# STUDIES IN CRYSTAL STRUCTURE

## PART I α-ETHYNYLACETIC ACID

## PART II n-HEXATRIACONTANE

THESIS
PRESENTED FOR THE DEGREE OF
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BY
H. M. M. SHEARER, B.Sc.

University of Glasgow
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## Preface

This thesis describes research in chemical crystallography, which was carried out during a three year period in the Chemistry Department of the University of Glasgow. It is expected that the work will be published.

I wish to express my sincere thanks to my supervisor, Professor J. M. Robertson, for suggesting the topics of research and for his constant guidance and encouragement. I am also much indebted to Dr. V. Vand, a former I.C.I. Research Fellow in this Department, for his many suggestions and a great deal of helpful discussion. In addition, I would like to thank Dr. Raphael of this Department for a supply of but-3-yne-1-ol and Mr. C. W. Bunn of I.C.I. Ltd. for some pure n-hexatriacontane.

In conclusion I am indebted to the Department of Scientific and Industrial Research for a maintainance allowance.

## Summary

The first part of this thesis describes an investigation, by X-ray methods, of ethynylacetic acid (prop-2-yne-1-carboxylic acid). The acid was found to exist in two crystal forms and one of these - the α-form - was studied in some detail. The dimensions of the two crystallographically independent molecules in the unit cell were obtained from projections along two of the cell axes and more accurate values of the molecular parameters were found by a process of averaging. An attempt was then made to determine the nature of the acetylenic carbon-hydrogen bond at the end of the molecular chain.

Part 2 describes an investigation of the monoclinic form of n-hexatriacontane. The signs of the reflecting planes in two of the lattice zones were obtained by means of sub-cell theory and the molecular structure was determined from projections down two of the cell axes. By assuming a regular repetition along the hydrocarbon chain, the molecular dimensions were determined with greater accuracy.

# Contents.

## Introduction

### (a) General

The introduction of modern physical methods of structure analysis has transformed the information derived from classical chemical and stereochemical theory from a qualitative to a quantitative basis. It is now possible to determine, not only the spatial arrangement of atoms in a molecule, but also the bond lengths and valence angles.

A number of methods are available for this purpose, of which the most accurate is undoubtedly the spectroscopic method[1]. This is restricted however to very simple molecules in the gaseous state but provides the most reliable information on standard interatomic distances.

Methods based on the diffration of electrons by gases or crystals and X-rays by crystals are less precise but can be applied to less simple molecules. Gas electron diffraction methods are applied to compounds which exist in the gaseous state or to solids with a high vapour pressure. A good account of the development of this method and a list of structures investigated has been published by Brockway[2]. Electron diffraction methods can also be applied, like X-rays, to crystals and some important results have recently been obtained.

X-rays crystallographic methods, on the other hand, can be applied to very complex molecules and provide information not only about intramolecular distances and angles but also about the electron density distribution and intermolecular distances.

A method of structure analysis arising from the diffraction of neutrons by crystals is also being developed. Theoretically, this method is very suitable for the determination of the light atoms in a compound but the experimental difficulties are considerable and it has been applied, as yet, only to very simple compounds.

## (b) Structure Determination by X-ray Methods

It is sometimes possible, in very simple cases, to deduce the structure of a compound from the knowledge of its space group and the intensities of the X-ray reflections. Such cases are extremely rare and normally systematic methods of refinement are required. Of these, the Fourier synthesis has proved the most valuable.

### 1. Fourier Synthesis.

W. H. Bragg[3] in 1915 suggested the application of the Fourier series method to the problem of X-ray analysis and in 1929 W. L. Bragg[4] extended the treatment and made the first practical use of it in the determination of the structure of diopide. In 1933, the first Fourier analysis of a complex organic structure was carried out by Robertson on anthracene[5].

The electron density at any point within a crystal can be expressed by means of the Fourier series:-

$$\rho(x,y,z) = \frac{1}{V} \underset{-\infty}{\overset{\infty}{\sum_{h}\sum_{k}\sum_{\ell}}} F(hk\ell)\, e^{-2\pi i\left(\frac{hx}{a}+\frac{ky}{b}+\frac{\ell z}{c}\right)}$$

where p(x,y,z) is the electron density at the point (x,y,z); V is the volume of the unit cell, a,b and c are the lengths of the crystal axes and F(hkl) is the structure factor of the reflection having Miller indices hkl. The structure factors F(hkl) are in general complex, and contain both a magnitude and phase component. The magnitude of F(hkl) in the case of mosaic crystals is proportional to the square root of the intensity of the reflection after correction by Lorentz and polarisation factors and hence can be determined experimentally. The phases of the structure factors must be found by indirect methods and much of the work of structure analysis by X-ray methods is concerned with determining these.

If the unit cell possesses a centre of symmetry and this is chosen as the origin of the coordinates, then the phase angles must be either 0 or $\pi$. The sign of the structure factor is either positive or negative and the determination of the phase of each of the terms of the series is reduced to the determination of the sign of its structure factor. The series may now be written:

$$\rho(x,y,z) = \frac{1}{V} \sum_{h}\sum_{k}\sum_{l=-\infty}^{\infty} \pm |F(hkl)| \cos 2\pi\left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}\right)$$

and for the projection in a direction parallel to b on to the ac plane:

$$\rho(x,z) = \frac{1}{A} \sum_{h}\sum_{l=-\infty}^{\infty} \pm |F(h0l)| \cos 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right)$$

where A is the area of projection.

The signs of F, the structure factors, are determined in many cases by "trial and error" methods. Atomic positions are chosen on the basis of the chemical structure of the molecule and the physical properties of the crystals. In addition, considerations of packing and the strength of some of the reflected planes are taken into account. The structure factors are then calculated and the atomic positions adjusted to bring the calculated values of the structure factors more into agreement with the observed values.

When reasonable agreement between the two sets of values is obtained a Fourier synthesis can be carried out, using the signs of the calculated structure factors of the stronger reflections together with their observed magnitudes. From the resulting electron density map more precise values of the atomic coordinates will generally be obtained and the structure factors are then recalculated. Signs can now be given to further reflections and the process repeated with a more complete Fourier series. When signs have been attributed to all the observed reflections and remain unaltered on the completion of a further Fourier synthesis, the process of refinement by this method is at an end.

If all the atoms are resolved in the electron density map, accurate values of the atomic coordinates are obtained but if, however, overlapping of the atoms occurs it may be necessary to resort to "trial" methods to obtain these.

During this process of refinement, it is usual to accept, as an index of reliability of a postulated structure, the quantity R, the discrepancy or figure of merit, given by

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

where Fo is the observed value of the structure factor and Fc the calculated value.

The equation for the electron density given on P.4 is true only for an infinite series of terms. In practice the series is terminated at a limit fixed by the sphere of reflection. The effect of this termination of the series is to introduce errors into the electron density map and hence into the coordinates obtained even for well resolved atoms. Booth[6] estimated that these errors will be of the order of ± 0.02A and put forward the following method of correction. The structure factors are calculated from the final atomic coordinates and these calculated values used as coefficients in a Fourier synthesis. The coordinates obtained from this synthesis will be slightly different to those from which the structure factors were calculated and these differences give the errors, with reversed sign, of the original coordinates and may be applied as corrections.

### 2. (Fo-Fc) Synthesis.

A method of refinement which has been developed within recent years is the (Fo-Fc) or difference synthesis. This is a Fourier synthesis whose coefficients are the differences between the observed and calculated values of the structure factors, and for the projection in a direction parallel to b on to the ac plane it is represented by the expression

$$D = \rho_o - \rho_c = \frac{1}{A}\sum_h \sum_\ell \left\{ F_o(h0\ell) - F_c(h0\ell) \right\} \cos 2\pi \left( \frac{hx}{a} + \frac{\ell z}{c} \right).$$

This function gives the difference between the observed electron density in the unit cell of the crystal and that calculated for a postulated arrangement of the atoms.

The resulting difference map then indicates the corrections to be applied to the atomic coordinates and scattering curves to bring the calculated values of the structure factors more into agreement with the observed values. It may also reveal fine details of the crystal structure such as hydrogen atoms or bonding electrons.

The use of this function was advocated by Booth[7] in 1948, but essentially the same method was used by Finbank and Norman[8] in 1948 in an endeavour to locate the hydrogen atoms in oxalic acid dihydrate and a closely related method was used by Brindley and Wood[9] in 1929 in an investigation of the structure of the chlorine ion. It proved of value in establishing the crystal structure of sodium benzyl penicillin[10] but the full potentialities of the method were established by Cochran[11 and 12] only in 1951.

The corrections to the atomic coordinates may be derived as follows. The electron density distribution of an atom, to a first approximation, is Gaussian and may be represented as

$$\rho_0(r) = \rho_0(0)\, e^{-pr^2}$$

where $\rho_0(r)$ is the electron density at a distance r from the centre of the atom where the electron density is $\rho_0(o)$.

This may be written

$$\rho_0(r) = \rho_0(0)\left\{1 - pr^2 + \frac{p^2r^4}{2!} - \cdots\cdots\right\}$$

$$\doteqdot \rho_0(0)\left\{1 - pr^2\right\} \qquad \text{for small values of r.}$$

If the origin is taken at the point assumed to be the atomic centre in calculating the structure factors, then

$$D(r) = \rho_o(r) - \rho_c(r)$$

$$= \rho_o(0)\left\{1 - p(r-\Delta)^2\right\} - \rho_c(0)\left\{1 - p'r^2\right\}$$

where $\Delta$ is the required correction to the atomic centre. If the correct scattering curve has been chosen so that $\rho_o(o) = \rho_c(o)$ and $p = p'$ then

$$D(r) = 2\rho_o(0)\, p r \Delta$$

and $$\Delta = \frac{\left(\frac{dD}{dr}\right)_{r=0}}{2p\rho_o(0)}$$

The factor p depends upon the thermal motion of the atoms and is normally derived experimentally. From the equation above

$$\rho_o(r) = \rho_o(0)\, e^{-pr^2}$$

so that $$\log_e \rho_o(r) - \log_e \rho_o(0) = -pr^2$$

and $$\log_e \rho_o(r) = -pr^2 + c.$$

An atom, which is well resolved in projection, is chosen and with its centre as origin the radius r of the innermost contour levels is found. The logarithms of the values of these contour levels are then plotted against the squares of the radius and the slope of the line through these points gives -p.

The direction of shift of the atomic coordinate is along the line of steepest ascent and the magnitude of this is determined by measuring the gradient of the slope at the atomic site and dividing by the factor $2p\rho_a(o)$ which can be taken as a constant for any one type of atom. The process of refinement comes to an end when the function D has zero slope at the atomic centres. These coordinates will be free from termination of series errors except in so far as the scattering curves used to calculate the Fc's are incorrect.

The coefficients of this Fourier series are (Fo-Fc) and hence it is desirable that the magnitudes (as well as the signs) of both Fo and Fc be obtained with a high degree of precision. To this end the integrated intensities of the X-ray reflections are sometimes measured, on a relative scale, by means of Geiger-counter techniques[13] and this leads to values of Fo quoted, in one instance, as being reproducible to within 2-3% whilst differing from the values of Fo, resulting from the visual estimation of the intensities, by 9%.

Considerable accuracy is also required in the Fc's and it is usually found necessary to include in these, the contributions of the hydrogen atoms in the structure. The atomic scattering factors are normally obtained from theoretical scattering curves modified by temperature factors to allow for the thermal motion of the atoms. These curves possess a certain theoretical basis and may conveniently be used, by the choice of suitable temperature factors, to assign separate scattering curves to different atoms or groups of atoms and to allow for their anisotropic motion. Corrections to these temperature factors may be obtained from the difference maps.

