13	1	3*	7.7	-8.9
14	1	3*	4.9	-5.6
15	1	3*	9.2	-10.7
16	1	3	48.8	46.3
17	1	3	27.4	-29.8
18	1	3	35.6	-38.0
19	1	3*	9.0	-7.7
20	1	3	28.5	-33.4
21	1	3*	9.7	-0.5
22	1	3	16.3	15.4
23	1	3*	9.7	10.3
24	1	3	18.3	-15.2
25	1	3*	9.9	5.9
26	1	3	25.4	26.4
27	1	3*	10.4	4.2
28	1	3	40.7	-39.4
29	1	3*	10.7	6.5
30	1	3	31.5	33.8
31	1	3*	10.7	3.1
32	1	3	31.3	-30.7
33	1	3*	10.7	-2.8
34	1	3	20.7	19.2
0	2	3	47.8	-44.5
1	2	3*	4.6	-1.2
2	2	3	23.4	19.2
3	2	3	14.2	-16.3
4	2	3	18.3	-20.3
5	2	3	20.3	-24.2
6	2	3	14.2	15.1
7	2	3	44.7	42.3
8	2	3*	8.2	8.6
9	2	3	34.6	-31.0
10	2	3*	8.2	-6.8
11	2	3*	5.2	8.1
12	2	3	18.3	18.4
13	2	3*	5.2	9.1
14	2	3*	9.0	-10.8
15	2	3	20.3	-19.5
16	2	3*	9.0	4.4
17	2	3*	5.7	10.6
18	2	3	20.3	-17.3
19	2	3*	5.7	-2.9
20	2	3*	10.7	9.4
21	2	3	17.3	18.3
22	2	3*	10.2	1.9
23	2	3	25.4	-31.6
24	2	3*	10.2	2.9
25	2	3	28.5	35.3
26	2	3*	10.7	1.0
27	2	3	22.4	-24.6
28	2	3*	10.7	6.5
29	2	3*	6.3	1.7
30	2	3*	10.7	-7.2
31	2	3	19.3	22.4
32	2	3*	10.7	1.4
33	2	3	15.2	-14.3
34	2	3*	10.7	-9.0
35	2	3*	6.3	8.7
36	2	3*	10.7	-1.6
37	2	3	15.2	-17.0
1	3	3	14.2	9.2
2	3	3*	5.4	2.1
3	3	3	14.2	-15.5
4	3	3	13.2	-12.2
5	3	3*	9.7	-0.6
6	3	3*	5.7	-0.9
7	3	3*	9.7	-3.8
8	3	3*	5.7	-7.6
9	3	3*	9.7	-6.5
10	3	3*	5.7	3.2
11	3	3*	9.9	10.1
12	3	3	20.3	-22.6
13	3	3	16.3	-16.0
14	3	3	30.5	23.5
15	3	3	16.3	27.3
16	3	3	57.9	-55.8
17	3	3*	10.2	-5.5
18	3	3	41.7	45.8
19	3	3*	10.2	17.9
20	3	3*	9.4	8.9
21	3	3*	10.7	-5.4
22	3	3	18.3	-17.5
23	3	3*	10.7	- 9.1

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
24	3	3	25.4	25.0	13	5	3	18.3	15.6
25	3	3*	10.7	10.4	14	5	3	18.3	-18.1
26	3	3	22.4	-27.5	15	5	3*	10.7	-16.3
27	3	3	16.3	-18.5	16	5	3	30.5	29.0
28	3	3	25.4	29.3	17	5	3*	10.7	10.3
29	3	3	16.3	13.2	18	5	3	22.4	-21.7
30	3	3	20.3	-20.7	19	5	3*	10.2	-9.1
31	3	3	18.3	-16.9	20	5	3*	6.0	-1.2
32	3	3	18.3	18.5	21	5	3*	9.9	3.0
33	3	3*	10.7	10.5	22	5	3	16.3	13.8
34	3	3	15.2	-13.8	23	5	3*	9.9	4.1
