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

CRYSTAL DATA AND EXPERIMENTAL DETAILS

(A) Sodium 2-oxo valerate (C₅H₇O₃Na) prepared by adding concentrated solution of sodium hydroxide to the alcoholic solution of L-keto valeric acid, is highly soluble in water. Crystals were grown from water-alcohol mixture as very thin flakes elongated on (100) face. 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 (Davies, 1960). Axial lengths a, b and c were measured from high angle reflexions in equatorial Wäissenberg photographs. These values are

a = 34.08 Å  
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

\[ n = \frac{V \cdot N \cdot \rho}{M} \]

where \( n \) is number of molecules per unit cell; \( V \) is volume of the unit cell; \( N \) is Avagadro's number; \( \rho \) 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:

\[ \mu \text{ cm}^{-1} \] for CuK$_\alpha$ radiation was calculated by the formula

\[ \mu = \frac{\rho \sum n \mu_g}{\sum n \omega} \text{ cm}^{-1} \]

where \(\rho\) is density in gm cm$^{-3}$, \(n\) is relative number of atoms present, \(\mu_g\) is gm atomic absorption coefficient, and \(\sum \omega\) is sum of the atomic weights of the elements present. \(\mu_g\) for carbon, oxygen and sodium is 66, 203 and 711 respectively. Thus \(\mu\) calculated for CuK$_\alpha$ 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 CuK$_\alpha$ radiations. The crystal used was roughly of 0.6 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, h0l, hkl, 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 reflection-spot which at the same time was well separated from other spots was chosen and the crystal was oscillated through \(10^\circ\) about the angle giving this reflection 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 follow:

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 \(2\theta\) consists only of the components of
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

\[
\frac{1}{L} = \left( \frac{\cos \theta}{\cos \theta_0} \right)^{-1}
\]

for equi-inclination photographs and

\[
\frac{1}{L} = \left( \sin^2 \theta \right)^{-1/2}
\]

for normal beam photographs. For zero layer \( \theta_0 = 0 \) and \( \cos \theta_0 = 2 \sin \theta \)

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

This can be interpreted as the relative time\( \Delta \) 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 obviously move slowly than those which are away.

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

\[
D = \frac{(\sin^2 2 \theta - \cos^2 \theta_0)^{1/2}}{1 + \cos^2 2 \theta}
\]

for normal beam photographs

\[
D = \frac{(\cos \theta_0 \cos \theta)}{1 + \cos^2 2 \theta}
\]

for equi-inclination

All the intensities were corrected for the \( Lp \) factor with the help of curves given by Oochran (1948).

Since the calculated absorption coefficient \( \mu \) for CuK\( \alpha \) radiation of the compound is quite small, therefore, absorption correction was neglected.

\( \text{(ii) Correction for spot extension:} \)

In upper-level Weisseneberg 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 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 divided 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 (1956) as

\[ W = \frac{A + \Delta A}{A} \]

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 \( I = \frac{W}{I_E} \).

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 (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 (1914) gave the relation

$$f = f_0 \exp \left(-B \frac{(\sin \theta)^2}{\lambda^2}\right)$$

where $f$ is scattering at a temp; $f_0$ 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 (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

$$\langle I_{\text{abs}} \rangle = \langle |F|^2 \rangle = \sum_{n=1}^{N} f_n^2$$

and

$$K \langle I_{\text{obs}} \rangle = \langle I_{\text{abs}} \rangle$$

$$K \langle I_{\text{obs}} \rangle = \sum_{n=1}^{N} f_0^2 e^{-2B \left(\frac{\sin \theta}{\lambda}\right)^2}$$
taking logarithms of both sides we get

$$\log_{e}K = \log_{e} \left( \frac{\sum_{n=1}^{N} f_{o}^2}{\langle I_{obs} \rangle} \right) - 2B \left( \sin \frac{\theta}{\lambda} \right)^2$$

or

$$\log_{e} \left( \frac{\sum_{n=1}^{N} f_{o}^2}{\langle I_{obs} \rangle} \right) = 2B \left( \sin \frac{\theta}{\lambda} \right)^2 + \log_{e}K$$

thus plot of \( \log_{e} \left( \frac{\sum_{n=1}^{N} f_{o}^2}{\langle I_{obs} \rangle} \right) \) against \( \left( \sin \frac{\theta}{\lambda} \right)^2 \) 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 \( \sin \theta \) (as shown in table 1 and 2). The mean value of observed intensities \( \langle I_{obs} \rangle \) 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. \( \sum f_{o}^2 \) was obtained by

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

McWeeny's 10 (1961) values of atomic scattering factors were used for carbon and oxygen; and for Na\(^+\) that of James and Brindley 11 (1931) was used. \( \log_{e}C \) was plotted against \( \left( \sin \frac{\theta}{\lambda} \right)^2 \) for each zone, where C is \( \sum_{n=1}^{N} f_{o}^2 / \langle I_{obs} \rangle \). 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 absences are:

- \( \text{hk}0 \) for \( \text{h} + \text{k} = \text{odd} \);
- \( \text{h}0\text{l} \) for \( \text{l} = \text{odd} \).
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**

<table>
<thead>
<tr>
<th>Sin θ</th>
<th>Sin²θ</th>
<th>&lt;I&gt;</th>
<th>(\sum f_n^2)</th>
<th>C = (\frac{\sum f_n^2}{&lt;I&gt;})</th>
<th>logₑC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 - 0.4</td>
<td>0.0379</td>
<td>2.17</td>
<td>1913</td>
<td>852</td>
<td>6.7822</td>
</tr>
<tr>
<td>0.3 - 0.4</td>
<td>0.0515</td>
<td>1.94</td>
<td>1585</td>
<td>817</td>
<td>6.7057</td>
</tr>
<tr>
<td>0.4 - 0.5</td>
<td>0.0851</td>
<td>1.34</td>
<td>1073</td>
<td>801</td>
<td>6.6859</td>
</tr>
<tr>
<td>0.55-0.65</td>
<td>0.1514</td>
<td>0.61</td>
<td>619</td>
<td>1014</td>
<td>6.9216</td>
</tr>
<tr>
<td>0.6 - 0.7</td>
<td>0.1779</td>
<td>0.57</td>
<td>521</td>
<td>914</td>
<td>6.8179</td>
</tr>
<tr>
<td>0.7 - 0.8</td>
<td>0.2371</td>
<td>0.35</td>
<td>377</td>
<td>1047</td>
<td>6.9537</td>
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</table>