One of the outstanding examples of the application of (Fo-Fc) syntheses to the problem of structure determination is the recent work of Cochran on salicyclic acid[14]. The integrated values of the intensities of the X-ray reflections were measured using Geiger-counter techniques and the atomic coordinates obtained from projections down two of the cell axes. Anistropic scattering curves were assigned to the carbon and oxygen atoms and very accurate values of the bond lengths and electron density distribution obtained. From the difference maps the presence of the hydrogen atoms in the molecule was shown and coordinates were assigned to them. The electron density at or near the centres of the bonds between atoms was found to be greater than that required for circularly symmetrical atoms and the magnitude of this bonding effect was estimated. Cochran also concluded as a result of this work that there was a transfer of a part of an electron from the hydrogen atoms to the oxygen atoms to which they were attached.

### 3. Comparison of Fourier and Difference Synthesis Methods.

The use of (Fo-Fc) synthesis methods postulates that a good approximation to the structure has already been obtained, and to this end it is often desirable to use the ordinary Fourier methods in the initial stages of refinement. Further refinement by difference syntheses methods compensates for termination of series errors.

Another advantage arises particularly in the case of two-dimensional methods of investigation where the ordinary Fourier methods are often limited in application by the poor resolution of the atoms. With difference synthesis methods, a large part of the electron density is subtracted and the remainder shown up with greater clarity so that the process of refinement may still be carried on. Again, with normal Fourier series methods this process comes to an end when, in the centrosymmetrical case, the correct signs have been assigned to all the planes but refinement by difference syntheses can be carried on beyond this point.

With difference syntheses methods, however, the calculated values of the structure factors are included in the coefficients of the Fourier series. If the atoms are assumed to be spherically symmetrical, to undergo isotropic thermal motion and, for any element, to possess equal diffracting power, errors will be introduced into these calculated values. These errors are systematic and their sources will be revealed in the following difference maps. Their effect on the atomic coordinates obtained from these maps is thought to be small[14].

The limiting factor in the accuracy of the difference maps and hence of the atomic coordinates obtained from them is more likely to be the accuracy of the experimental values of the structure factors where visual estimations of the intensities of the X-ray reflections are employed. If the accuracy of the intensity measurements is assumed to be of the order of 10-15%, then the accuracy of any individual Fo will be 5-7% and that of $[Fo-Fc]$ considerably less, even neglecting any source of error in Fc. Reflections for which $|Fo-Fc|$ is small must then be neglected since the signs of these may well be incorrect. The errors in Fo are, however, random and will, for a large number of reflections, tend to cancel out when used to determine $(\rho_a-\rho_e)$. With Fourier synthesis methods, the errors in atomic coordinates due to this cause have been shown to be small[15] and it is presumed that this will also hold for coordinates obtained as a result of difference synthesis methods. The magnitudes of these errors can be determined by statistical methods.

### 4. The Accuracy of Electron Density Maps.

A number of statistical methods have been devised for assessing the accuracy of the electron density maps obtained in X-ray structure analysis. In comparison with the true electron density, the values of the electron density calculated within a unit cell by means of a Fourier series are liable to three sources of error:

(I) errors in the experimental |F| values,

(II) effects of termination of the series at a finite (hkl) value, and

(III) computational errors.

Booth[16] discussed the first two of these. He considered that the electron density distribution of an atom may be represented by a Gaussian equation of the form given earlier and derived expressions for the deviation in coordinate resulting from the effects of random errors in the experimental |F| values. For the two dimensional case this was given as

$$\sigma(x_r) = \frac{2}{N_r}\left(\frac{\pi}{\lambda p}\right)^2\left(\frac{\pi}{A}\right)^{\frac{1}{2}}\sigma(F_o)$$

where $\sigma(x_r)$ is the standard deviation of the x-coordinate of the $r^{th}$ atom, Nr is its atomic number, A is the area of projection and $\sigma$(Fo) is the standard deviation of the experimental values of |F|. Booth argued that the value of $\sigma$(Fo) would be greatly overestimated by deriving it from the values of |Fo-Fc| since Fc is generally calculated for non-bonded atoms and makes no allowance for their anisotropic thermal motion. In a small number of cases he obtained a value for $\sigma(Fo)$ by a comparison of two sets of Fo's estimated by independent workers. Booth also considered that the standard deviation of the coordinates in the one-, two- and three-dimensional cases are in the ratio 10:3:1.

The effect of the termination of the series was also discussed and the method of correction, which has already been mentioned for a polyatomic structure, was put forward.

The accuracy of the electron density maps was also discussed by Cruikshank[17], who calculated the effects of random errors in the experimental values of $|F|$ and found that in the two dimensional case:

$$\sigma(\rho) = \frac{1}{A}\left\{\sum_2 (\Delta F)^2\right\}^{\frac{1}{2}}$$

where $\sigma(\rho)$ is the standard deviation in electron density, A is the area of projection and $\sum_2$ indicates that the summation is carried out over the planes with due regard to their multiplicity,

Also, from his work it can be shown that

$$\sigma(x) = \frac{\frac{2\pi}{aA}\left\{\sum_2 h^2(\Delta F)^2\right\}^{\frac{1}{2}}}{2p\rho(0)}$$

where $\sigma(x)$ is the standard deviation in the $x$-coordinate of the atom and h is the Miller index related to the $a$ crystal axis.

In general

$$\sigma(x) \simeq \sigma(y) \simeq \sigma(z)$$

and the R.M.S. radial error of position will be

$$\sigma(r) = \sqrt{3}\left\{\sigma^2(x) + \sigma^2(y) + \sigma^2(z)\right\}^{\frac{1}{2}}.$$

Cruikshank argued that the difference between two equally reliable sets of experimental $|F|$ values will lead to values of $\Delta F$ which are too low since no allowance will be made for systematic errors common to both sets of observations; whilst the differences between a set of F values calculated for a postulated structure and the experimentally obtained values will result in values of $\Delta F$ which are too high. The latter basis was recommended as being the more reliable and it will also allow for residual finite series errors due to imperfections in the calculated values of the structure factors.

Errors of computation were also discussed and found to be so small as to be negligible with the usual methods of calculation.

Further equations were given in a paper by Ahmed and Cruikshank[18]. If the positions of two atoms forming a bond are independent the standard deviation of the bond length is given by

$$\sigma^2(\ell) = \left\{\sigma^2(x_1) + \sigma^2(x_2)\right\}\cos^2\alpha + \left\{\sigma^2(y_1) + \sigma^2(y_2)\right\}\cos^2\beta + \left\{\sigma^2(z_1) + \sigma^2(z_2)\right\}\cos^2\gamma,$$

where $\sigma(x_1)$, $\sigma(y_1)$, $\sigma(z_1)$ are the standard deviations of the coordinates of the first atom and $\cos\alpha$, $\cos\beta$ and $\cos\gamma$ are the direction cosines of the line joining the atoms.

If the positions of the three atoms 1, 2, 3forming an angle at 2 are independent the standard deviation of the angle is given by

$$\sigma^2(\theta) = (1/\ell m \sin\theta)^2\Big[(x_2 - x_3)^2\sigma^2(x_1) + (x_1 - 2x_2 + x_3)^2\sigma^2(x_2) + (x_2 - x_1)^2\sigma^2(x_3) +$$

$$+ \text{similar terms in } y \text{ and } z\Big],$$

where l and m are the lengths of the two bonds, $\theta$ is the angle and x, y and z are the coordinates referred to orthogonal axes.

The order of magnitude of these errors can be seen in the case of hydroxyl-$\ell$-proline which was studied by Zussman[19] who explored two projections involving 220 reflections with the aid of (Fo-Fc) syntheses. It was also investigated by Donohue and Trueblood[20] who carried out a three-dimensional survey with the aid of 650 reflections and obtained the atomic coordinates by least squares methods. A comparison of the two sets of atomic peremeters revealed an average difference of 0.02A and a maximum difference of 0.08A; for the nine intramolecular bond distances and the three hydrogen bond distances the average difference is 0.018A and the maximum 0.074A; and for the twelve inter-bond angles the average difference is 2.1° and the maximum 5.1°.

The number of electrons associated with each atom may be evaluated as follows.[11] (11). If $n_o$ and $n_c$ are the numbers of electrons in an area S, where the electron densities are $\rho_o$ and $\rho_c$,

$$n_o - n_c = \int_S (\rho_o - \rho_c)\, dS = \int_S D\, dS$$

or approximately $$n_o = n_c + \delta S . \Sigma D,$$

where the sum is taken over the points inside S at which

D ( $= \rho_o - \rho_c$) was evaluated and

$$\delta S = A\,\delta x.\delta z / ac.$$

If the area is bounded by the lines $x = x_1, x_2$ and $z = z_1, z_2$, then

$$\sigma(n_0) = \sqrt{2}\,\sigma(F_0)\,\frac{x_2-x_1}{a}\cdot\frac{z_2-z_1}{c}\left[\sum_h\sum_l\left\{\frac{\sin \pi h(x_2-x_1)/a}{\pi h(x_2-x_1)/a}\right\}^2\left\{\frac{\sin \pi l(z_2-z_1)/c}{\pi l(z_2-z_1)/c}\right\}^2\right]^{\frac{1}{2}}$$

where $\sigma(F_o)$ is the standard deviation of $|F_o|$ and is given by

$$\sigma(F_0) = \left\{\overline{(\Delta F)^2}\right\}^{\frac{1}{2}}.$$

## 5. Tests of Significance.

When the structure of a compound has been determined by X-ray methods, it is often wished to make a comparison with some theoretical structure and find out whether the two are compatible. Similarly it may be desired to compare different experimental determinations of the same chemical compound or group of atoms. Normally the molecular dimensions will be different and these differences may be so small as to be readily explained by the experimental errors or large enough to suggest that they are real. A method of effecting this comparison and tests of significance have been put forward by Cruikshank and Robertson[21].

The experimental data will give an estimated bond length $l_0$, with an estimated standard deviation $s_0$, having v degrees of freedom; where v is the difference between the number of crystallographically independent planes observed and the number of independent parameters derived from the data. In a large number of cases v is large and for this a value of $v > 30$ is put forward, so that $s_0$ may be regarded as a reasonably accurate estimate of $\sigma_0$, the true standard deviation of the bond length $l_0$. If it is desired to compare the value $l_0$ with the theoretical value $\lambda_0$ then, on the supposition that $\lambda_0$ is the true value,

$$t_0 = (l_0 - \lambda_0) / \sigma_0$$

where $t_0$ is a value of the random variable t having a Student distribution with v degrees of freedom.

The probability P that $|t| \geqslant |t_0|$ can be found from the tables of this distribution. When P is small, the supposition that $\lambda_0$ is the true value of the bond length is rendered unlikely on the basis of the experimental results and may be denied; when P is large, the supposition may well be true although the statistical examination does not provide evidence of this.

The degrees of significance to be attached to different values of P are arbitrary but the following table was put forward:

$P \geqslant 0.05$ not significant
$0.05 > P \geqslant 0.01$ possibly significant
$0.01 > P \geqslant 0.001$ significant
$0.001 > P$ highly significant.

When v is large, the value of $t_e$ at the various significance points are

$P = 0.05$ $t_e = 1.960$
$P = 0.01$ $t_e = 2.576$
$P = 0.001$ $t_e = 3.291$

By similar means, it is possible to compare two experimentally determined bond lengths and to examine the supposition that the true lengths are the same. In this case the experimental data will give the estimated bond lengths $l_1$ and $l_2$, with the estimated standard deviations $s_1$ on $v_1$ degrees of freedom and $s_2$ on $v_2$ degrees of freedom. When both $v_1$ and $v_2$ are large, $s_1$ and $s_2$ may be taken as $\sigma_1$ and $\sigma_2$ and

$$t_0 = (\ell_1 - \ell_2) / (\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}$$

when the two determinations are taken as independent.