35	3	3*	10.2	3.3	24	5	3	19.3	-19.2
36	3	3*	5.9	1.1	25	5	3*	9.7	-11.1
37	3	3*	9.5	-7.1	26	5	3	19.3	14.4
38	3	3*	5.9	5.4	0	6	3*	9.9	3.3
39	3	3*	5.6	3.1	1	6	3	25.4	-26.5
40	3	3	16.3	-14.7	0	0	4*	7.0	-12.1
41	3	3*	8.7	-5.5	1	0	4	44.7	44.0
42	3	3	16.3	14.3	2	0	4*	7.0	8.2
43	3	3*	7.7	4.3	4	[illegible]	4		
44	3	3	13.2	-10.4	5	0	4*	8.1	2.3
0	4	3*	10.2	16.3	6	0	4	16.8	-18.8
1	4	3	25.4	28.8	7	0	4*	8.3	8.8
2	4	3*	10.2	4.9	8	0	4	26.4	23.9
3	4	3*	6.3	5.2	9	0	4*	8.3	-18.9
4	4	3*	10.7	3.5	10	0	4*	7.2	-5.9
5	4	3*	6.3	13.0	11	0	4*	8.4	-3.9
6	4	3*	10.7	-9.5	12	0	4*	7.9	4.6
7	4	3	15.2	-18.9	13	0	4	21.3	-22.8
8	4	3*	10.7	-3.0	14	0	4	31.5	26.3
9	4	3*	6.3	6.7	15	0	4	15.2	15.1
10	4	3*	10.7	-4.5	16	0	4	42.7	-46.1
11	4	3*	6.3	7.7	17	0	4*	8.9	-11.2
12	4	3*	10.7	-4.0	18	0	4	26.4	-29.5
13	4	3	15.8	-15.1	19	0	4	15.2	11.8
14	4	3*	10.7	-4.0	20	0	4	13.2	10.4
15	4	3	20.3	21.0	21	0	4*	9.3	6.4
1	5	3*	10.7	0.4	22	0	4	27.4	28.8
2	5	3*	6.3	-10.9	23	0	4*	9.5	9.0
3	5	3*	10.7	3.5	24	0	4	23.4	-19.6
4	5	3*	6.3	11.6	25	0	4*	9.5	8.0
5	5	3*	10.7	2.6	26	0	4	20.3	18.7
6	5	3*	6.3	4.0	27	0	4*	9.5	-5.8
7	5	3*	10.7	-4.8	28	0	4*	8.7	-3.0
8	5	3*	6.3	-7.5	29	0	4*	9.5	-3.4
9	5	3*	10.7	6.5	30	0	4*	8.7	-10.2
10	5	3*	6.3	7.8	31	0	4*	9.5	7.6
11	5	3*	10.7	-13.7	32	0	4	19.3	19.9
12	5	3*	6.0	4.8	33	0	4*	9.5	-11.5
					34	0	4	17.3	-18.1

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
1	1	4	14.5	-11.7	8	3	4*	8.5	-5.3
2	1	4*	5.9	4.8	9	3	4*	7.3	-8.2
3	1	4*	4.9	3.7	10	3	4*	8.7	8.9
4	1	4*	5.9	-1.3	11	3	4*	7.3	-2.6
5	1	4	12.1	9.8	12	3	4*	8.7	-0.4
6	1	4*	6.3	3.6	13	3	4	15.2	13.4
7	1	4*	5.3	-7.2	14	3	4*	8.7	-7.2
8	1	4*	6.3	6.9	15	3	4	17.3	-17.7
9	1	4*	5.3	7.6	16	3	4*	8.7	15.7
10	1	4*	6.8	-8.2	17	3	4	17.3	16.3
11	1	4*	6.1	3.2	0	4	4	36.6	46.4
12	1	4*	7.3	0.8	1	4	4*	9.0	-0.8
13	1	4	14.2	-14.8	2	4	4	34.6	-40.6
14	1	4*	7.8	6.9	3	4	4*	9.0	-7.1
15	1	4	18.3	20.6	4	4	4	31.5	32.8
17	1	4	18.3	-20.2	5	4	4*	9.0	10.1