From the graph No. 1a, B = 1.1 Å² and K = 23

**TABLE 2**

<table>
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<tr>
<th>Sin θ</th>
<th>Sin²θ</th>
<th>&lt;I&gt;</th>
<th>(\sum f_n^2)</th>
<th>C = (\frac{\sum f_n^2}{&lt;I&gt;})</th>
<th>logₑC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 - 0.4</td>
<td>0.0379</td>
<td>3.158</td>
<td>1913</td>
<td>605.8</td>
<td>6.4066</td>
</tr>
<tr>
<td>0.3 - 0.4</td>
<td>0.0515</td>
<td>3.129</td>
<td>1583</td>
<td>861.7</td>
<td>6.7589</td>
</tr>
<tr>
<td>0.4 - 0.5</td>
<td>0.0851</td>
<td>0.909</td>
<td>1073</td>
<td>1181.0</td>
<td>7.0742</td>
</tr>
<tr>
<td>0.5 - 0.6</td>
<td>0.1273</td>
<td>0.441</td>
<td>735</td>
<td>1665.2</td>
<td>7.4176</td>
</tr>
<tr>
<td>0.6 - 0.7</td>
<td>0.1779</td>
<td>0.223</td>
<td>521</td>
<td>2332.1</td>
<td>7.7546</td>
</tr>
<tr>
<td>0.7 - 0.8</td>
<td>0.2371</td>
<td>0.179</td>
<td>377</td>
<td>1397.3</td>
<td>7.5482</td>
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</table>

From the graph No. 1b, B = 3.6 Å² and K = 25
CHAPTER 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.

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

where \((x, y, z)\) 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:

(1) 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

\[ P(u, v, w) = V \sum_{x} \sum_{y} \sum_{z} \rho(x, y, z) \rho(x+u, y+v, z+w) \, dx \, dy \, dz \ldots . \]  --(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:
\[ P(u, v, w) = \frac{1}{V} \sum_{h}^{+\infty} \sum_{k}^{+\infty} |F(hkl)|^2 \exp\left[-2\pi \frac{i}{h} (hu + kv + lw)\right] \] ..... (3)

If \( |F(hkl)| = |\tilde{F}(hkl)| \) the above equation (3) simplifies to
\[ P(u, v, w) = \frac{1}{2V} \sum_{h}^{+\infty} \sum_{k}^{+\infty} |\tilde{F}(hkl)|^2 \cos 2\pi (hu + kv + lw) \] ..... (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. Nevertheless, 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 obscure or distort the neighbouring peaks. For this, instead of $|F^2|$ coefficient $|F^2_M|$ are used as coefficient where $|F^2_M| = M(S) |F^2|$ and $M(S)$ is any modifying (or sharpening) function.

Patterson (1936 b) used the following modification to increase the resolution of peaks in case of CuSO$_4$·5H$_2$O which is

$$M(S) = \left( \frac{1}{\hat{F}} \right)^2 \exp \left[ - \frac{\pi^2}{p} S^2 \right]$$

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

Schomaker and Shoemaker suggested (unpublished) the following modification:

$$M(S) = \left( \frac{1}{\hat{F}} \right)^2 S^2 \exp \left[ - \frac{\pi^2}{p^2} S^2 \right]$$

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 lattice 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 \(1\ \text{r.l.u.} = 20\ \text{cms for } a^* \) (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:

\[
\begin{align*}
x, y, z; & \quad \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z; \quad \frac{1}{2}+x, \frac{1}{2}-y, z; \quad \overline{x}, y, \frac{1}{2}-z \\
\overline{x}, \overline{y}, \overline{z}; & \quad \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z; \quad \frac{1}{2}-x, \frac{1}{2}+y, z; \quad x, \overline{y}, \frac{1}{2}+z
\end{align*}
\]

origin being at \(\overline{1}\).

\(x\) 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 \(Na(\overline{x}, \overline{y})\) falling at \((2x, 0)\).

**Peak No. 2** was presumed to be due to interaction between \(Na(x, y)\) and \(Na(\overline{x}, \overline{y})\) 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 \(c = 5.97\) \(\AA\); while those of sodium 2-oxo-caprylate (Tavale, Pant and Biswas, 1964) are similar except that of 'a' which is longer by about 15.5 \(\AA\). Assuming the usual bond-lengths and angles this is the expected decrease in 'a' axis of 20x0 valerate for a structure iso-typic with 2oxo 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

<table>
<thead>
<tr>
<th>Atoms</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.217</td>
<td>0.230</td>
<td>0.000</td>
</tr>
<tr>
<td>O1</td>
<td>0.219</td>
<td>0.158</td>
<td>0.383</td>
</tr>
<tr>
<td>O2</td>
<td>0.150</td>
<td>0.161</td>
<td>0.200</td>
</tr>
<tr>
<td>O3</td>
<td>0.195</td>
<td>0.377</td>
<td>0.670</td>
</tr>
<tr>
<td>C1</td>
<td>0.193</td>
<td>0.238</td>
<td>0.490</td>
</tr>
<tr>
<td>C2</td>
<td>0.161</td>
<td>0.245</td>
<td>0.370</td>
</tr>
<tr>
<td>C3</td>
<td>0.117</td>
<td>0.290</td>
<td>0.503</td>
</tr>
<tr>
<td>C4</td>
<td>0.078</td>
<td>0.240</td>
<td>0.402</td>
</tr>
<tr>
<td>C5</td>
<td>0.042</td>
<td>0.235</td>
<td>0.573</td>
</tr>
</tbody>
</table>

(B) Electron density projection and refinement of parameters:

Structure factor and electron density expressions for (hko) projection are derived which contribute to:

\[
F(hko) = \sum_{n=1}^{N} 8f_n \cos 2\pi h x_n \cos 2\pi k y_n \ldots \ldots (1)
\]

\[
\rho(x,y,z) = \frac{1}{A} \left[ F(000) + 2\sum_{h=1}^{\infty} F(h00) \cos 2\pi h x + \sum_{k=1}^{\infty} F(0k0) \cos 2\pi k y \right] + 4 \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} F(hk0) \cos 2\pi h x \cos 2\pi k y \ldots \ldots (2)
\]

(1) 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 $\theta$ 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, Mckeeny'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 ($B=1.1\,\text{Å}$) obtained by Wilson's method (Part I, chapter 1) was used.