(c) The Determination of the Hydrogen Atoms.

The most reliable method for determining interatomic distances and bond angles is the spectroscopic and by means of this the carbon-hydrogen bond distances are known with considerable accuracy and are shown in Table I[22].

Table I

| Hybridisation | Molecule | C - H bond length (A) | Stretching force constant ($10^5$ dynes/cm) | Bond energy (kcal/mole.) |
|---|---|---|---|---|
| sp | Acetylene | 1.057 | 5.88 | ~ 121 |
| $sp^2$ | Ethylene | 1.079 | 5.05 | ~ 106 |
| $sp^3$ | Methane | 1.094 | 4.88 | ~ 103 |

The increased bond length and decreased force constant, along the series acetylene, ethylene and methane are related to the decrease in bond energy and the smaller overlap of the atomic orbitals.

X-ray diffraction methods may also be used to determine the location of the hydrogen atoms in a crystal structure. Their diffracting power is much less than that of the atoms with which they are normally associated and their contribution to the total diffracting power of a molecule may not be great. Nevertheless a careful study of the electron density in the neighbourhood of the positions of the other atoms will often reveal indications of the presence and position of these hydrogen atoms.

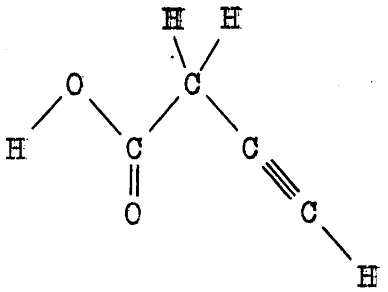
With two-dimensional methods of investigation, the hydrogen atoms, in the positions calculated by assuming normal bond lengths and valence angles, are found often to project more or less directly on to the heavier atoms to which they are attached. In other cases however this does not happen and much of the fine detail of the electron density distribution of these compounds can be explained in this way. This can be seen in the cases of sebacic acid and of hexamethylenediamine, especially of the latter where overlapping of the hydrogen atoms occurs[23].

As has been seen, three-dimensional analyses provide much more accurate values of the electron density and possess the additional advantage in that the effects of overlapping are much reduced. More accurate values of the carbon-hydrogen bond distances can thus be obtained by this method and these were found to average 1.08A in the case of naphthalene[24] and 1.10A for anthracene[25]. The result of the work on hydroxy-ℓ-proline[20] which contains a saturated ring system gave an average value of 1.10A for this distance.

Parameters have also been assigned to the hydrogen atoms on the basis of difference maps obtained by (Fo-Fe) syntheses where the contribution of all the atoms other than the hydrogens has been subtracted. The carbon-hydrogen bonds, in the case of salicyclic acid[14], have an average length of 0.89A with a standard deviation of about 0.1A. This is considerably smaller than the accepted distance but Cochran points out that there is no reason to suppose in this case that the point of maximum electron density coincides with the proton. The oxygen-hydrogen bond distance of the carboxyl group was found to be 0.91A, which is also less than the value normally taken for this bond.

## Part I The Crystal and Molecular Structure of α-Ethynylacetic Acid.

### (a) Introduction



Ethynylacetic acid (prop-2-yne-1-carboxylic acid) possesses the structure shown above, and the aim of this investigation was to determine the position of the hydrogen atom at the end of the carbon chain and if possible the nature of its bonding to the adjacent carbon atom.

The configuration of this acid made appear favourable the determination of the position of this hydrogen atom by X-ray methods using two-dimensional methods of investigation. The sp hybridisation of the two carbon atoms of the triple bond results in these two atoms, the carbon atom of the methylene group and the terminal hydrogen atom being collinear. Thus in a projection in which these carbon atoms are resolved, the terminal hydrogen atom will be fairly well displaced from the adjacent carbon atom.

The nature of a carbon-hydrogen bond depends upon the type of molecule in which it is present. Methane would seem to have a small bond dipole in the direction $C^{+} H^{-}$. In ethylene, the hydrogen atom becomes more positive so that the C - H bonds appear to possess zero dipole moment or a small one of sign $C^{-} H^{+}$. In acetylene, this effect is continued so that the C - H bonds have a fairly large bond dipole of sign $C^{-} H^{+}$.

Walsh[26] has suggested that these changes in the bond dipoles can be explained by the differing types of the hybrid orbitals of carbon. The s-component of the carbon orbitals increases in the ratio $\frac{1}{4}$, $\frac{1}{3}$ and $\frac{1}{2}$ on going along the above series. In an s-orbital the electrons are more close to the carbon nucleus than in a p-orbital. Similarly in an s-component of a hybrid orbital the electrons will be nearer to the carbon nucleus than in a p-component. The electron pair forming the bond is thus increasingly displaced towards the carbon nucleus and away from the hydrogen on proceeding along the above series and hence the hydrogen atom becomes increasingly positive. In this way it is possible to explain the acidic nature of acetylene and the increased electron-attracting nature of the ethynyl group as compared with the ethylenic, as is shown by the dissociation constants of the substituted acids and a study of reaction velocities[27].

There are thus four main types of carbon-hydrogen bonds, the three kinds mentioned above plus the aromatic ones which are thought to be similar to those in ethylene. The polarity of these is reflected in their electron density distribution but the effect is somewhat obscured by the differing thermal motions of the atoms.

Ethynylacetic acid was chosen as the mono-substituted acetylenic compound most suitable for examination by X-ray methods and it was hoped that a careful study of its electron density would reveal to what extent the terminal C - H bonds had become polarised. Alternatively, this bond may be considered as arising from resonance between the structures

$$R-C\equiv C-H \qquad R-C\equiv \overset{-}{C}:\ \overset{+}{H} \qquad R-C\equiv \overset{+}{C}\ \ :\overset{-}{H}$$

I II III

The contribution of form III is likely to be so small that this structure can be neglected and the hybrid considered as arising from resonance between the covalent form I and the ionic form II.

(b) Crystal Data.

α-Ethynylacetic Acid $C_4H_4O_2$; M 84.07; m.p. 83.5°C; d, calc 1.293, found 1.306. Monoclinic prismatic, $a = 8.06 \pm 0.02$, $b = 4.20 \pm 0.01$, $c = 25.78 \pm 0.06$A, $\beta = 98°8' \pm 30'$. Absent spectra, (h0l) when h is odd, (0k0) when k is odd, and (0kl) when l is odd. Space Group $C_{2h}^5 - P2_1/a$. Eight molecules per unit cell. Molecular symmetry, nil. Volume of the unit cell 864.0$A^3$. Absorption coefficient for X-rays, ($\lambda = 1.542$) $u = 10.37 cm^{-1}$. Total number of electrons per unit cell, F(000) = 352.

(c) Polymorphism.

The investigation of the structure of this acid was hampered by the presence, at first unrecognised, of a second crystal form. This form, the β-form, has a unit cell with the dimensions,

$$a = 8.06 \pm 0.1,$$
$$b = 4.20 \pm 0.03,$$
$$c = 25.55 \pm 0.06A. \qquad \beta = 90 \pm 1°.$$

It will be noted that the a and b axes in both the α and β forms are equivalent in length whilst the c axial lengths correspond closely on allowing for the change in the value of the angle β. Other similarities between the two forms are apparent. The two sets of (h0l) reflections, as observed on rotation photographs about the b axes, appear indistinguishable although considerable differences were noticed in the case of the (h1l) reflections. The structures of the two forms must agree closely in projection along the b axes but they will differ considerably in space. The β-form was not however studied in any detail.

The difficulty in recognising the existence of these polymorphic forms was due largely to their considerable similarity. It was increased by the volatile nature of the crystals which resulted, until this polymorphism was recognised, in fragments of different crystals being examined at succeeding stages of the work and, in some cases, being used to collect all the data about one axial direction.

In the initial X-ray examination, crystals were set up about axes which were later found to be the a and b axes of the α-form and the c axis of the β-form. As the two forms are very similar the axial reflections, which are common to two of the zones, appeared to correspond. On this basis, the c axis was 25.6A in length the β angle very nearly 90° and the unit cell pseudo-orthorhombic with the apparent space group Pcan-$D_{2h}^{11}$ or $C_{2v}^{5c}$. Attempts were made to derive a trial structure using methods similar to those outlined below for the α-form but without success. The reason for this became apparent on solving the latter structure.

In the continuation of the experimental work, a first-layer Weissenberg film was obtained about the b axis. This indicated that the smallest unit cell would have a long axis of length 25.9A and an angle β of 99° approximately, whereas a value of the β angle of 90° would correspond to a cell of twice this size with an axis 51A in length. The unit cell dimensions were reinvestigated to explain this discrepancy and a rotation photograph about the b axis was obtained which, when compared with a previous photograph supposedly about the same axis, was found to be very similar in the zero layer line but differed in a number of respects in the first layer line. Polymorphism was immediately suggested and was borne out by the discovery, for one type of crystal, of an axis of length 51A and normal to both the a and b axis. The true c axis of this crystal was found to be displaced from this by about 9° in the direction of the a axis.

The experimental data for this form, which was named the α-form, was then obtained using portions of one large crystal.

(d) General Arrangement of the Molecules.

The α-form is monoclinic but possesses a pseudo-orthorhombic structure. Thus, in the (h0l) series of reflections, the $(20\bar{1})$ is an approximate plane of symmetry. The (200) and $(20\bar{2})$ reflections are of nearly equal intensity and spacing as are also the (201) and $(20\bar{3})$, the (202) and $(20\bar{4})$. This approximate symmetry breaks down to some extent with the high order reflections, the most noticeable example being the (805) plane which is weak whilst the $(80\overline{13})$ is of medium strength. These differences between these reflections help to distinguish between the two very similar crystal directions in which the c axis could lie. Thus if this were taken in the $(20\bar{2})$ plane its length would be 25.90A instead of 25.78A and the angle β 99°47′ instead of 98°8′.

The space group $C_{2h}^{5}$ – $P2_1/a$ possesses four asymmetric units in the unit cell which contains in this case eight molecules i.e. two molecules in the asymmetric unit.

Normally carboxylic acids are grouped in dimers round a centre of symmetry between the carboxyl groups but other arrangements are possible and three cases arise.

1. The molecules may not be arranged in dimers involving the use of any of the elements of symmetry.

2. The molecules may be arranged in dimers which possess an element or elements of symmetry which do not coincide with any of the crystal elements of symmetry. The full symmetry of the molecular grouping is not used in forming the crystalline arrangement. It is not uncommon for molecules, which appear to possess planes or axes of symmetry, to fail to use them in building up the crystal. Examples of this are seen in naphthalene and anthracene. In general, use is made of a centre of symmetry if this is present or can readily be produced by a suitable arrangement of the molecules but pyrene and 1:2:5:6-dibenzanthracene appear to be exceptions.

3. The molecules are arranged in dimers about a centre of symmetry which coincides with a centre of symmetry within the crystal. The unit cell of the space group $C_{2h}^{5}$ - $P2_1/a$ contains eight centres of symmetry of which only two are normally occupied by centro-symmetrical molecules or groupings of molecules. This is sufficient

to fulfil the symmetry of the space group but there is no reason to suppose that this number cannot be exceeded so that four centres may be occupied by centrosymmetrical groupings. In many cases this will lead to the formation of a space group of higher symmetry but this cannot be assumed in every case.

α-Ethynylacetic acid has now been shown to belong to this last group. The eight molecules in the unit cell are arranged in dimers round centres of symmetry which coincide with the crystal centres. This arrangement permits an explanation of the pseudo-orthorhombic structure of the compound and can be used to account for the non-space group absences. Similar arrangements have been observed in the case of stilbene, azobenzene and tolane[28].