0	2	4	24.4	-27.0	7	4	4*	9.0	-11.5
1	2	4	24.4	-21.3	8	4	4*	7.5	-4.0
2	2	4	23.4	24.6	9	4	4*	9.0	-0.6
3	2	4	11.2	16.3	10	4	4	21.3	13.9
4	2	4	27.4	-26.6	11	4	4*	9.0	5.0
5	2	4	10.2	-6.6	12	4	4	20.3	-19.1
6	2	4	21.3	17.2	13	4	4*	9.0	-16.5
7	2	4*	7.3	2.5	14	4	4	25.4	28.0
8	2	4*	6.5	-7.9	15	4	4*	9.0	10.9
9	2	4*	7.8	8.8	16	4	4	25.4	-31.9
10	2	4*	6.5	-9.6	1	5	4	18.3	-19.1
11	2	4*	7.8	1.8	2	5	4*	8.7	0.4
12	2	4	19,3	12.7	0	6	4	19,3	-17.6
13	2	4	17.1	20.4	1	6	4*	7.3	-0.2
14	2	4	36.6	-34.4	2	6	4	19.3	16.0
15	2	4*	8.5	-13.6	3	6	4*	7.3	6.2
16	2	4	37.6	46.1	4	6	4	19.3	-16.1
1	3	4	20.3	24.6	0	0	6	36.6	45.2
2	3	4*	8.5	-6.7	2	0	6	30.5	-28.7
4	3	4*	8.5	1.7	3	0	6	21.3	-18.4
5	3	4*	7.1	-9.7	16	0	6	16.3	-19.8
6	3	4*	8.5	-10.8	20	0	6	13.2	-15.0
7	3	4*	7.1	3.7	22	0	6	14.2	12.8

SODIUM PYRUVATE

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
6	0	0	23.4	19.2	16	0	2	9.7	-12.6
8	0	0	67.8	-60.8	18	0	2	9.1	9.1
10	0	0	61.7	53.1	20	0	2	8.6	-8.5
12	0	0	15.7	-11.5	2	0	-2	45.9	47.8
14	0	0	18.1	-17.6	4	0	-2	48.8	-47.8
16	0	0	10.4	-8.9	6	0	-2	20.8	19.7
18	0	0	12.5	6.1	10	0	-2	32.9	-30.6
20	0	0	-24.8~~2~~	25.7	12	0	-2	21.0	21.6
22	0	0	10.2	-12.2	16	0	-2	18.0	17.4
24	0	0	5.0	6.0	18	0	-2	6.2	-7.5
26	0	0	8.0	-7.2	24	0	-2	10.8	-9.1
0	0	1	29.8	-30.1	26	0	-2	12.8	13.2
2	0	1	18.0	-18.6	4	0	3	5.0	-7.5
4	0	1	36.1	-38.4	18	0	3	8.2	7.6
6	0	1	7.3	-9.1	1	0	- 3	13.3	-13.8
8	0	1	38.5	45.0	12	0	-3	4.4	5.7
12	0	1	14.9	-23.1	14	0	-3	4.7	-5.5
14	0	1	15.0	19.6	16	0	-3	4.2	-6.7
20	0	1	7.9	8.6	18	0	-3	15.3	12.2
22	0	1	19.1	-16.1	20	0	-3	5.6	-7.4
24	0	1	5.2	-2.6	0	0	4	11.3	-16.7
26	0	1	6.6	6.0	2	0	4	6.5	10.1
2	0	-1	18.8	19.1	4	0	-4	9.0	9.3
4	0	-1	54.5	54.6	6	0	-4	7.1	-6.3
6	0	-1	14.5	-16.3	8	0	-4	13.8	14.4
8	0	-1	38.5	-34.1	10	0	-4	7.4	-7.9
10	0	-1	42.8	35.1	14	0	-4	8.5	8.2
12	0	-1	18.9	14.8	6	1	0	11.4	-12.8
14	0	-1	14.0	-12.6	7	1	0	22.2	16.3
16	0	-1	11.1	10.2	8	1	0	52.3	48.0
18	0	-1	35.9	-30.4	9	1	0	40.4	-35.7