Atomic scattering values at the required temperature were obtained by

$$f_n = f_0\, e^{-B\left(\frac{\sin \theta}{\lambda}\right)^2}$$

where $f_0$ 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 $F_o$ values. The reliability index 'A' given by

$$R = \frac{\sum \left( |F_o| - |F_c| \right)}{\sum |F_o|}$$

came out to be $\approx 0.22$ for observed reflections 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. Every-
time 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>
<thead>
<tr>
<th>Atoms</th>
<th>Trial</th>
<th>I Fourier</th>
<th>II Fourier</th>
<th>III Fourier</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>y</td>
<td>x</td>
<td>y</td>
<td>x</td>
</tr>
<tr>
<td>Na</td>
<td>0.217</td>
<td>0.230</td>
<td>0.217</td>
<td>0.237</td>
</tr>
<tr>
<td>O1</td>
<td>0.219</td>
<td>0.158</td>
<td>0.219</td>
<td>0.162</td>
</tr>
<tr>
<td>O2</td>
<td>0.150</td>
<td>0.161</td>
<td>0.150</td>
<td>0.165</td>
</tr>
<tr>
<td>O3</td>
<td>0.195</td>
<td>0.377</td>
<td>0.195</td>
<td>0.379</td>
</tr>
<tr>
<td>Cl</td>
<td>0.193</td>
<td>0.238</td>
<td>0.193</td>
<td>0.258</td>
</tr>
<tr>
<td>C2</td>
<td>0.151</td>
<td>0.245</td>
<td>0.151</td>
<td>0.240</td>
</tr>
<tr>
<td>C3</td>
<td>0.117</td>
<td>0.290</td>
<td>0.117</td>
<td>0.276</td>
</tr>
<tr>
<td>C4</td>
<td>0.078</td>
<td>0.240</td>
<td>0.078</td>
<td>0.206</td>
</tr>
<tr>
<td>C5</td>
<td>0.042</td>
<td>0.235</td>
<td>0.042</td>
<td>0.270</td>
</tr>
<tr>
<td>( R \approx 0.220 )</td>
<td>( R \approx 0.190 )</td>
<td>( R \approx 0.175 )</td>
<td>( R \approx 0.158 )</td>
<td></td>
</tr>
</tbody>
</table>

In all these cases \( R \approx \) factor was calculated excluding
1800, & 020 reflexions (reflexion 1800 showed serious dis-
agreement 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
effects 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

\[ R_1 = \sum_{\text{U}} \omega_1 (hkl) (|F_0(hkl)| - |F_c(hkl)|)^2 \]

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. "\( \sum_{\text{U}} \)" denotes the summation over all structure factors included in refinement. Fo has the sign of Fc. Shoemaker and collaborator (1950) suggested the minimization of function \( R_2 \) which is given as:

\[ R_2 = \sum_{\text{U}} \omega_2 (hkl) (|F_0(hkl)|^2 - |F_c(hkl)|^2)^2 \]

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 \( \Delta x_n \) in the x-coordinate of the \( n^{th} \) atom is

\[ \frac{F_c}{x_n} \Delta x_n. \]

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

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

The correct \( \Delta x_n, \Delta y_n \) & \( \Delta z_n \) are those which most nearly equate \( \Delta Fc \) to \( (F_0 - F_c) \). This implies that as many equations .
shall be available as many structure factors are included in refinement. Obviously, the number of this type of equations should be considerably greater than the independent coordinates to be refined.

Multiplying both sides by $\frac{\partial F_c}{\partial \Delta x_n}$ to (3) and putting $(F_o-F_c)$ for $\Delta F_c$ and summing up for all the terms (reflections) we get

$$\sum \frac{\partial F_o}{\partial \Delta x_n} \frac{\partial F_c}{\partial \Delta x_n} = \sum \left( \frac{\partial F_c}{\partial \Delta y_n} \frac{\partial F_c}{\partial \Delta y_n} + \frac{\partial F_c}{\partial \Delta z_n} \frac{\partial F_c}{\partial \Delta z_n} \right)$$

where $\sum$ denotes sum over all atoms except $n^{th}$. The next normal equation can be formed by multiplying both sides by $\frac{\partial F_c}{\partial \Delta x_{n+1}}$ and getting equations as earlier. Thus getting as many normal equations as many unknowns are to be solved, one can get $\Delta x_n$, $\Delta y_n$ and $\Delta z_n$ 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 $\sum \frac{\partial F_c}{\partial \Delta x_n} \frac{\partial F_c}{\partial \Delta x_n}$ are likely to be comparably smaller than $\sum \frac{\partial F_c}{\partial \Delta x_n}$ and if the axes are orthogonal or nearly so then $\sum \frac{\partial F_c}{\partial \Delta x_n} \frac{\partial F_c}{\partial \Delta y_n}$ are small enough to be neglected and therefore equation (4) reduces to

$$\sum \frac{\partial F_o}{\partial \Delta x_n} \frac{\partial F_c}{\partial \Delta x_n} = \Delta x_n \sum \frac{\partial F_c}{\partial \Delta x_n}$$

or

$$\Delta x_n = \frac{\sum \frac{\partial F_c}{\partial \Delta x_n}}{\sum \frac{\partial F_c}{\partial \Delta x_n}}$$

similarly we can derive equations for $\Delta y_n$ and $\Delta z_n$.