In addition to the spectra required to be absent by the symmetry of the space group, the (0kl) reflections, with the possible exception of the (01l) which in any case would be very weak, were found to be absent when l is odd. These absences can be explained by the mutual interaction of the two molecules in the asymmetric unit. If these molecules are so arranged that, when an atom of the first molecule is in the position (y, z), the corresponding atom of the second molecule is at either $(-y, \frac{1}{2} - z)$ or $(\frac{1}{2} + y, \frac{1}{2} - z)$ then the values of the structure factors of the (0kl) planes will be zero when l is odd. With the c axis chosen as above the atoms of the second molecule were found to be in the general position $(\frac{1}{2} + y, \frac{1}{2} - z)$ from a study of the intensities of the (hk0) reflections. Had the c axis been chosen to lie along the $(20\bar{2})$ plane, the other relationship would have applied.

The projection of the unit cell on the (100) thus contains eight asymmetric units i.e. one molecule per asymmetric unit and there is introduced an additional centre of symmetry one quarter way along the c axis in this projection. The structure factor equations for the (0kl) planes with l even then simplify to

$$A = 8 \cos 2\pi ky \cos 2\pi lz \quad \text{when } k = 2n,$$

$$\text{and} \quad A = -8 \sin 2\pi ky \sin 2\pi lz \quad \text{" } k = 2n + 1.$$

and the summation is carried out over one molecule.

The pseudo-orthorhombic structure can be explained by adopting an arrangement of the molecules similar to that found for stilbene. The eight molecules in the unit cell are grouped in dimers round the centres of symmetry at (000), ($\frac{1}{2}\frac{1}{2}0$).($0\frac{1}{2}\frac{1}{2}$) and ($\frac{1}{2}0\frac{1}{2}$). Alternatively the last two dimers might be placed at ($00\frac{1}{2}$) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) but this is ruled out by a consideration of the intensities of the (hk0) reflections. The dimer at ($0\frac{1}{2}\frac{1}{2}$) can, to a first approximation, be derived from the one situated at (000) by a rotation of 180° about the a axis, a translation of $\frac{c}{2}$ and reflection in a plane parallel to the (010) but with a displacement of $\frac{1}{4}$ b. This movement is not a real symmetry operation of the crystal and the variations in the intensities of the (h0l) reflections show that it cannot be quite exact.

The axes a, b and c′ were chosen to correspond with the pseudo-orthorhombic structure of the crystal. Thus c′ lies in the ($20\bar{1}$) plane and will, to a first approximation, be perpendicular to the crystal axes a and b and of length c sin β. The positions of the atoms of the two molecules in the asymmetric unit are, to a first approximation, given by the relationship ($x'$, $y$, $z'$) and ($x' - \frac{1}{4}$, $\frac{1}{2} + y$, $\frac{1}{2} - z'$). Structure factor equations for the (h0l′) series of reflections of this pseudo-orthorhombic cell were evaluated and it was found that:

$$A = 8 \cos 2\pi hx' \cos 2\pi lz' \text{ when } \tfrac{1}{2}h + l' = 2n,$$

$$\text{and } A = -8 \sin 2\pi hx' \cos 2\pi lz' \quad \text{"} \quad \tfrac{1}{2}h + l' = 2n + 1,$$

when the summation is carried out over one molecule. The indices $(h0l')$ are related to the $(h0l)$ by $l' = \frac{1}{2}h + l$.

(e) Analysis of the Structure.

From the size and shape of the unit cell, the postulated grouping of the molecules and taking into account considerations of packing it appeared that the length of the molecule lay approximately along the long c axis with the plane of the molecule inclined at about 30-40° to the (010).

The projection along the short b axis was studied first. The axial planes (0,0,32), (0,0,30) and (0,0,22) are very strong and assuming a molecular structure with normal bond lengths and valence angles and, as a first approximation, a planar configuration, it was soon possible to position the molecule in the asymmetric unit of the pseudo-orthorhombic cell so that good agreement was obtained between the calculated and observed values of the structure factors of the (00l) planes. By carrying out a one-dimensional Fourier synthesis the z-coordinates of the atoms were obtained with greater precision.

With these coordinates and taking into account the approximate tilt of the plane of the molecule and the strong values of the (202), (207) and (2,0,22) planes - referred to the a, b and c′ axes - a trial structure for the pseudo-orthorhombic cell was soon obtained which gave a discrepancy of 34.4% over the 112 observed (h0l′) planes. Signs were attributed to 96 of these and a Fourier synthesis F1 was carried out over the pseudo-cell, taking $|F(h0\bar{l}')| = |F(h0l')|$. All the atoms except $C_1$ were resolved. New atomic positions were obtained and the discrepancy was found to have fallen to 25.4%.

The second Fourier synthesis F2 was carried out over the true monoclinic cell. The $(h0\bar{l}')$ reflections were included at their observed values which increased the discrepancy to 26.6%. The signs of these planes were obtained by means of the transformation,

$$F(h0\bar{l}') = F(h0l') \qquad \text{when } \tfrac{1}{2}h + l' = 2n,$$

and $$F(h0\bar{l}') = -F(h0l') \qquad \text{"} \quad \tfrac{1}{2}h + l' = 2n + 1.$$

The planes were reindexed to accord with the monoclinic cell and signs were given to 188 of these. This Fourier synthesis and the introduction of an empirical composite scattering curve for the carbon and oxygen atoms resulted in the discrepancy falling to 21.1%. The number of planes to which signs were given was 193.

A difference synthesis D1 was then carried out. Planes with a value of $2\sin\theta < 0.4$ were omitted from this since they were most likely to be affected by the fact that the contributions of the hydrogen atoms were not included in the calculated values of the structure factors. Planes with a value of $|Fo-Fc| < 1$ were also omitted from this and all subsequent difference syntheses. The discrepancy was found to be 18.6%.

The (100) projection was then examined. Approximate values of the x- and z-coordinates of the atoms were known and from these and the expected values of the bond lengths values of the y-coordinates were deduced. This structure gave a discrepancy of 36% over the (Okl) reflections and allowed signs to be assigned to 43 of the 51 planes observed. The scattering curve derived in the (010) projection was also applied here. A Fourier synthesis F3 was carried out but the resolution of the atoms was very poor owing to the overlapping of the atoms $C_1$ and $O_2$ and the merging of the atoms $C_4$, $O_1$ and $O_2$ with similar atoms of adjacent molecules. Coordinates were assigned to the atoms and the discrepancy was found to have fallen to 31.5%. Signs were given to 45 planes.

As the resolution of the atoms in this zone was very poor, it was decided to refine this projection by means of (Fo-Fc) syntheses. Accordingly two difference syntheses D2 and D3 were carried out from which were omitted the contributions of the planes with $2\sin\theta < 0.4$. The z-coordinates obtained from the (010) projection were maintained unaltered. As a result of these signs could be given to all the observed planes and the value of the discrepancy was reduced to 15.3%.

At this stage it was thought desirable to adopt atomic scattering curves with some theoretical foundation and those derived by McWeeny[29] were used. These theoretical curves are then modified by a temperature factor to allow for the thermal motion of the atoms, as follows:

$$f = f_{th}\, e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$$

where $f$ is the desired atomic scattering factor for a given value of $\sin\theta$, $f_{th}$ is the theoretical value at the same $\sin\theta$ and B is a constant depending on the thermal motion of the atoms. For the carbon atoms, the values of the valence state were taken and for the oxygen atoms, those given by $\frac{1}{3}(f^{\parallel} + 2f^{\perp})$ , where $f^{\parallel}$ and $f^{\perp}$ are the scattering factors parallel and perpendicular to the symmetry axis of an unbonded neutral atom (defined by that 2p orbital which contains a different number of electrons from the other 2p orbitals). From these a composite scattering curve for the carbon and oxygen atoms was derived by weighting their contributions in the proportion of their scattering power in the molecule.

The difference maps obtained above showed, in some instances, the presence of peaks corresponding to the expected positions of the hydrogen atoms. These peaks were liable to cause incorrect shifts to be applied to the carbon and oxygen atoms. To guard against this the positions of the hydrogen atoms were calculated assuming normal valence angles and a carbon-hydrogen bond length of 1.09A except for $C_4 - H_4$ and $C_8 - H_8$ where a length of 1.06A was taken. The contributions of these atoms to the structure factors of the planes with a value of $2\sin\theta \leqslant 1.2$ were calculated as beyond this their contributions were not thought to be significant due to the rapid falling off of the scattering curve. The theoretical atomic scattering curve due to McWeeny was used with an arbitrary value of $2.0 \times 10^{-16}$ being assumed for B.

From the observed values of the structure factors of the (h0l) reflections were subtracted the calculated values of the hydrogen contributions; the remainder represents the contributions of the carbon and oxygen atoms. The reflections were then divided into groups according to their values of 2sinθ. The mean value of the scattering factors in each of the groups is given by

$$\bar{f} = \frac{F_1 + F_2 + \text{----} + Fn}{G_1 + G_2 + \text{----} + Gn}$$

where Fr is the contribution of the carbon and oxygen atoms to the observed values of the structure factors of the $r^{th}$ reflection, Gr is the value of the geometrical structure factor obtained by weighting the contributions of the carbon and oxygen atoms in the ratio 6:8 and n is the number of reflections in the group.

For each group,

$$\bar{f} = f_{th}\, e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$$

and $$\log_e \frac{\bar{f}}{f_{th}} = -B\left(\frac{\sin\theta}{\lambda}\right)^2.$$

By graphical methods it was possible to obtain the value of B which gave the best fit of these mean values of the scattering factors to the theoretical curve.

This method gave a value of B = $4.0 \times 10^{-16}$ for the composite carbon-oxygen curve and this value was also assumed for the hydrogens. The structure factors were recalculated using these scattering curves and including the contributions of the hydrogen atoms. The discrepancies were found to be 16.8% for the (h0l) series of reflections and 13.6% for the (0kl).

Difference syntheses D4 and D5 were carried out in these projections respectively. The contributions of all the planes, to which signs had been given, were included except (002) which was observed low possibly due to extinction. New atomic positions were obtained for the atoms, the z-coordinates from the two projections being averaged with greater weight given to those obtained from the (010) projection. Almost all the atoms were seen to lie in regions of the difference map where $(\rho_o - \rho_c)$ was negative indicating that the chosen value of B was too small. Cochran[11] has shown that there is a difference of $0.15 e\text{Å}^{-2}$ at the atomic centre between the electron densities of two carbon atoms whose temperature factor B differs by $0.1 \times 10^{-16}$. The application of this method of correction indicated a mean value of B of $4.2 \times 10^{-16}$. This change, in most instances, gave an estimated value of $(\rho_o - \rho_c)$ which was negative at the centres of the carbon atoms and positive at the centres of the oxygen atoms. An effect of this nature would be introduced by the choice of a composite scattering curve in place of separate ones for the carbon and oxygen atoms. It was decided therefore to introduce separate scattering curves for these atoms with a value of B of $4.2 \times 10^{-16}$ in both cases. A similar value of B was assigned to the hydrogen atoms. The discrepancies were then 14.3% for the (h0l) series of reflections and 12.2% for the (0kl).