20	0	-1	4.4	-4.4	10	1	0	17.1	-16.2
22	0	-1	25.3	22.4	11	1	0	13.0	-7.9
0	0	2	32.7	-34.7	12	1	0	22.6	-19.6
2	0	2	16.1	-15.3	13	1	0	6.3	4.5
4	0	2	47.0	52.4	14	1	0	17.9	19.8
6	0	2	23.1	-26.7	15	1	0	11.3	9.4
8	0	2	18.1	25.1	16	1	0	33.0	-30.6
10	0	2	5.3	-7.4	17	1	0	12.2	9.1
12	0	2	5.5	-11.4	18	1	0	8.8	8.1
14	0	2	6.2	6.9	19	1	0	13.4	-13.1

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
20	1	0	7.1	8.7	25	1	-1	5.7	5.8
21	1	0	3.7	-2.4	26	1	-1	4.6	-5.6
22	1	0	7.2	-9.8	27	1	-1	2.8	4.0
23	1	0	4.1	3.8	0	1	2	25.4	-27.5
24	1	0	6.3	9.0	1	1	2	5.2	5.6
25	1	0	3.4	3.6	2	1	2	6.7	6.2
0	1	1	35.6	-41.6	3	1	2	8.1	8.8
3	1	1	17.4	19.6	4	1	2	7.8	-7.7
4	1	1	15.6	17.8	5	1	2	8.8	-8.7
5	1	1	8.1	7.6	6	1	2	18.1	19.3
6	1	1	43.2	-36.1	7	1	2	5.3	-4.8
7	1	1	30.6	-32.8	9	1	2	7.5	9.3
8	1	1	17.8	20.3	10	1	2	13.1	-16.6
9	1	1	12.6	12.5	12	1	2	15.6	22.2
10	1	1	12.7	-13.8	13	1	2	3.5	-3.9
11	1	1	10.7	-10.4	14	1	2	5.1	-4.8
12	1	1	11.4	-11.9	15	1	2	3.5	4.9
13	1	1	19.2	20.5	17	1	2	6.0	-5.8
14	1	1	8.3	6.1	20	1	2	13.9	-13.8
15	1	1	9.8	1.7	21	1	2	4.7	3.7
16	1	1	9.0	5.6	22	1	2	3.9	3.2
17	1	1	19.3	-18.0	23	1	2	4.3	-3.8
18	1	1	13.8	12.3	1	1	-2	5.3	-5.2
19	1	1	12.9	11.5	2	1	-2	4.9	5.8
20	1	1	8.3	-6.7	3	1	-2	9.4	9.1
21	1	1	7.8	-6.6	5	1	-2	14.9	-17.7
22	1	1	3.0	2.8	6	1	-2	10.4	-8.7
23	1	1	6.0	4.6	7	1	-2	4.6	-4.7
24	1	1	3.7	-3.1	8	1	-2	22.3	-22.4
25	1	1	3.0	2.3	9	1	-2	11.1	16.8
26	1	1	4.4	-4.2	10	1	-2	25.0	25.8
1	1	-1	7.5	9.1	12	1	-2	18.0	-16.8
2	1	-1	64.0	-76.6	13	1	-2	3.5	1.1
3	1	-1	54.0	-61.0	14	1	-2	6.7	-6.1
4	1	-1	2.5	0.7	15	1	-2	7.1	-5.0
5	1	-1	35.3	33.1	16	1	-2	12.0	11.6
6	1	-1	9.5	10.9	18	1	-2	16.1	-13.9
7	1	-1	16.8	14.6	19	1	-2	4.4	3.9
8	1	-1	20.0	-20.1	20	1	-2	18.8	17.7
10	1	-1	30.8	32.6	22	1	-2	3.1	3.7
11	1	-1	20.1	15.0	24	1	-2	9.4	-8.6
12	1	-1	5.3	-3.9	25	1	-2	7.8	-7.2
13	1	-1	33.4	-38.2	0	1	3	3.4	3.5
15	1	-1	19.5	13.8	1	1	3	6.3	-7.4
17	1	-1	15.1	8.8	2	1	3	20.8	21.9