However, if $i^{th}$ and $j^{th}$ atoms in any projection are not well resolved than the quantities such as $\sum \frac{\partial F_c}{\partial \Delta x_n} \frac{\partial F_c}{\partial \Delta y_n}$ cannot be neglected compared to $\sum \left( \frac{\partial F_c}{\partial \Delta x_n} \right)^2$ and so the equations...
\[ \Delta x_i \sum \frac{\partial F_c}{\partial x_i} + \Delta y_j \sum \frac{\partial F_c}{\partial x_j} = \sum \frac{(F_0 - F_c)}{q} \Delta x_i \quad \text{and} \quad \Delta x_i \sum \frac{\partial F_c}{\partial x_i} \Delta y_j + \Delta x_i \sum \frac{(\partial F_c)}{\partial y_j} = \sum \frac{(F_0 - F_c)}{q} \Delta y_j \]

be solved for \( \Delta x_i \) and \( \Delta y_j \). Similarly equations for \( \Delta y_j \), \( \Delta x_i \), and \( \Delta z_j \) could be deduced.

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

For \( (hk0) \) projection the formula is

\[ F(hk0) = \sum_{n=1}^{N} 8 f_n \cos 2\pi h x_n \cos 2\pi k y_n \]

differentiating this with respect to \( x_n \), we get

\[ \frac{\partial F_c}{\partial x_n} = -8 f_n 2\pi h \sin 2\pi h x_n \cos 2\pi k y_n \sum \frac{(F_0 - F_c)}{q} (-8 \pi h f_n \sin 2\pi h x_n \cos 2\pi k y_n) \]

\[ \therefore \Delta x_n = \frac{-8 \pi h f_n \sin 2\pi h x_n \cos 2\pi k y_n \sum (F_0 - F_c)}{(-8 \pi h f_n \sin 2\pi h x_n \cos 2\pi k y_n)^2} \]

and similarly for \( \Delta y_n \) and \( \Delta z_n \) could be obtained.

First least squares refinement gave the coordinates \((x_{r1}, y_{r1})\) which improved R-factor to 0.142. Second least squares \((x_{r2}, y_{r2})\) refinement, however, spoiled the agreement and consequently the R-factor. It was noted that with \( x_{r1} \) parameters, \( h00 \) type of reflections showed much better agreement and were thought to be the best. \( Y \)-parameters were again refined by least squares and new parameters \( y_{r3} \) with \( x_{r1} \) 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

$$K_1 \frac{F_0}{F_c} = e^{-(B_2 - B_1) \left( \frac{\sin \theta}{\lambda} \right)^2}$$

or

$$K_1 \times C = e^{-\Delta B \left( \frac{\sin \theta}{\lambda} \right)^2}$$

where $F_0/F_c = C$; 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>
<thead>
<tr>
<th>$(\sin \theta/\lambda)^2$</th>
<th>$\sum F_c$</th>
<th>$\sum F_0$</th>
<th>$C = \sum F_0/\sum F_c$</th>
<th>$\log_e C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.026</td>
<td>285</td>
<td>305</td>
<td>1.0702</td>
<td>0.0677</td>
</tr>
<tr>
<td>0.052</td>
<td>518</td>
<td>507</td>
<td>0.9788</td>
<td>-0.0215</td>
</tr>
<tr>
<td>0.086</td>
<td>477</td>
<td>498</td>
<td>1.0440</td>
<td>0.0430</td>
</tr>
<tr>
<td>0.127</td>
<td>270</td>
<td>270</td>
<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.178</td>
<td>451</td>
<td>451</td>
<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.236</td>
<td>393</td>
<td>374</td>
<td>0.9517</td>
<td>-0.0496</td>
</tr>
</tbody>
</table>

(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 POS & FCS VALUES
but instead of varying \(x, y, z\) coordinates, now \(B\) is varied. The temperature factor correction \(\Delta B_n\) for the \(n\)th atom is given

\[
\Delta B_n = \left( \sum_q \Delta F_q / \delta B_n \right) / \left( \sum_q (\Delta F_q / \delta B_n)^2 \right) \ldots (6)
\]

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

\[
F(hko) = \sum_{n=1}^{N} 8 f_{0_n} \exp \left( -B_n \left( \sin \theta / \lambda \right)^2 \right) \cos 2\pi hx_n \cos 2\pi ky_n
\]

where \(f_0\) 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 \(B_n\)

\[
\delta F_c / \delta B_n = -\left( \sin \theta / \lambda \right)^2 8 f_{0_n} \exp \left[ -B_n \left( \sin \theta / \lambda \right)^2 \right] \cos 2\pi hx_n \cos 2\pi ky_n
\]

or

\[
\delta F_c / \delta B_n = \left( \frac{3}{2} / \lambda \right)^2 \cdot F_{\alpha n}
\]

where \(F_{\alpha n}\) is the contribution of \(n\)th atom to the total structure factor

or

\[
\delta F_c / \delta B_n = -\left( \frac{3}{2} / \lambda \right)^2 \cdot F_{\alpha n} \ldots \ldots \ldots \ldots \ldots (7)
\]

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

\[
\Delta B_n = \frac{-4 \lambda \sum \Delta F.P}{\sum P^2} \quad \text{where} \quad P = F_{\alpha n} \cdot S^2
\]

After getting \(x_{r1}, y_{r3}\) parameters, it was tried to calculate individual temperature factor as explained above. With the new temperature factors again \(F_c\) 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.
Refinement of $x$ and $y$ parameters by L.S. Method