Another set of difference syntheses D6 and D7 were carried out. The shifts in atomic coordinates were fairly small having, in the (010) projection an average value of 0.009A and a maximum of 0.015A for $O_1$ and $O_3$ and in the (100) projection an average of 0.008A and a maximum of 0.014A for $O_1$. The thermal motion of the oxygen atoms varies considerably from one atom to another but a mean value of B of $4.4 \times 10^{-16}$ was taken. For the other atoms the value of B was maintained unchanged at $4.2 \times 10^{-16}$. The discrepancies were evaluated and found to be 13.1% for the (h0l) reflections, 11.8% for the (0kl) and 18.0% for the (hk0), the overall discrepancy being 13.7%. If the unobserved planes are included with values of Fo equal to zero, the discrepancies are 16.3% for the (h01) reflections and 14.9% for the (0kl).

Signs had now been given to all but two of the (h01) planes and all but one of the (0kl). Fourier syntheses F4 and F5 were carried out with (002) included at its calculated value and reveal the electron density in the projections on the (010) and (100). These are shown in Figs. 1 and 3 respectively whilst Fig. 2 indicates the arrangement of the molecules in the projection on the (010). The two crystallographically independent molecules in the asymmetric unit in the projection on the (010) are shown side by side in Fig. 4 and the very great similarity between them is easily seen.

The (Fo-Fc) synthesis D8 was evaluated for the projection on the (010) in which Fc represented the calculated contributions of the carbon and oxygen atoms and this is included as Fig. 5. This difference map shows that part of the electron density which is due to the hydrogen atoms. It also reveals the imperfections of the model used in calculating the Fc's. Thus small shifts in the atomic coordinates of the atoms $C_5$,$O_1$ and $O_3$ are indicated. The map also reveals the thermal motions

Fig. 1. F.4. Electron-density projection along the b axis on the (010). Each contour line represents a density increment of one electron per $A^2$, the one electron line being dotted.

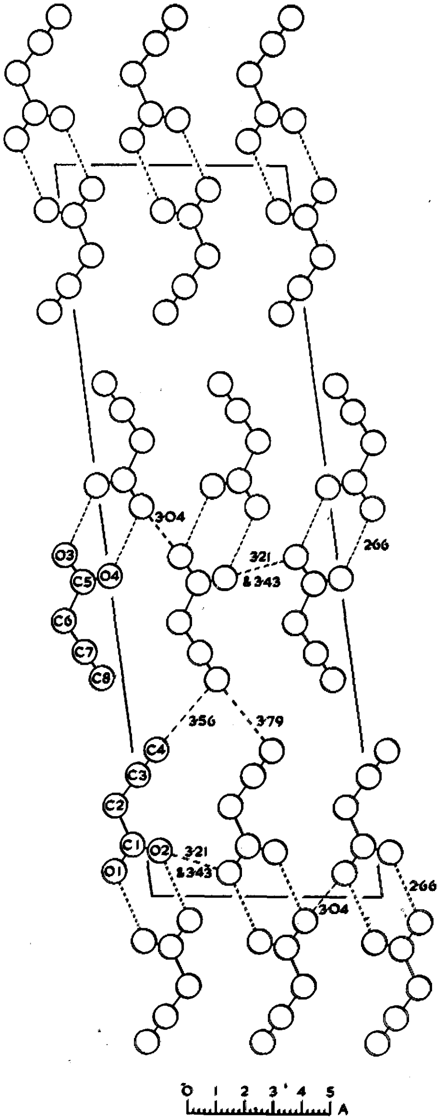


Fig. 2. Projection along the b axis on the (010) showing the general arrangement of the molecules.

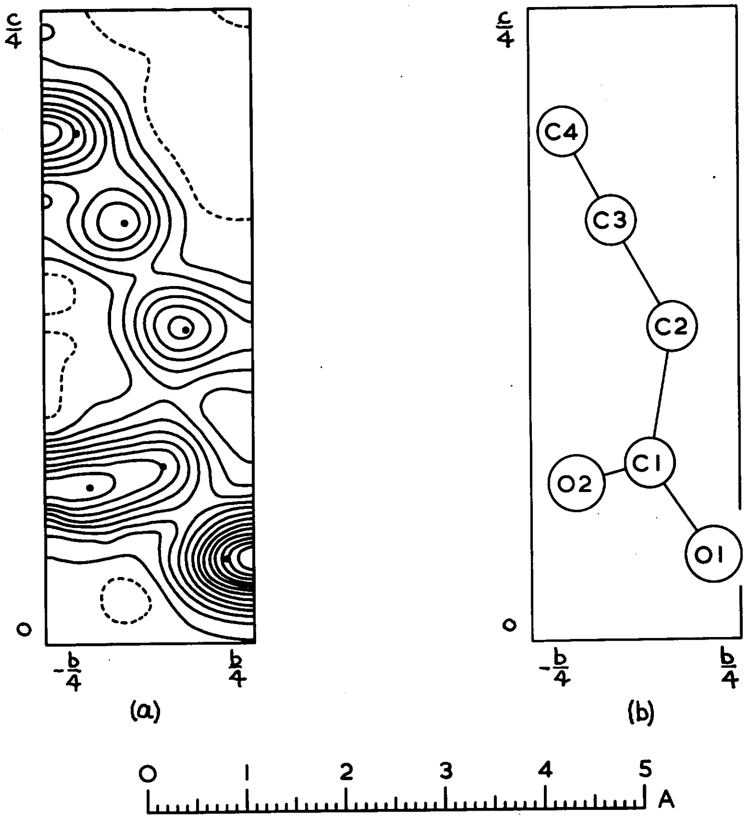


Fig. 3. (a) F.5 Electron density projection along the a axis on the (100). Each contour line represents a density increment of one electron per $A^2$, the one electron line being dotted.

(b) Same projection showing the arrangement of the atoms.

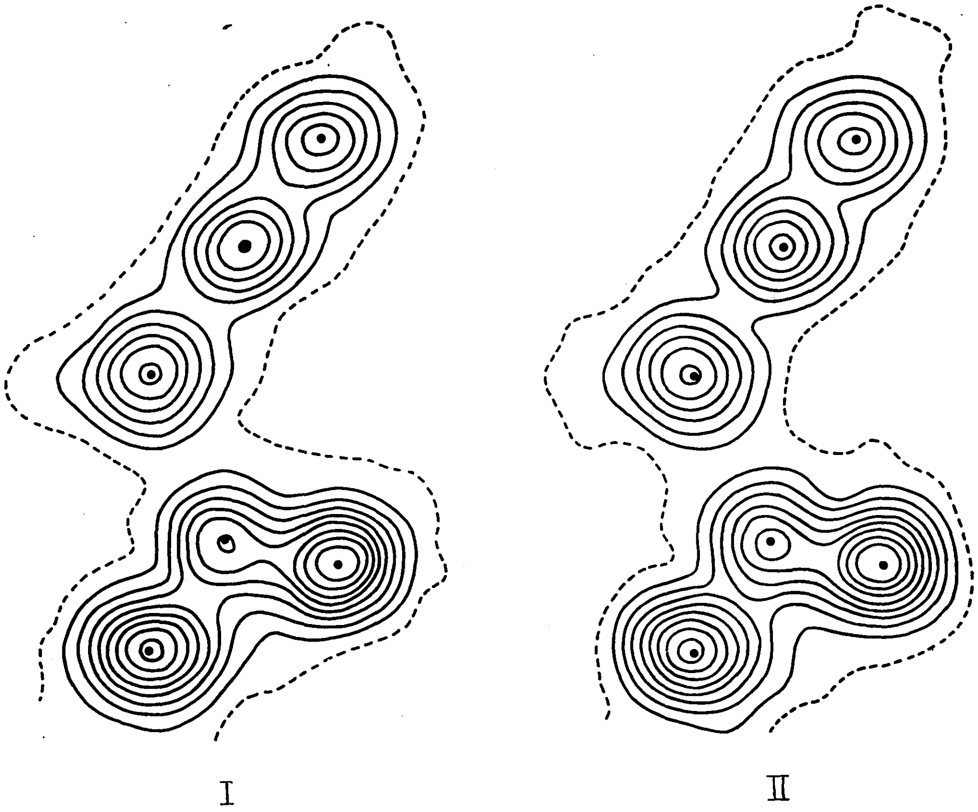


Fig. 4. Comparison of the two molecules in the asymmetric unit in the projection on the (010) and shown in Fig. 1. Molecule I is situated at centre of symmetry at (000) and molecule II at ($0\frac{1}{2}\frac{1}{2}$).

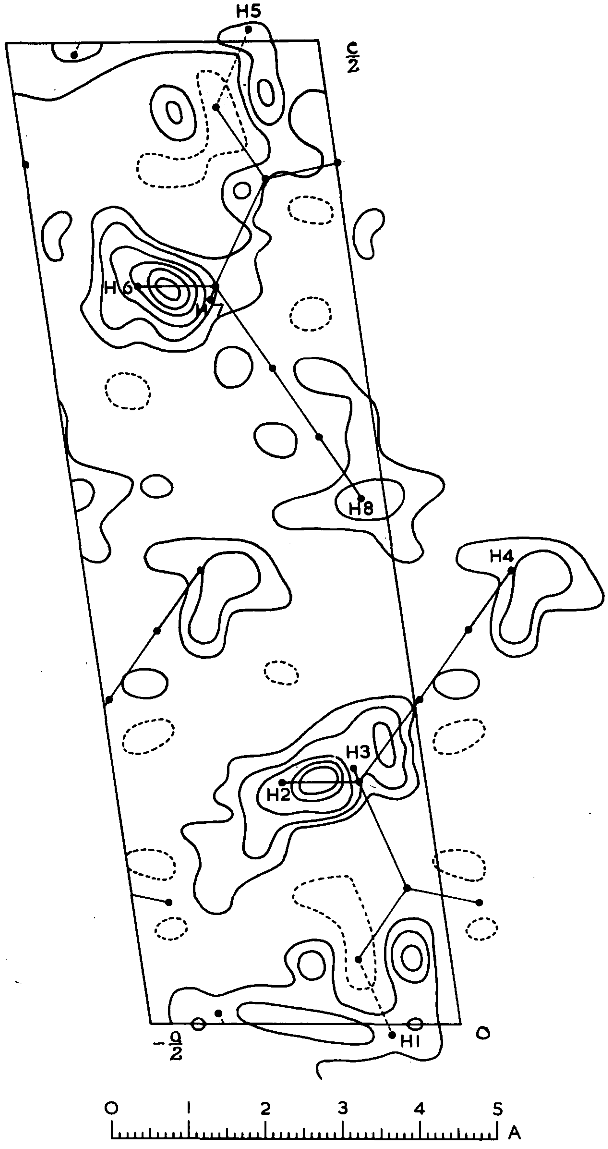


Fig. 5. D.8. Difference between electron density projected on the (010) and that calculated for isolated carbon and oxygen atoms. Each contour line represents a density increment of 0.25 electrons per $A^2$ with the negative contours dotted and the zero line omitted.

of the molecules. The atoms $C_7$ and $C_8$ and, to a lesser extent $C_3$ and $C_4$ are seen to be vibrating in a direction more or less perpendicular to the carbon chains whilst the large peaks in the map adjacent to $O_1$ and $O_3$ show that these atoms possess considerable anisotropic motion in a direction almost parallel to the a axis.

The other large peaks in this map are seen to be associated with the positions of the hydrogen atoms but in view of the likely accuracy of $(\rho_o - \rho_c)$ no attempt was made to position these atoms from the map. The electron density peaks due to $H_1$ and $H_5$ are seen to be liable to considerable distortion due to the choice of incorrect scattering curves for $O_1$ and $O_3$ and the atoms $H_2$ and $H_3$ and $H_6$ and $H_7$ overlap considerably. Atoms $H_4$ and $H_8$ are revealed most clearly; $H_8$ is seen to correspond very closely with its calculated position but $H_4$ is displaced slightly in the direction of the a axis.