18	1	-1	4.4	2.1	3	1	3	9.5	10.2
21	1	-1	6.2	3.3	4	1	3	7.8	-7.2
22	1	-1	13.9	-10.9	5	1	3	7.8	-7.5
23	1	-1	15.3	-13.5	6	1	3	5.7	5.4
24	1	-1	5.4	5.6	8	1	3	7.7	-7.5

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
9	1	3	5.0	-4.5	1	2	0	6.5	-7.5
11	1	3	3.0	4.4	2	2	0	9.3	-5.6
12	1	3	5.7	4.7	3	2	0	23.1	20.2
13	1	3	5.5	4.8	4	2	0	12.3	-9.3
14	1	3	5.8	-6.4	5	2	0	2.4	1.4
15	1	3	8.0	-8.2	6	2	0	17.7	-11.9
17	1	3	7.3	6.2	7	2	0	9.5	-7.2
18	1	3	5.8	-5.2	8	2	0	23.3	15.2
1	1	-3	6.2	7.0	9	2	0	7.4	8.2
2	1	-3	13.9	15.5	10	2	0	17.9	16.1
3	1	-3	4.4	4.2	11	2	0	19.3	-15.4
4	1	-3	7.0	-9.3	12	2	0	5.9	3.4
5	1	-3	17.6	-17.9	13	2	0	14.3	13.4
6	1	-3	16.6	15.1	14	2	0	2.4	-0.5
7	1	-3	17.8	19.3	15	2	0	2.4	-1.6
8	1	-3	6.6	-6.0	16	2	0	7.3	-8.2
9	1	-3	7.7	-8.7	17	2	0	7.9	-7.8
10	1	-3	6.3	-4.1	19	2	0	7.2	6.6
11	1	-3	4.0	-2.9	21	2	0	6.2	-9.7
12	1	-3	13.8	14.4	23	2	0	4.5	6.6
13	1	-3	8.3	9.4	25	2	0	1.7	3.8
14	1	-3	5.6	-4.7	26	2	0	1.4	-2.8
15	1	-3	8.4	-11.2	0	2	1	8.4	-8.6
17	1	-3	6.5	5. 4	1	2	1	4.4	-3.9
18	1	-3	10.4	-8.1	2	2	1	27.4	30.5
19	1	-3	2.9	-1.0	3	2	1	49.0	44.8
22	1	-3	4.0	3.0	4	2	1	31.5	-29.4
0	1	4	9.6	9.4	5	2	1	39.7	-37.2
1	1	4	7.9	7.4	6	2	1	31.9	31.7
2	1	4	6.8	-5.6	7	2	1	11.3	-7.7
3	1	4	7.1	-7.5	9	2	1	11.2	7.6
4	1	4	5.5	-6.1	10	2	1	15.6	-17.2
5	1	4	4.2	-4.4	11	2	1	11.2	-11.7
6	1	4	2.5	2.7	12	2	1	13.6	11.0
7	1	4	2.5	4.1	13	2	1	22.2	23.6
8	1	4	6.3	-6.7	14	2	1	24.1	-24.1
9	1	4	2.6	2.5	15	2	1	9.6	-7.9
10	1	4	7.0	5.8	16	2	1	13.2	10.7
3	1	-4	4.7	-3.6	17	2	1	9.7	-8.7
4	1	-4	5.7	-5.2	19	2	1	4.5	4.2
6	1	-4	3.4	1.7	20	2	1	2.8	3.6
7	1	-4	6.5	-6.9	22	2	1	8.5	7.0
9	1	-4	3.7	2.2	23	2	1	4.9	4.9
10	1	-4	6.2	-6.9	24	2	1	4.2	-3.5
11	1	-4	6.5	7.4	1	2	-1	3.4	3.5
12	1	-4	5.3	6.0	2	2	-1	9.2	8.7
13	1	-4	3.9	-2.7	3	2	-1	8.8	-8.1
14	1	-4	3.0	-2.1	4	2	-1	15.1	18.3
15	1	-4	3.0	-2.9	5	2	-1	21.0	26.1
16	1	-4	8.3	7.3	6	2	-1	37.0	-46.6
					7	2	-1	26.2	-25.4

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