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$x_{r1}$</th>
<th>$y_{r1}$</th>
<th>$x_{r2}$</th>
<th>$y_{r2}$</th>
<th>$x_{r1}$</th>
<th>$y_{r3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.2170</td>
<td>0.2330</td>
<td>0.2175</td>
<td>0.2310</td>
<td>0.2170</td>
<td>0.2360</td>
</tr>
<tr>
<td>O1</td>
<td>0.2195</td>
<td>0.1560</td>
<td>0.2200</td>
<td>0.1550</td>
<td>0.2195</td>
<td>0.1500</td>
</tr>
<tr>
<td>O2</td>
<td>0.1515</td>
<td>0.1620</td>
<td>0.1515</td>
<td>0.1590</td>
<td>0.1515</td>
<td>0.1590</td>
</tr>
<tr>
<td>O3</td>
<td>0.1957</td>
<td>0.3850</td>
<td>0.1945</td>
<td>0.3800</td>
<td>0.1957</td>
<td>0.3850</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1925</td>
<td>0.2610</td>
<td>0.1915</td>
<td>0.2600</td>
<td>0.1925</td>
<td>0.2660</td>
</tr>
<tr>
<td>C2</td>
<td>0.1517</td>
<td>0.2380</td>
<td>0.1517</td>
<td>0.2380</td>
<td>0.1517</td>
<td>0.2440</td>
</tr>
<tr>
<td>C3</td>
<td>0.1145</td>
<td>0.2930</td>
<td>0.1135</td>
<td>0.2930</td>
<td>0.1145</td>
<td>0.2930</td>
</tr>
<tr>
<td>C4</td>
<td>0.0765</td>
<td>0.2130</td>
<td>0.0760</td>
<td>0.2110</td>
<td>0.0765</td>
<td>0.2090</td>
</tr>
<tr>
<td>C5</td>
<td>0.0430</td>
<td>0.2630</td>
<td>0.0420</td>
<td>0.2680</td>
<td>0.0430</td>
<td>0.2700</td>
</tr>
</tbody>
</table>

$R = 0.142$ \hspace{1cm} $R = 0.153$ \hspace{1cm} $R = 0.124$

(iv) **Final (001) electron density projection:**

The electron density map fig. 6 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 Seevers-Lipson's strips, 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 $h+l = 2n$

$$F(h0l) = \sum_{n=1}^{N} s_{f_{n}} \cos 2\pi h_{x_{n}} \cos 2\pi l_{z_{n}}$$
FIG. 7: ELECTRON DENSITY PROJECTION ON (010). CONTOURS ARE DRAWN AT INTERVALS OF 1 e/Å². FIRST FIVE CONTOURS AROUND Na⁺, O₁, AND O₂ ATOMS ARE AT 1 e/Å² INTERVALS AND THEN ALTERNATE CONTOURS ARE DRAWN. 1 e/Å² CONTOUR IS DASHED.
for \( h+1 = 2n+1 \)

\[
F(h\ell) = -\sum_{n=1}^{N} 8 f_n \sin 2\pi h x_n \sin 2\pi l z_n
\]

\[
\rho(x_0 y) = \frac{1}{A_c} \left[ F(x_0 y) + 2 \left( \sum_{h=1}^{\infty} F(h\ell) \cos 2\pi h x + \sum_{l=1}^{\infty} F(l\ell) \cos 2\pi l y \right) \right]
\]

\[
+ \left( \sum_{h=1}^{\infty} \sum_{l=1}^{\infty} F(h\ell) \cos 2\pi h x \cos 2\pi l y \right) \left( \sum_{h=1}^{\infty} \sum_{l=1}^{\infty} F(h\ell) \sin 2\pi h x \sin 2\pi l y \right)
\]

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 \(\sigma^2\) 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 photosommatre 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 \((F_0-F_c)\) values instead of \(F_0\) 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 \(f_n = F_0 \exp(-B(\sin \theta/\lambda)^2)\) for isotropically vibrating atom by residual 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 ($\Delta r_n$) in atomic position can be calculated by

$$\Delta r_n = \frac{(\beta D/\beta r)_n / 2}{p (\beta_o)_n}$$

(Lipson and Cochran, 1953)$^{20}$

where $\beta_o$ is the observed density at the centre of atom; $\beta D$ is the value of $\beta_o - \beta c$ at the distance $r$ from the centre of the atom and $p$ is a constant which is given by

$$p = Z (p/\pi)^{3/2} \exp\left[-pr^2\right]$$

(Costain, 1941)

where $\beta$ 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 $\log \beta$ versus $r^2$. In practice, $p$ is taken equal to $5.0^2$. The value of $(\beta_o)_n$ 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 $\approx 0.194$.

<table>
<thead>
<tr>
<th>Na</th>
<th>01</th>
<th>02</th>
<th>03</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-parameters</td>
<td>0.217</td>
<td>0.219</td>
<td>0.150</td>
<td>0.195</td>
<td>0.193</td>
<td>0.151</td>
<td>0.115</td>
<td>0.077</td>
</tr>
<tr>
<td>z-parameters</td>
<td>0.000</td>
<td>0.383</td>
<td>0.200</td>
<td>0.070</td>
<td>0.485</td>
<td>0.370</td>
<td>0.503</td>
<td>0.402</td>
</tr>
</tbody>
</table>

(vii) The 'Least-Squares' refinement:

By this time (hko) projection was refined to 0.124. The final $x_{1}$-parameters with the $z_{1}$-parameters obtained by first least square refinement gave $R$-factor $\approx 0.165$. $z_{2}$-parameters
from second least square cycle with the revised temperature factor of 1.1 Å° 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>
<thead>
<tr>
<th>Atoms</th>
<th>$x_{r1}$</th>
<th>First L.S. $z_{r1}$</th>
<th>Second L.S. $z_{r2}$</th>
<th>Third L.S. $z_{r3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.2170</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>01</td>
<td>0.2195</td>
<td>0.337</td>
<td>0.393</td>
<td>0.400</td>
</tr>
<tr>
<td>02</td>
<td>0.1515</td>
<td>0.190</td>
<td>0.185</td>
<td>0.179</td>
</tr>
<tr>
<td>03</td>
<td>0.1957</td>
<td>0.665</td>
<td>0.662</td>
<td>0.661</td>
</tr>
<tr>
<td>C1</td>
<td>0.1925</td>
<td>0.438</td>
<td>0.488</td>
<td>0.496</td>
</tr>
<tr>
<td>C2</td>
<td>0.1517</td>
<td>0.377</td>
<td>0.371</td>
<td>0.367</td>
</tr>
<tr>
<td>C3</td>
<td>0.1145</td>
<td>0.506</td>
<td>0.512</td>
<td>0.517</td>
</tr>
<tr>
<td>C4</td>
<td>0.0765</td>
<td>0.392</td>
<td>0.390</td>
<td>0.390</td>
</tr>
<tr>
<td>C5</td>
<td>0.0430</td>
<td>0.557</td>
<td>0.549</td>
<td>0.543</td>
</tr>
</tbody>
</table>

$R \approx 0.165 \quad R \approx 0.140 \quad R \approx 0.133$

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 Beevers-Lipson's strips along one quarter of $a$-axis and half of the $c$-axis at interval of $1/120^{th}$ along $a$ and $1/60^{th}$ along $c$. 