The coordinates of the atoms in the asymmetric crystal unit are given in Table I where x, y and z are referred to the monoclinic crystal axes and x′, y and z′ to the orthogonal axes a, b and c′, where c′ is perpendicular to a and b.

Then $x' = x + z \cos \beta$,

$z' = z \sin \beta$.

The dimensions of the two molecules in the asymmetric crystal unit as shown in Table II. It will be seen that good agreement is obtained between the two sets of values, the greatest difference being 0.024A between $C_2 - C_3$ and $C_6 - C_7$ and 0.8° between $O_1 - C_1 - C_2$ and $O_3 - C_5 - C_6$ and also between $O_2 - C_1 - C_2$ and $O_4 - C_5 - C_6$. The average difference is 0.012A in length and 0.6° in angle. The averaged molecular dimensions are shown in Table III.

The number of electrons associated with the atoms $C_4$, $C_8$, $H_4$ and $H_8$ were then determined from the difference map D8. The limits of the areas over which the electron counts were made were fixed by perpendiculars drawn through the mid points of the bonds $C_3 - C_4$, $C_4 - H_4$, $C_7 - C_8$ and $C_8 - H_8$ and by a circle of radius 1.1A drawn with the atomic site as centre. The areas allotted to the atoms $C_4$ and $C_8$ were 2.18A$^2$ and to $H_4$ and $H_8$ 3.34A$^2$.

## Table I.

Atomic Coordinates

Centre of symmetry as origin;
x, y, z, x′ and z′ in A.

| Atom | $\frac{x}{a}$ | $\frac{y}{b}$ | $\frac{z}{c}$ | x | y | z | x′ | z′ |
|---|---|---|---|---|---|---|---|---|
| $C_1$ | −0.0539 | 0.0347 | 0.0697 | −0.434 | 0.146 | 1.797 | −0.688 | 1.779 |
| $C_2$ | −0.1061 | 0.0900 | 0.1236 | −0.855 | 0.378 | 3.187 | −1.306 | 3.155 |
| $C_3$ | 0.0100 | −0.0539 | 0.1658 | 0.081 | −0.226 | 4.275 | −0.523 | 4.232 |
| $C_4$ | 0.1047 | −0.1681 | 0.2011 | 0.844 | −0.706 | 5.185 | 0.111 | 5.133 |
| $C_5$ | −0.1164 | 0.5347 | 0.4303 | −0.938 | 2.246 | 11.093 | −2.507 | 10.982 |
| $C_6$ | −0.2214 | 0.5900 | 0.3764 | −1.784 | 2.478 | 9.704 | −3.156 | 9.607 |
| $C_7$ | −0.1492 | 0.4461 | 0.3342 | −1.202 | 1.874 | 8.615 | −2.420 | 8.529 |
| $C_8$ | −0.0897 | 0.3319 | 0.2989 | −0.723 | 1.394 | 7.706 | −1.813 | 7.629 |
| | | | | | | | | |
| $O_1$ | −0.1486 | 0.1847 | 0.0333 | −1.198 | 0.776 | 0.859 | −1.319 | 0.850 |
| $O_2$ | 0.0594 | −0.1425 | 0.0619 | 0.479 | −0.599 | 1.597 | 0.253 | 1.581 |
| $O_3$ | −0.1792 | 0.6847 | 0.4667 | −1.444 | 2.876 | 12.031 | −3.145 | 11.911 |
| $O_4$ | 0.0036 | 0.3575 | 0.4381 | 0.029 | 1.501 | 11.293 | −1.568 | 11.180 |
| | | | | | | | | |
| $H_1$ | 0.113 | −0.168 | 0.006 | 0.91 | −0.70 | 0.15 | 0.88 | 0.15 |
| $H_2$ | −0.230 | −0.013 | 0.124 | −1.86 | −0.05 | 3.19 | −2.31 | 3.15 |
| $H_3$ | −0.112 | 0.346 | 0.131 | −0.90 | 1.45 | 3.37 | −1.38 | 3.33 |
| $H_4$ | 0.189 | −0.272 | 0.232 | 1.52 | −1.14 | 5.99 | 0.68 | 5.93 |
| $H_5$ | 0.107 | 0.333 | 0.494 | 0.87 | 1.40 | 12.74 | −0.94 | 12.62 |
| $H_6$ | −0.345 | 0.488 | 0.376 | −2.78 | 2.05 | 9.70 | −4.16 | 9.61 |
| $H_7$ | −0.233 | 0.846 | 0.369 | −1.87 | 3.55 | 9.52 | −3.22 | 9.43 |
| $H_8$ | −0.036 | 0.228 | 0.268 | −0.29 | 0.96 | 6.91 | −1.27 | 6.84 |

## Table II

### Molecular Dimensions.

| | | | |
|---|---|---|---|
| $C_1 - C_2$ | 1.526 ± 0.020 A | $C_5 - C_6$ | 1.538 ± 0.020 A |
| $C_2 - C_3$ | 1.462 ± 0.024 | $C_6 - C_7$ | 1.438 ± 0.024 |
| $C_3 - C_4$ | 1.202 ± 0.024 | $C_7 - C_8$ | 1.188 ± 0.024 |
| $C_1 - O_1$ | 1.298 ± 0.022 | $C_5 - O_1$ | 1.291 ± 0.022 |
| $C_1 - O_2$ | 1.217 ± 0.025 | $C_5 - O_2$ | 1.214 ± 0.025 |

| | | | |
|---|---|---|---|
| $C_1{-}C_2{-}C_3$ | 112.6 ± 1.3° | $C_5{-}C_6{-}C_7$ | 113.0 ± 1.3° |
| $C_2{-}C_3{-}C_4$ | 178.9 | $C_6{-}C_7{-}C_8$ | 178.4 |
| $O_1{-}C_1{-}C_2$ | 112.0 ± 1.6 | $O_3{-}C_5{-}C_6$ | 111.2 ± 1.6 |
| $O_2{-}C_1{-}C_2$ | 123.6 ± 1.3 | $O_4{-}C_5{-}C_6$ | 124.4 ± 1.3 |
| $O_1{-}C_1{-}O_2$ | 123.8 ± 1.5 | $O_3{-}C_5{-}O_4$ | 124.4 ± 1.5 |

## Table III

### Averaged Molecular Dimensions.

| | | | |
|---|---|---|---|
| $C_1 - C_2$ | 1.532 ± 0.019 A | $C_1{-}C_2{-}C_3$ | 112.8 ± 1.1° |
| $C_2 - C_3$ | 1.450 ± 0.022 | $C_2{-}C_3{-}C_4$ | 178.8 |
| $C_3 - C_4$ | 1.195 ± 0.021 | $O_1{-}C_1{-}C_2$ | 111.6 ± 1.4 |
| $C_1 - O_1$ | 1.294 ± 0.020 | $O_2{-}C_1{-}C_2$ | 124.0 ± 1.2 |
| $C_1 - O_2$ | 1.216 ± 0.022 | $O_1{-}C_1{-}O_2$ | 124.1 ± 1.3 |

The number of electrons associated with these atoms is (see p. 19)

$$n_\theta = n_e + \delta S.\Sigma D.$$

where the summation is carried out over the points inside S at which D was evaluated. The synthesis was evaluated at interval of $^{a}/30$ and $^{c}/120$ so that $\delta S = A/3600$. The values of $n_e$ were taken as 0 for the hydrogen atoms and 5.95e for the carbon atoms, the latter value being due to Cochran[30]. The results are shown in Table IV.

Table IV

Number of Electrons

| Atom | $n_e$ | $n_\theta$ | Average $n_\theta$. |
|---|---|---|---|
| $C_4$ | 5.95 | 6.22 | 6.23 |
| $C_8$ | 5.95 | 6.24 | |
| $H_4$ | 0 | 0.73 | 0.78 |
| $H_8$ | 0 | 0.82 | |

The total for the averaged group $C_4H_4$ is 7.01e.

## Geometry of the Molecules.

The equation of the plane through the points $C_1, C_2$ and

$C_4$ referred to the orthogonal axes a, b and c′, where c′ is perpendicular to a and b, is given by

$$x' + 1.627y + 0.175z' + 0.139 = 0,$$

and that through the points $C_1$, $O_1$ and $O_2$ is

$$x' + 1.223y + 0.150z' + 0.242 = 0.$$

The angle between these planes is 7.6°.

The equation to the plane through the points $C_5$, $C_6$ and $C_8$ is given by

$$x' + 1.606y - 0.201z' + 1.107 = 0,$$

and that through the points $C_5$, $O_3$ and $O_4$ is

$$x' + 1.223y - 0.143z' + 1.331 = 0.$$

The angle between these planes is 7.4°.

The plane of the carboxyl group is inclined to the plane through the carbon atoms by an angle of 7.5°, on averaging the above results.

## Intermolecular Distances.

The more important intermolecular distances are indicated by dotted lines in Fig. 2. The closest approach between molecules occurs in the hydrogen bridges of length 2.66A which connect the oxygen atoms of adjacent carboxyl groups. Certain other oxygen-oxygen distances especially those of 3.04 and 3.21A are shorter than is usual, although distances of 3.11A have been reported for β-succinic acid[31]. The other distances are all greater than 3.4A. The figures are collected in Table V where A refers to the standard molecules, B the reflected molecules, C the molecules one translation along the C axis and D the molecules one translation along the b axis.

## Table V

### Intermolecular Distances.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $O_1$(A) | .... | $O_2^1$(A) | 2.66A | $O_4$(A) | .... | $C_5$(B) | 3.51 |
| $O_2$(A) | .... | $O_1^1$(A) | 2.66 | $C_4$(A) | .... | $C_8$(B) | 3.56 |
| $O_3$(A) | .... | $O_4^1$(C) | 2.66 | $C_4$(D) | .... | $C_3$(B) | 3.70 |
| $O_4$(A) | .... | $O_3^1$(C) | 2.66 | $O_4$(D) | .... | $C_6$(B) | 3.72 |
| $O_1$(B) | .... | $O_1^1$(A) | 3.04 | $C_8$(A) | .... | $C_7$(B) | 3.73 |
| $O_3$(B) | .... | $O_3^1$(C) | 3.04 | $C_4$(D) | .... | $C_2$(B) | 3.73 |
| $O_2$(A) | .... | $O_1$(B) | 3.21 | $O_2$(A) | .... | $C_2$(B) | 3.74 |
| $O_4$(D) | .... | $O_3$(B) | 3.21 | $C_8$(A) | .... | $C_6$(B) | 3.78 |
| $O_2$(D) | .... | $O_1$(B) | 3.43 | $C_4$(A) | .... | $C_8$(A) | 3.79 |
| $O_4$(A) | .... | $O_3$(B) | 3.43 | $C_4$(D) | .... | $C_8$(A) | 3.79 |
| $O_4$(A) | .... | $C_6$(B) | 3.46 | $C_4$(A) | .... | $C_7$(B) | 3.83 |
| $O_2$(D) | .... | $C_2$(B) | 3.48 | $C_3$(A) | .... | $C_2$(B) | 3.94 |
| $O_2$(D) | .... | $C_1$(B) | 3.51 | $C_7$(D) | .... | $C_6$(B) | 3.98 |

## (f) Accuracy of the Results.

The estimated standard deviation of the atomic coordinates is (see p. 16)

$$\sigma(x) = \frac{\frac{1}{A}\,\frac{2\pi}{a}\left\{\sum_{z} h^2(\Delta F)^2\right\}^{\frac{1}{2}}}{2p\,\rho(0)}$$

By taking $\Delta F = |F_o - F_c|$ an overestimate of the combined experimental and residual finite-series errors is obtained. The value of p was found to be 3.9 from measurements of well resolved atoms in the final projection on the (010). The values obtained are shown in Table VI.