8	2	-1	13.3	12.3	24	2	-2	5.3	4.0
9	2	-1	2.2	0.6	25	2	-2	6.1	6.0
10	2	-1	25.2	-22.7	11	2	-2	3.5	3.4
11	2	-1	5.7	2.5	0	2	3	11.3	11.0
12	2	-1	9.7	9.0	1	2	3	9.3	10.1
13	2	-1	2.7	3.9	2	2	3	13.7	-14.1
14	2	-1	15.5	15.9	3	2	3	20.4	-20.7
15	2	-1	13.5	11.9	4	2	3	4.5	6.2
16	2	-1	16.4	-15.7	5	2	3	5.8	5.4
17	2	-1	15.4	-13.6	6	2	3	9.2	9.1
18	2	-1	15.5	14.4	7	2	3	17.9	19.5
19	2	-1	4.0	4.1	8	2	3	6.6	-7.6
20	2	-1	7.6	-5.0	9	2	3	11.1	-13.9
22	2	-1	4.7	3.0	10	2	3	10.3	13.6
23	2	-1	2.4	-2.0	11	2	3	2.5	2.3
24	2	-1	4.2	4.4	12	2	3	6.5	-8.0
25	2	-1	4.4	3.9	13	2	3	5.4	-4.2
26	2	-1	9.4	-8.5	15	2	3	3.9	-4.3
2	2	2	3.1	-2.4	16	2	3	3.2	2.7
3	2	2	4.0	-2.7	1	2	-3	5.2	4.5
4	2	2	4.8	-5.6	2	2	-3	12.9	-13.7
5	2	2	17.1	-15.9	3	2	-3	6.3	-7.9
6	2	2	4.7	-4.2	4	2	-3	2.8	1.7
7	2	2	3.4	2.2	5	2	-3	8.4	-8.5
9	2	2	8.4	8.6	7	2	-3	14.7	14.4
11	2	2	11.2	14.3	8	2	-3	6.3	-6.2
13	2	2	7.8	-9.6	9	2	-3	4.9	6.6
14	2	2	3.6	4.4	10	2	-3	12.3	12.3
15	2	2	10.9	-11.1	12	2	-3	6.4	-7.0
16	2	2	4.6	3.6	13	2	-3	14.5	-14.1
17	2	2	9.0	9.2	14	2	-3	9.1	10.1
18	2	2	2.6	-0.8	17	2	-3	8.2	4.5
19	2	2	3.1	-3.6	18	2	-3	7.7	-5.3
21	2	2	4.9	5.1	20	2	-3	8.6	6.5
22	2	2	2.9	-0.1	21	2	-3	6.6	5.4
1	2	-2	12.9	-12.5	1	2	4	2.3	2.2
3	2	-2	13. 6	-12.9	2	2	4	2.4	2.1
4	2	-2	11.3	13.4	3	2	4	2.3	2.3
5	2	-2	35.9	35.8	4	2	4	2.2	1.8
6	2	-2	6.3	7.4	1	2	-4	9.8	10.9
7	2	-2	4.5	-6.7	5	2	-4	9.5	-10.2
8	2	-2	3.3	-3.0	6	2	-4	4.0	4.3
9	2	-2	15.2	-13.7	7	2	-4	7.1	7.2
10	2	-2	3.4	4.8	8	2	-4	6.1	-4.5
12	2	-2	9.3	-9.6	9	2	-4	6.0	-5.9
13	2	-2	15.6	-15.0	10	2	-4	4.1	-4.6
15	2	-2	15.5	16.0	11	2	-4	4.3	4.7
17	2	-2	6.8	5.5	13	2	-4	8.5	7.6
18	2	-2	6.0	-6.5	14	2	-4	3.0	-3.8
19	2	-2	9.5	-9.1	1	3	0	10.1	-10.6

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
2	3	0	5.6	3.2	12	3	-1	2.9	1.7
3	3	0	26.0	24.0	13	3	-1	8.8	5.9
4	3	0	26.4	-23.0	14	3	-1	20.0	-16.1
5	3	0	42.2	-38.3	15	3	-1	5.5	3.1
7	3	0	36.1	29.5	16	3	-1	3.9	2.5
8	3	0	8.0	6.6	17	3	-1	5.5	-4.2