(viii) (010) electron density projection:
FIG. 6: ELECTRON DENSITY PROJECTED ON (001). CONTOURS ARE DRAWN AT INTERVALS OF $1 \text{ e/}^2$. FIRST FOUR CONTOURS AROUND $\text{Na}^+$ AND $\text{O}_1$ ATOMS ARE AT $1 \text{ e/}^2$ 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

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

Geometrical structure factor part for the space group Pbcn is

$$A = \cos 2\pi (h x + (h + k)/4) \cos 2\pi (k y + 1/4) \cos 2\pi (l z - (h + k)/4)$$

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.

$$f_0 = A \exp(-a x^2) + B \exp(-b x^2) + C$$ where $$x = \sin \theta /\lambda$$

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

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 (1961) and are tabulated in table 8.

**Table 8**

<table>
<thead>
<tr>
<th>Atoms</th>
<th>A</th>
<th>b</th>
<th>a</th>
<th>b</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>6.298</td>
<td>1.938</td>
<td>3.751</td>
<td>11.842</td>
<td>1.764</td>
</tr>
<tr>
<td>C</td>
<td>1.620</td>
<td>2.988</td>
<td>6.785</td>
<td>28.126</td>
<td>1.380</td>
</tr>
</tbody>
</table>

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

$$f = f_0 \times \exp [-B(\sin \theta /\lambda)^2]$$ 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 \( F_c \) for each plane, it computes \( \sin \theta; F_{obs} - F_c \) and prints out \( h, k, l; \sin \theta; F_{obs}; F_{cal}; \) and \( \Delta F \) (i.e. \( F_{obs} - F_c \)). 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 \( h+k+1 = 2n+1 \) 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 \( h+k+1 = 2n+1 \) 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 \( \cos 2 \pi l z \) 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 \( \phi \) differs from zero by an amount \( 1/n_1 \) is given as

\[
J(h+w, k, l) = n_2^2 n_3^2 A^2 \sin^2 \frac{\phi}{2} \frac{n_1}{n_2} (\sin^2 \frac{\phi}{2} (h+w) n_1)/(\sin^2 \frac{\phi}{2} (h+w)) + n_1 n_2^2 n_3^2 \frac{B^2}{1 - 2(1-2\lambda)^2 \cos \omega + (1-2\lambda)^4}
\]

The first term contains the factor \( \sin^2 \frac{\phi}{2} \frac{n_1}{n_2} \) which implies that when \( w \) is even the term vanishes; that means the reflections with \( h+k+1 = \text{odd} \) do not appear and obviously this term therefore corresponds to sharp reflexions. When \( h+k+1 = \text{even} \) (i.e. \( w \) even) 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

\[
\text{Id} \propto B^2 Q \left\{(1-2\lambda) \cos \frac{\lambda}{2} \pi \omega + l^2 \right\} \left\{1 - (1-2\lambda)^4 \right\}
\]

where \( Q = \frac{1 - 2(1-2\lambda)^2 \cos \omega \pi \omega + (1-2\lambda)^4}{1 - 2(1-2\lambda)^2 \cos \omega \pi \omega + (1-2\lambda)^4} \)

The plots of \( Q \) against \( \omega \) are shown for \( \phi = 0.1, 0.3, 0.7, 0.9 \) respectively. The curves are symmetrical about \( \omega = 0 \) having maxima at \( \omega = 0 \) when \( \phi < 0.5 \) and at \( \omega = 1 \) when \( \phi > 0.5 \). Which means for \( \phi < 0.5 \) the curves have maxima at reciprocal points with \( h+k+1 = \text{odd} \). Since the diffuse spots in the X-ray photographs show maxima near reciprocal lattice points with \( h+k+1 = \text{odd} \), obviously \( \phi \) is close to zero or so. This implies that the
structure is closer to ordered structure of space group Pccn 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 diffused 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.

Intensity of all the diffuse reflexions was 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) Standard-deviations:

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

<table>
<thead>
<tr>
<th>Atoms</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Zn &lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.2167</td>
<td>0.2368</td>
<td>-0.0025</td>
<td>1.77</td>
</tr>
<tr>
<td>O1</td>
<td>0.2195</td>
<td>0.1519</td>
<td>0.3958</td>
<td>1.72</td>
</tr>
<tr>
<td>O2</td>
<td>0.1508</td>
<td>0.1596</td>
<td>0.1759</td>
<td>2.20</td>
</tr>
<tr>
<td>O3</td>
<td>0.1934</td>
<td>0.3836</td>
<td>0.6550</td>
<td>1.92</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1913</td>
<td>0.2600</td>
<td>0.4890</td>
<td>1.99</td>
</tr>
<tr>
<td>C2</td>
<td>0.1515</td>
<td>0.2316</td>
<td>0.3631</td>
<td>2.01</td>
</tr>
<tr>
<td>C3</td>
<td>0.1155</td>
<td>0.3015</td>
<td>0.5022</td>
<td>2.03</td>
</tr>
<tr>
<td>C4</td>
<td>0.0784</td>
<td>0.2020</td>
<td>0.3927</td>
<td>2.72</td>
</tr>
<tr>
<td>C5</td>
<td>0.0411</td>
<td>0.2799</td>
<td>0.5270</td>
<td>3.72</td>
</tr>
</tbody>
</table>

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 ≤ F² ≤ F <sub>min</sub> 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 μ - I min/3 (Walter C. Hamilton, 1955)<sup>22</sup> and refinement was carried out with few cycles. R-factor at the start was 0.1380 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

\[
\sigma(x_n) = \left( \frac{K}{\sqrt{2}} \right) \left( \frac{N}{2p} \right)^{5/4} \left( \frac{N}{\sum_{i=1}^{N} z_i^2} \right)^{1/8} - \text{(Lipson & Cochran, 1953)}
\]

In the equation \( K = (\sum \Delta F) / |F_0| \), which is the \( \Delta \)-factor at the end of refinement; \( p \) is constant given by Costain's equation, and has been taken as \( 5.0 \) \( \AA^{-2} \). \( z_n \) 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 atoms 1 and 2 respectively.