Table VI

Estimated Standard Deviations of the Atomic Coordinates.

| | | σ(x),A | σ(y),A | σ(z),A |
|---|---|---|---|---|
| (010) projection | Carbon | 0.019 | | 0.013 |
| | Oxygen | 0.014 | | 0.010 |
| (100) projection | Carbon | | 0.023 | 0.017 |
| | Oxygen | | 0.017 | 0.012 |

Taking for the carbon atoms $\sigma(x) = 0.019$, $\sigma(y) = 0.023$ and $\sigma(z) = 0.013$A the R. M. S. radial error of position was found to be 0.019A. For the oxygen atoms $\sigma(x) = 0.014$, $\sigma(y) = 0.017$ and $\sigma(z) = 0.010$A giving the R. M. S. radial error of position as 0.014A. The mean standard deviation for a carbon-carbon bond is thus 0.027A and for a carbon-oxygen bond 0.024A. The standard deviation of the individual bond lengths and angles were calculated by means of the formulae already quoted and are shown in Table II.

The standard deviation in the electron density is given by (see p.16)

$$\sigma(\rho_o) = \sigma(\rho_o - \rho_c) = \frac{1}{A}\left\{\sum_2 (\Delta F)^2\right\}^{\frac{1}{2}}$$

For the projection on the (010) $\sigma(\rho_o) = 0.24$e.A$^{-2}$ and for that on the (100) $\sigma(\rho_o) = 0.30$e.A$^{-2}$.
The peaks in the difference map D8 corresponding to $H_4$ and $H_8$ are seen to be significant and may be attributed to these atoms.

The standard deviation in the number of electrons in a given area is (see p. 20)

$$\sigma(n_e) = \sqrt{2}\,\sigma(Fo)\,\frac{x_2-x_1}{a}\,\frac{z_2-z_1}{c}\left[\sum_h\sum_l\left\{\frac{\sin\pi h(x_2-x_1)/a}{\pi h(x_2-x_1)/a}\right\}^2\left\{\frac{\sin\pi l(z_2-z_1)/c}{\pi l(z_2-z_1)/c}\right\}^2\right]^{\frac{1}{2}}$$

$$\text{where } \sigma(Fo) = \left\{\overline{(\Delta Fo)^2}\right\}^{\frac{1}{2}} = 2.22.$$

and $(x_2-x_1)/a = \frac{1}{5}$ and $(z_2-z_1)/c = \frac{1}{14}$. The latter corresponds to an area of 2.94 $A^2$, which is about equal to the average area over which the electron counts were made.

Then $\sigma(n_e) = 0.18e$.

A comparison of the results obtained for the two sets of crystallographically independent molecules within the unit cell revealed that the differences between them were not significant so far as the bond lengths and angles between the carbon and oxygen atoms, and the positions, maximum electron density and number of electrons in the atoms $C_4$ and $C_8$ and $H_4$ and $H_8$ were concerned. There may be some very small real differences in their internal structures due to their different crystallographic environment but the deviations observed are not significant. More accurate values of the molecular parameters may then be obtained by a process of averaging and these values of the bond lengths and angles are given in Table III. Other averaged values are as follows: the maximum electron density of $H_4$ is 0.70e.A$^{-2}$, the number of electrons in $H_4$ is 0.78e and in $C_4$ is 6.23e. The standard deviations of these mean values may now be estimated.

The bond lengths of the two sets of molecules in the unit cell are not independent since the y- and z-coordinates of similar atoms are related by the pseudo-symmetry. If this relationship is an exact one and the two types of molecules are indeed identical so far as their internal arrangements are concerned then the x-components of similar bonds must be equal in length.

The standard deviation in the distance in the direction of the a axis between two symmetrically independent atoms is given by

$$\sigma(dx) = \left\{\sigma^2(x_1) + \sigma^2(x_2)\right\}^{\frac{1}{2}}$$

If two independent measurements of this are made with equal accuracy, the standard deviation of the mean is

$$\sigma(\bar{dx}) = \frac{1}{\sqrt{2}}\left\{\sigma^2(x_1) + \sigma^2(x_2)\right\}^{\frac{1}{2}} =$$

$$= \left\{\left[\frac{\sigma(x_1)}{\sqrt{2}}\right]^2 + \left[\frac{\sigma(x_2)}{\sqrt{2}}\right]^2\right\}^{\frac{1}{2}}$$

The two estimations of the differences in the x-coordinates between pairs of similar atoms in the two types of molecules were regarded as independent but not those between the y- and z-coordinates which were obtained by means of the apparent symmetry between these molecules.

The mean standard deviation for the averaged carbon-carbon bond was found to be 0.024A and for the averaged carbon-oxygen bond 0.021A. in comparison with the values of 0.027 and 0.024A found respectively for the non-averaged bond lengths. The standard deviations of the averaged bond lengths and angles were also calculated and are shown in Table III. Also at points, in the projection on the (010), similarly situated with regard to the two types of molecules the standard deviation of the averaged electron density will be $\frac{0.24}{\sqrt{2}} = 0.17e.A^{-2}$ since the two estimations of this may be considered as independent. Similarly the standard deviation of the mean of the number of electrons is a given area will be 0.13e.

## (g) Discussion.

The structure of α-ethynylacetic acid is unusual in that it possesses the space group $C^5_{2h}$ - $P2_1/a$ with eight molecules in the unit cell, but similar arrangements have been observed for stilbene, azobenzene and tolane[28]. It is presumed that the intermolecular forces, in particular those due to the ethynyl groups at the end of the carbon chains, and the requirements of good packing are better satisfied by this arrangement than by one composed of crystallographically equivalent molecules.

The values of the bond lengths (Table III) obtained by averaging over the two molecules in the asymmetric unit are seen to be in good agreement with those obtained for similar compounds. The length of the triple bond $C_3 - C_4$ was found to be 1.20A compared with the value of 1.204A found for acetylene by spectroscopic methods[32]. The adjacent bond $C_2 - C_3$ is 1.45A long and this contraction from the normal single bond length of 1.54A is highly significant. For allylene[33] the equivalent bond length was found to be 1.460A by spectroscopic methods. The bond $C_1 - C_2$ with a length of 1.53A does not differ significantly from the standard carbon-carbon single bond length. The angle $C_1 - C_2 - C_3$ is 112.8° but this increase over the normal tetrahedral angle of 109.5° is not significant although similar values have been observed for other compounds e.g. β-succinic acid[31]. The dimensions of the carboxyl group agree closely with those found for other acids in similar arrangements and a number of the most accurate examples are shown in Table VII.

Table VII

Dimensions of the Carboxyl Group.

| | $C-O_1$ | $C-O_2$ | $C-C-O_1$ | $C-C-O_2$ | $O_1-C-O_2$ | $O_1 .. H .. O_2$ |
|---|---|---|---|---|---|---|
| Oxalic acid dehydrate(18) | 1.29A | 1.19A | 112.6° | 121.6° | 125.8° | - |
| α-Anhydrous oxalic acid(34) | 1.29 | 1.19 | 109.2 | 122.7 | 128.2 | 2.71 |
| Salicylic Acid (14) | 1.33 | 1.24 | 117.0 | 122.7 | 120.2 | 2.63 |
| α-Ethynylacetic Acid | 1.29 | 1.22 | 111.6 | 124.0 | 124.1 | 2.66 |

The sum of the angles round $C_1$ is 359.7° indicating that $C_1$, $C_2$, $O_1$ and $O_2$ are very nearly planar.

As a result of the sp hybridisation associated with the triple bond the atoms $C_2$, $C_3$ and $C_4$ should be collinear as should also be $C_6$, $C_7$ and $C_8$. The atom $C_3$ was found to lie on the line $C_2 - C_4$ and $C_7$ on the line $C_6 - C_8$ to within less than 0.01A. The angles $C_2$-$C_3$-$C_4$ and $C_6$-$C_7$-$C_8$ and their averaged value do not differ significantly from 180°. These atoms may then be taken as collinear within the limits of experimental error.

The mean maximum electron density of the averaged atoms $H_4$ and $H_8$ was found to be $0.70 e.A^{-2}$ from the difference map D8 and comparison with the standard deviation of the averaged electron density shows that this value is highly significant. The electron distribution of an isolated hydrogen atom was calculated by forming the two-dimensional transform of $f_{th}\, e^{-4.2\left(\frac{\sin\theta}{\lambda}\right)^2}$ and the maximum electron density found to be $0.66\ e.A^{-2}$. This calculated electron distribution will be only approximately correct since it assumes isotropic thermal motions of these atoms and the difference map reveals that they are vibrating in a direction almost perpendicular to the bonds with the carbon atoms.

The number of electrons associated with the atoms $C_4$, $C_8$, $H_4$ and $H_8$ was estimated by an electron count in their areas and is shown in Table IV. The averaged value obtained for the group $C_4H_4$ agrees closely with the theoretical value but there is a transfer of about 0.2e from $H_4$ to $C_4$. The direction of this electron transfer is in agreement with that demanded by theoretical considerations. Thus the terminal carbon-hydrogen bond is mainly covalent but would appear to possess about 20% ionic character.

The determination of the number of electrons associated with a particular atom is liable to a number of errors in addition to the experimental one already discussed. The areas allocated to the atoms are to some extent arbitrary so that electrons which really belong to one atom may be counted as belonging to another and this difficulty arises especially where the atoms lie close together in projection. Also the electron distribution of the hydrogen atoms will spread to some extent outside the boundaries of the areas assigned to them. This will result in the values of $n_o$ for $H_4$ and $H_8$ being too small. In addition, the use of incorrect scattering curves for the carbon atoms must be considered. The change from isotropic to anisotropic scattering curves for these atoms to allow for their thermal motion being mainly in a direction almost perpendicular to the carbon chain will result in a transference of electron density from the direction perpendicular to the chain to that along the chain. Thus the electron density will be increased in the region between the atoms $C_4$ and $H_4$ and $C_8$ and $H_8$ and this might result in an apparent transfer of electrons from the carbon to the hydrogen atoms. As a result of these factors the standard deviation of the mean of the number of electrons will be increased from 0.13 to about 0.25e. The observed transfer of 0.2e from $C_4$ to $H_4$ is therefore not significant.

## (h) Experimental

### 1. Preparation of the acid

Ethynylacetic acid was prepared by the oxidation in acetone solution of but-3-yne-1-ol by means of chromic acid solution[35]. Extraction with ether followed by distillation and repeated crystallisation of the extract from light petroleum (40–60°) gave the acid as thin plates, m.p. 83.5°C.

Analysis showed the acid to be C 57.15%, H 4.8%. $C_4H_4O_2$ requires C 57.23%, H 4.77%.

### 2. Stability

Ethynylacetic acid was found to be quite stable but some decomposition was observed in the solid state on long standing and in solution on crystallising out on the sides of the beaker in contact with the air.

It was however found to be very volatile; a crystal of size suitable for X-ray investigation disappearing within a few hours. Various methods of protecting the crystal was tried, the most effective being to seal the crystal inside a thin-walled capillary tube. Tubes made of lithium borate glass were used on account of their low absorption of X-rays.

## 3. Preparation of the crystals

The acid crystallised from a mixture of equal parts of benzene and light petroleum (60-80°) in flat diamond-shaped plates with the a and b crystal axes lying in the plane of the plate and bisecting the interfacial angles. The crystals show well-developed (001) and (110) faces with marked cleavage on the latter. Crystals, suitable for X-ray work could be obtained from these by cutting.

## 4. Determination of crystal data.

Nickel-filtered copper Kα radiation, $\lambda = 1.542$A, was employed in all the measurements. Rotation, oscillation and moving-film photographs of all the principal zones were taken. The axial lengths were obtained from the rotation photographs on which were superimposed powder lines from a piece of copper wire. The lattice constants of the latter are very accurately known and this allowed the radius of the camera and hence the axial length to be determined with some precision.