9	3	0	7.1	-6.7	18	3	-1	8.6	7.9
10	3	0	7.8	-6.1	19	3	-1	5.3	4.6
11	3	0	4.9	-2.4	20	3	-1	3.6	-3.7
12	3	0	3.6	5.2	22	3	-1	3.1	3.6
13	3	0	20.0	19.8	23	3	-1	2.3	3.4
14	3	0	3.0	2.9	25	3	-1	1.8	-2.4
15	3	0	22.6	-23.0	1	3	2	19.2	21.1
17	3	0	9.9	1.5	2	3	2	4.8	-5.1
18	3	0	3.6	4.4	3	3	2	25.1	-29.0
19	3	0	2.9	-2.9	4	3	2	16.3	17.6
20	3	0	3.4	3.2	5	3	2	18.1	14.9
21	3	0	3.2	-4.6	6	3	2	7.2	7.5
22	3	0	2.4	-3.0	8	3	2	14.6	-15.0
23	3	0	5.2	5.3	9	3	2	20.3	-18.4
24	3	0	3.1	-3.6	10	3	2	6.8	-8.7
25	3	0	4.8	-5.7	11	3	2	21.2	21.0
0	3	1	10.4	-11.6	13	3	2	14.5	-12.4
2	3	1	13.1	-13.1	14	3	2	4.1	4.9
3	3	1	4.5	4.9	15	3	2	4.6	3.4
4	3	1	4.9	4.4	16	3	2	5.7	6.8
5	3	1	3.8	-4.5	17	3	2	5.7	6.8
6	3	1	12.3	11.4	19	3	2	6.6	-6.2
7	3	1	5.7	5.6	20	3	2	4.3	-4.2
8	3	1	9.1	9.5	1	3	-2	10.8	-10.7
9	3	1	3.5	-0.8	2	3	-2	3.2	1.2
10	3	1	11.2	8.3	3	3	-2	2.8	1.8
12	3	1	20.2	-16.0	4	3	-2	2.8	-2.2
13	3	1	6.1	-5.4	5	3	-2	12.4	12.9
16	3	1	7.3	7.3	6	3	-2	14.2	-16.0
17	3	1	5.3	4.2	7	3	-2	10.8	-12.0
18	3	1	4.8	-3.9	8	3	-2	5.3	5.5
19	3	1	3.1	-4.5	9	3	-2	13.7	14.5
21	3	1	3.9	5.3	10	3	-2	19.6	18.0
22	3	1	4.4	-5.2	11	3	-2	13.4	-15.6
1	3	-1	5.4	-5.9	12	3	-2	4. 3	3.2
2	3	-1	2.1	-1.9	13	3	-2	5.5	7.8
3	3	-1	14.5	14.0	14	3	-2	3.0	-4.7
4	3	-1	9.8	-10.7	15	3	-2	3.0	1.3
5	3	-1	6.5	-8.2	16	3	-2	3.2	-5.7
6	3	-1	18.0	15.4	17	3	-2	11.0	-12.4
7	3	-1	11.7	-11.1	19	3	-2	13.4	12.7
9	3	-1	9.7	8.1	21	3	-2	7.6	-9.0
10	3	-1	6.5	-6.5	23	3	-2	2.1	2.6
11	3	-1	7.6	-9.0	0	3	3	3.8	3.3

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
1	3	3	4.5	4.1	6	4	0	6.4	-4.7
2	3	3	3.8	4.2	7	4	0	13.9	12.8
3	3	3	2.9	-1.9	8	4	0	3.0	-2.9
6	3	3	7.4	-8.3	9	4	0	17.4	-16.7
11	3	3	3.6	2.5	10	4	0	5.1	-4.0
13	3	3	6.9	-3.9	11	4	0	10.0	8.7
14	3	3	6.7	1.4	12	4	0	15.1	-16.0
1	3	-3	1.9	4.2	14	4	0	11.7	12.3
2	3	-3	4.2	-5.2	15	4	0	3.3	3.5
3	3	-3	8.6	9.7	16	4	0	4.9	6.1
4	3	-3	6.4	7.6	17	4	0	3.3	3.7
5	3	-3	9.2	9.9	18	4	0	5.0	-6.4