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

\[
\sigma^2(\theta) = \sigma^2(r_1)/l_1^2 + \sigma^2(r_2)/l_2^2 + \sigma^2(r_3)/l_3^2 + \sigma^2(r_1/r_2)\cdot l_1^2 + \sigma^2(r_2/r_3)\cdot l_2^2 + \sigma^2(r_1/r_3)\cdot l_3^2
\]

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**

<table>
<thead>
<tr>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B in Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.2166 ± 0.0002</td>
<td>0.2366 ± 0.0008</td>
<td>-0.0010 ± 0.0008</td>
<td>1.62</td>
</tr>
<tr>
<td>01</td>
<td>0.2193 ± 0.0002</td>
<td>0.1516 ± 0.0011</td>
<td>0.3962 ± 0.0011</td>
<td>1.24</td>
</tr>
<tr>
<td>02</td>
<td>0.1607 ± 0.0002</td>
<td>0.1601 ± 0.0011</td>
<td>0.1774 ± 0.0011</td>
<td>2.03</td>
</tr>
<tr>
<td>03</td>
<td>0.1931 ± 0.0002</td>
<td>0.3837 ± 0.0011</td>
<td>0.6599 ± 0.0011</td>
<td>1.57</td>
</tr>
<tr>
<td>C1</td>
<td>0.1916 ± 0.0003</td>
<td>0.2576 ± 0.0014</td>
<td>0.4863 ± 0.0014</td>
<td>1.60</td>
</tr>
<tr>
<td>C2</td>
<td>0.1513 ± 0.0003</td>
<td>0.2272 ± 0.0014</td>
<td>0.3549 ± 0.0014</td>
<td>2.01</td>
</tr>
<tr>
<td>C3</td>
<td>0.1157 ± 0.0003</td>
<td>0.3000 ± 0.0014</td>
<td>0.5014 ± 0.0014</td>
<td>1.53</td>
</tr>
<tr>
<td>C4</td>
<td>0.0782 ± 0.0003</td>
<td>0.2062 ± 0.0014</td>
<td>0.3935 ± 0.0014</td>
<td>2.30</td>
</tr>
<tr>
<td>C5</td>
<td>0.0410 ± 0.0003</td>
<td>0.2770 ± 0.0014</td>
<td>0.5341 ± 0.0014</td>
<td>4.08</td>
</tr>
</tbody>
</table>
CHAPTER IV

RESULTS AND DISCUSSION

(1) The final atomic coordinates 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:

\[
\cos \theta = \frac{r_1^2 + r_2^2 - r_3^2}{2r_1r_2}
\]

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 \(\alpha\)-keto valerate group are shown in Fig. 8 and tabulated in Table 12.

**TABLE 11**

<table>
<thead>
<tr>
<th>Atoms</th>
<th>(X)</th>
<th>(Y)</th>
<th>(Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>7.3339</td>
<td>1.4527</td>
<td>-0.0059</td>
</tr>
<tr>
<td>O1</td>
<td>7.4759</td>
<td>0.9308</td>
<td>2.3415</td>
</tr>
<tr>
<td>O2</td>
<td>5.1374</td>
<td>0.9830</td>
<td>2.0484</td>
</tr>
<tr>
<td>O3</td>
<td>6.5828</td>
<td>2.3559</td>
<td>3.9000</td>
</tr>
<tr>
<td>Cl</td>
<td>6.5282</td>
<td>1.5817</td>
<td>2.8753</td>
</tr>
<tr>
<td>C2</td>
<td>5.1573</td>
<td>1.3950</td>
<td>2.1566</td>
</tr>
<tr>
<td>C3</td>
<td>3.9442</td>
<td>1.8420</td>
<td>2.9633</td>
</tr>
<tr>
<td>C4</td>
<td>2.6658</td>
<td>1.2661</td>
<td>2.3256</td>
</tr>
<tr>
<td>C5</td>
<td>1.3977</td>
<td>1.7008</td>
<td>3.1565</td>
</tr>
</tbody>
</table>
Fig. 8  BOND LENGTHS (Å) AND BOND ANGLES (°) IN 
4-KETO VALERATE GROUP.
TABLE - 12

Final bond lengths and angles along with their estimated standard deviations

<table>
<thead>
<tr>
<th></th>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁-O₁</td>
<td>1.288 ± 0.011 Å</td>
<td>O₁-C₁-O₃</td>
</tr>
<tr>
<td>C₁-O₃</td>
<td>1.285 ± 0.011</td>
<td>O₁-C₁-C₂</td>
</tr>
<tr>
<td>C₁-C₂</td>
<td>1.559 ± 0.012</td>
<td>O₃-C₁-C₂</td>
</tr>
<tr>
<td>C₂-O₂</td>
<td>1.182 ± 0.011</td>
<td>C₁-C₂-C₃</td>
</tr>
<tr>
<td>C₂-C₃</td>
<td>1.523 ± 0.012</td>
<td>C₁-C₂-O₂</td>
</tr>
<tr>
<td>C₃-C₄</td>
<td>1.540 ± 0.012</td>
<td>C₃-C₂-O₂</td>
</tr>
<tr>
<td>C₄-C₅</td>
<td>1.578 ± 0.012</td>
<td>C₂-C₃-C₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₃-C₄-C₅</td>
</tr>
</tbody>
</table>

(11) 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 O₁, O₃, C₁ and C₂

\[-0.2032 \times -0.7778 \times + 0.5946 \times + 0.3483 = 0\]

The normal distances of O₁, O₃, C₁ and C₂ from this plane are -0.002, -0.002, +0.002 and -0.002 Å respectively.