6	3	-3	9.7	-11.4	19	4	0	5.2	-5.3
7	3	-3	6.6	-8.6	20	4	0	2.6	2.6
8	3	-3	3.2	-5.8	21	4	0	4.1	4.8
10	3	-3	7.4	-6.0	0	4	1	2.3	-4.4
11	3	-3	8.5	9.2	1	4	1	8.0	6.4
12	3	-3	3.5	4.2	2	4	1	4.0	2.9
13	3	-3	8.4	-8.6	3	4	1	4.2	-2.7
14	3	-3	9.9	11.5	4	4	1	2.9	-3.3
16	3	-3	7.9	-5.1	5	4	1	21.3	12.4
19	3	-3	7.0	-5.5	6	4	1	3.4	4.7
1	3	4	7.9	-8.7	7	4	1	17.3	-12.1
3	3	4	3.1	4.0	8	4	1	16.1	-14.4
1	3	-4	10.6	9.9	10	4	1	4.9	3.6
2	3	-4	3.8	-2.6	11	4	1	16.3	13.5
3	3	-4	5.7	-4.9	12	4	1	17.9	15.5
4	3	-4	3.0	3.0	13	4	1	10.9	-8.6
6	3	-4	7.9	7.9	14	4	1	8.2	-7.4
10	3	-4	3.9	-4.3	15	4	1	6.2	5.6
2	4	0	3.3	2.1	16	4	1	6.6	5.6
3	4	0	12.7	-12.8	17	4	1	6.2	-5.6
4	4	0	21.6	17.3	18	4	1	3.8	-3.1
5	4	0	8.9	-8.2	19	4	1	8.0	-7.6
					20	4	1	5.5	-5.1

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
21	4	1	7.2	7.3	3	4	-2	15.5	17.1
1	4	-1	3.5	5.6	4	4	-2	5.2	-6.1
2	4	-1	3.4	-3.0	5	4	-2	8.4	-7.3
3	4	-1	8.0	9.6	6	4	-2	2.6	1.6
4	4	-1	8.0	-7.1	7	4	-2	6.2	8.0
5	4	-1	3.2	-2.3	8	4	-2	9.7	-9.0
6	4	-1	4.4	4.9	9	4	-2	3.3	3.8
7	4	-1	5.7	6.2	10	4	-2	9.1	7.8
8	4	-1	23.7	23.3	11	4	-2	12.3	-13.3
9	4	-1	15.3	-15.1	12	4	-2	3.2	5.2
10	4	-1	12.1	-13.1	13	4	-2	7.1	10.3
11	4	-1	5.7	5.8	14	4	-2	7.2	-8.0
13	4	-1	4.9	4.0	16	4	-2	9.4	6.2
15	4	-1	12.6	-12.1	19	4	-2	5.7	-4.5
16	4	-1	11.0	-9.9	20	4	-2	1.5	-0.5
17	4	-1	9.5	8.7	21	4	-2	4.2	-4.6
18	4	-1	11.7	11.3	0	4	3	10.4	4.9
19	4	-1	4.3	-4.5	1	4	3	9.0	-12.4
20	4	-1	3.1	-3.9	4	4	3	2.1	0.7
22	4	-1	8.7	-6.7	5	4	3	2.2	-1.0
0	4	2	6.6	5.5	6	4	3	2.3	-3.1
1	4	2	6.8	7.4	8	4	3	2.3	-5.6
3	4	2	14.9	-12.2	9	4	3	8.3	8.4
4	4	2	2.8	-1.6	10	4	3	3.5	4.3
5	4	2	6.8	5.3	11	4	3	10.9	-7.9
7	4	2	10.4	-10.0	1	4	-3	3.0	-4.7
8	4	2	5.8	6.0	3	4	-3	3.0	-4.9
9	4	2	6.0	7.9	4	4	-3	3.0	5.2
10	4	2	2.3	-4.3	6	4	-3	2.3	-2.6
12	4	2	2.3	1.4	7	4	-3	2.2	1.1
13	4	2	4.1	-5.3	9	4	-3	5.2	5.9
16	4	2	8.0	-6.2	10	4	-3	2.7	4.3
17	4	2	6.3	-4.7	11	4	-3	7.1	-7.6
1	4	-2	17.8	-20.0	12	4	-3	8.2	-9.2
2	4	-2	3.3	-5.7					