Plane (2) through C₁, C₂, O₂ and C₃

\[0.0309 \times + 0.9273 \times -0.3655 \times -0.9332 = 0\]

The atoms C₁, C₂, O₂ and C₃ 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\textsubscript{2}, C\textsubscript{3}, C\textsubscript{4} and C\textsubscript{5}

\[0.0311X - 0.8151Y + 0.5737Z - 0.5286 = 0\]

The atoms C\textsubscript{2}, C\textsubscript{3}, C\textsubscript{4} and C\textsubscript{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 \(\pm 0.012\ \text{Å}\). 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\textsuperscript{25} (form-B) (Dumbleton, J.H. et al., 1965) (2.557 ± 0.005 Å). The rather unnatural C\textsubscript{4}-C\textsubscript{5} distance (fig 8) 1.573 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\textsuperscript{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\textsuperscript{27},
pimelic acid\textsuperscript{28} and sebacic acid\textsuperscript{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\textsubscript{2}, C\textsubscript{3}, C\textsubscript{4} and C\textsubscript{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\textsuperscript{30} (Frederick, J. et.
al., 1962), butyric acid\textsuperscript{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)\textsuperscript{32}
on the basis of the difference in single-double bond character
of the two bonds. The predicted configuration of carboxylate
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\textsubscript{1}-C\textsubscript{1}-O\textsubscript{3} = 127.7° and C\textsubscript{1}-O\textsubscript{1} = 1.288 \pm 0.011 Å and C\textsubscript{1}-O\textsubscript{3} = 1.285 \pm 0.011 Å
are in favour of almost purely ionic form of the carboxylate
group in the present compound. An elegant illustration has been
provided by the structure of sodium and lithium dihydrogen
citrate\textsuperscript{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 \textsuperscript{m} 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 attached 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>
<thead>
<tr>
<th>Compounds</th>
<th>C-O (Å)</th>
<th>C-O (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono pyridine copper (II)</td>
<td>1.248</td>
<td>1.250</td>
<td>Hanic, F. et al.</td>
</tr>
<tr>
<td>acetate (orthorhombic form)</td>
<td>1.236</td>
<td>1.250</td>
<td>1964</td>
</tr>
<tr>
<td>Monopyridine copper (II)</td>
<td>1.247</td>
<td>1.231</td>
<td>Barclay &amp; Kennard</td>
</tr>
<tr>
<td>acetate (monoclinic form)</td>
<td>1.247</td>
<td>1.231</td>
<td>1961</td>
</tr>
<tr>
<td>L-glycine</td>
<td>1.261</td>
<td>1.265</td>
<td>Marsh, 1958</td>
</tr>
<tr>
<td>DL-serine</td>
<td>1.268</td>
<td>1.261</td>
<td>Shoemaker et al.</td>
</tr>
<tr>
<td>β-alanine</td>
<td>1.292</td>
<td>1.287</td>
<td>Jose, P., et al.</td>
</tr>
</tbody>
</table>

The angles O₁-C₁-O₃, O₁-C₁-C₂ and O₃-C₁-C₂ 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., 196)

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) where the maximum 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/16). Similar short bond has been observed in tri-ketoindane (Bolton, W., 1964), anhydrous barbituric acid (Bolton, W., 1963) and tetra chlorobenzoquinone (Chu, S. C., et al., 1963) 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 - O_1 (x, y, z) 2.406 Å
Na - O_1 (x, 1-y, z-1/2) 2.462 Å
Na - O_1 (1/2-x, 1/2-y, z-1/2) 2.370 Å
Na - O_2 (x, y, z) 2.526 Å
Na - O_3 (x, 1-y, z-1) 2.642 Å
Na - O_3 (x, y, z-1) 2.340 Å
These Na-0 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; Shiono, 1961) $^{43}$ (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:

\[
\begin{align*}
C_5 (x, y, z) - C_5 (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 4.506 \text{ Å} \\
C_5 (x, y, z) - C_5 (x, \bar{y}, \frac{1}{2}-z) & \quad 4.166 \\
C_5 (x, y, z) - C_5 (x, y, \frac{3}{2}-z) & \quad 3.786 \\
C_5 (x, y, z) - C_5 (\bar{x, y, 1-z}) & \quad 4.422 \\
C_5 (x, y, z) - C_5 (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 4.029 \\
C_5 (x, y, z) - C_5 (\bar{x}, 1-y, z) & \quad 3.934 \\
C_1 (x, y, z) - C_1 (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 4.329 \\
C_2 (x, y, z) - C_2 (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 4.054 \\
C_2 (x, y, z) - C_2 (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 4.467 \\
C_3 (x, y, z) - C_3 (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 4.722 \\
C_3 (x, y, z) - C_3 (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 3.842 \\
C_4 (x, y, z) - C_4 (x, \bar{y}, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 3.891 \\
C_4 (x, y, z) - C_4 (x, 1-y, \frac{1}{2}+z \text{ or } z-\frac{1}{2}) & \quad 4.663
\end{align*}
\]

The short Na-Na contact distances are

\[
\begin{align*}
Na (x, y, z) - Na (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z) & \quad 3.733 \text{ Å} \\
Na (x, y, z) - Na (\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}) & \quad 3.733 \\
Na (x, y, z) - Na (\frac{1}{2}-x, \frac{1}{2}+y, z) & \quad 3.830 \\
Na (x, y, z) - Na (\frac{1}{2}-x, y-\frac{1}{2}, z) & \quad 3.830
\end{align*}
\]

The strong Na-0 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-0 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), potassium caprate (Vand, Lomer and Lang, 1949), and potassium caproate (Lomer, 1952).

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REFERENCES

20. Lipson, H. and Cochran, W., The determination of crystal structures, p. 283, 301.
23. Same as
46. Same as 43