## 5. Measurement of the density.

The density was found by flotation methods using a mixture of light petroleum and carbon tetrachloride.

The value obtained was 1.306 gms/cc which would correspond to a cell containing 8.08 molecules. The number of molecules in the cell was taken as 8 and the density was calculated to be 1.293 gms/cc.

## 6. Intensity measurements and corrections

The (0kl), (h0l) and (hk0) reflections were obtained from Weissenberg films of the zero-layer lines of crystals rotated about the a, b and c axes. The intensities were measured on a relative scale by the method of visual estimation by means of the multiple film technique[36].

Table VIII shows the dimensions of the crystals used and it will be seen that the crystal specimens were quite uniform in cross-section. No corrections were applied to the observed intensities for the absorption of the X-ray beam in the crystal. The intensities were however corrected by the normal Lorentz and polarisation factors.

## Table VIII

| Reflections. | Cross-section of crystal in mm. | No. of reflections observed. | % of theoretical. | Range of intensities. |
|---|---|---|---|---|
| (Okl) | 0.27 x 0.24 | 51 | 64.6 | 8,000:1 |
| (hOl) | 0.24 x 0.21<br>0.32 x 0.36 | 204 | 79.1 | 6,600:1 |
| (Okl) | 0.25 x 0.28 | 23 | 51.1 | 840:1 |

As can be seen from the above table, two different crystals were used for the (hOl) reflections. A comparison of the two sets of reflections revealed that the intensities were identical within the limit of observational error. The absorption effects of the lithium borate capillary tubes were considered uniform in all directions and were ignored. The use of the two crystals increased the range of intensity which could be accurately measured and the larger crystal was used for the weak reflections.

The observed values of the structure factors were later placed on an absolute scale by comparison with the calculated values.

## 7. Fourier analyses.

For the projection on the (010), the electron density was computed at 900 points on the asymmetric unit, the a axis being subdivided into 30 parts of 0.269A and the c into 120 parts 0.215A. The summations were carried out using three-figure strips[37] and the results were plotted on a scale of 5 cm per A. by graphical interpolation from the summation totals. The projection on the (100) was computed similarly at 450 points in the asymmetric unit the summation intervals being $^{b}/30$ = 0.140A and c sinβ/120 = 0.213A.

# Table IX

Observed and Calculated values of the Structure Factors. Planes marked * were omitted from final syntheses owing to uncertainty of sign.

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 200 | 0.386 | 43.9 | +45.0 | 00,30 | 1.810 | 15.1 | +12.8 |
| 400 | 0.772 | 19.0 | −21.1 | 00,32 | 1.931 | 5.3 | + 4.3 |
| 600 | 1.158 | 5.4 | + 5.6 | | | | |
| 800 | 1.544 | 4.1 | + 3.6 | 020 | 0.733 | 5.7* | − 0.2 |
| 10,00 | 1.930 | < 1.6 | + 1.0 | 040 | 1.467 | < 2.9 | − 8.2 |
| | | | | | | | |
| 002 | 0.121 | 62.9 | +71.5 | $20,\overline{33}$ | 1.975 | 2.8 | − 3.9 |
| 004 | 0.241 | 19.3 | −17.8 | $20,\overline{32}$ | 1.915 | 2.4 | + 2.0 |
| 006 | 0.362 | 5.3 | − 5.0 | $20,\overline{31}$ | 1.857 | < 2.1 | + 0.4 |
| 008 | 0.483 | 70.0 | −72.6 | $20,\overline{30}$ | 1.796 | 6.8 | + 4.3 |
| 00,10 | 0.603 | 40.0 | −42.9 | $20,\overline{29}$ | 1,739 | 2.9 | + 1.8 |
| 00,12 | 0.724 | 35.9 | −36.2 | $20,\overline{28}$ | 1,679 | 10.1 | − 6.8 |
| 00,14 | 0.845 | 4.8 | + 7.3 | $20,\overline{27}$ | 1.622 | < 3.0 | − 0.8 |
| 00,16 | 0.965 | 20.4 | +20.6 | $20,\overline{26}$ | 1.563 | 4.3 | − 2.0 |
| 00,18 | 1.086 | 5.4 | + 3.7 | $20,\overline{25}$ | 1.505 | 12.5 | +10.1 |
| 00,20 | 1.207 | 17.3 | −15.9 | $20,\overline{24}$ | 1.446 | 16.1 | −12.1 |
| 00,22 | 1.327 | 25.3 | −24.8 | $20,\overline{23}$ | 1.387 | 23.3 | +20.3 |
| 00,24 | 1.448 | 7.1 | + 5.7 | $20,\overline{22}$ | 1.330 | 6.7 | − 5.8 |
| 00,26 | 1.569 | 3.1 | + 1.1 | $20,\overline{21}$ | 1.271 | 3.2 | + 3.2 |
| 00,28 | 1.690 | 2.8 | + 1.3 | $20,\overline{20}$ | 1.213 | 17.8 | +15.6 |

Table IX (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 20,$\overline{19}$ | 1.157 | 5.1 | − 4.3 | 207 | 0.612 | 47.7 | +44.9 |
| 20,$\overline{18}$ | 1.101 | 14.4 | +12.5 | 208 | 0.660 | 53.3 | −51.2 |
| 20,$\overline{17}$ | 1.046 | 5.5 | + 4.9 | 209 | 0.711 | 20.4 | +21.0 |
| 20,$\overline{16}$ | 0.988 | 30.4 | +30.3 | 20,10 | 0.761 | 16.8 | +13.6 |
| 20,$\overline{15}$ | 0.933 | 4.0 | − 4.9 | 20,11 | 0.814 | 11.8 | +13.0 |
| 20,$\overline{14}$ | 0.879 | 27.8 | +27.6 | 20,12 | 0.869 | 25.7 | +26.1 |
| 20,$\overline{13}$ | 0.826 | 13.2 | −12.0 | 20,13 | 0.922 | 3.9 | + 5.5 |
| 20,$\overline{12}$ | 0.772 | 20.1 | +16.8 | 20,14 | 0.979 | 29.2 | +31.2 |
| 20,$\overline{11}$ | 0.721 | 20.5 | −19.9 | 20,15 | 1.032 | 4.7 | − 5.3 |
| 20,$\overline{10}$ | 0.669 | 56.5 | −45.8 | 20,16 | 1.089 | 13.8 | +13.3 |
| 20$\overline{9}$ | 0.621 | 51.1 | −45.1 | 20,17 | 1.146 | 3.6 | + 4.1 |
| 20$\overline{8}$ | 0.575 | 81.3 | −77.3 | 20,18 | 1.203 | 16.9 | +16.8 |
| 20$\overline{7}$ | 0.531 | 6.9 | − 4.9 | 20,19 | 1.261 | < 3.1 | − 1.8 |
| 20$\overline{6}$ | 0.491 | 24.7 | +19.8 | 20,20 | 1.319 | 4.4 | − 4.5 |
| 20$\overline{5}$ | 0.456 | 23.7 | −21.7 | 20,21 | 1.377 | 20.5 | −19.9 |
| 20$\overline{4}$ | 0.426 | 28.9 | −30.3 | 20,22 | 1.433 | 14.9 | −12.6 |
| 20$\overline{3}$ | 0.403 | 82.1 | −82.9 | 20,23 | 1.493 | 12.5 | −11.0 |
| 20$\overline{2}$ | 0.389 | 41.2 | +40.6 | 20,24 | 1.549 | 4.3 | − 2.2 |
| 20$\overline{1}$ | 0.382 | 5.0 | − 3.7 | 20,25 | 1.610 | < 3.0 | + 0.5 |
| 201 | 0.399 | 79.4 | +81.4 | 20,26 | 1.669 | 9.0 | − 7.4 |
| 202 | 0.422 | 28.4 | −29.3 | 20,27 | 1.727 | < 2.7 | + 1.9 |
| 203 | 0.450 | 23.5 | +26.6 | 20,28 | 1.786 | 6.4 | + 3.9 |
| 204 | 0.485 | 24.5 | +23.6 | 20,29 | 1.843 | < 2.2 | + 0.7 |
| 205 | 0.524 | 5.1 | + 3.5 | 20,30 | 1.904 | 2.6 | + 2.5 |
| 206 | 0.566 | 77.8 | −74.7 | 20,31 | 1.962 | 4.3 | + 3.7 |

## Table IX (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| $40,\overline{32}$ | 1.974 | < 0.9 | + 0.1 | $40\overline{7}$ | 0.827 | 28.1 | +32.2 |
| $40,\overline{31}$ | 1.922 | 1.9 | - 1.9 | $40\overline{6}$ | 0.807 | 8.5 | + 6.2 |
| $40,\overline{30}$ | 1.866 | 3.9 | - 2.8 | $40\overline{5}$ | 0.789 | 25.5 | +26.8 |
| $40,\overline{29}$ | 1.812 | < 2.3 | + 0.2 | $40\overline{4}$ | 0.777 | 19.1 | -20.7 |
| $40,\overline{28}$ | 1.757 | 5.4 | - 3.9 | $40\overline{3}$ | 0.769 | 6.6 | + 9.1 |
| $40,\overline{27}$ | 1.704 | 3.3 | - 1.9 | $40\overline{2}$ | 0.766 | 4.0 | - 3.2 |
| $40,\overline{26}$ | 1.650 | 5.3 | - 4.3 | $40\overline{1}$ | 0.767 | 5.8 | - 5.7 |
| $40,\overline{25}$ | 1.597 | < 3.0 | + 0.1 | 401 | 0.784 | 22.3 | -25.0 |
| $40,\overline{24}$ | 1.544 | 4.5 | - 3.9 | 402 | 0.799 | 6.7 | + 4.5 |
| $40,\overline{23}$ | 1.492 | 4.7 | - 3.6 | 403 | 0.819 | 27.9 | -34.3 |
| $40,\overline{22}$ | 1.440 | 14.2 | +13.2 | 404 | 0.842 | 3.7 | - 7.1 |
| $40,\overline{21}$ | 1.387 | 6.7 | - 6.3 | 405 | 0.870 | < 2.5 | - 5.8 |
| $40,\overline{20}$ | 1.338 | 4.4 | + 3.5 | 406 | 0.899 | 24.3 | -28.4 |
| $40,\overline{19}$ | 1.289 | 5.2 | + 4.0 | 407 | 0.932 | 21.2 | -24.2 |
| $40,\overline{18}$ | 1.242 | 10.1 | + 8.8 | 408 | 0.968 | 8.6 | + 8.4 |
| $40,\overline{17}$ | 1.195 | 10.7 | -10.5 | 409 | 1.006 | 27.1 | -30.3 |
| $40,\overline{16}$ | 1.149 | 12.4 | +14.7 | 40,10 | 1.045 | 3.8 | - 1.9 |
| $40,\overline{15}$ | 1.105 | 19.0 | -16.4 | 40,11 | 1.089 | 12.6 | +13.3 |
| $40,\overline{14}$ | 1.063 | 3.9 | - 1.4 | 40,12 | 1.132 | 10.8 | +13.2 |
| $40,\overline{13}$ | 1.022 | 27.5 | +25.6 | 40,13 | 1.178 | 12.5 | +12.5 |
| $40,\overline{12}$ | 0.983 | 9.0 | + 9.3 | 40,14 | 1.224 | 10.5 | +10.4 |
| $40,\overline{11}$ | 0.947 | 25.9 | +26.6 | 40,15 | 1.271 | 4.9 | - 3.7 |
| $40,\overline{10}$ | 0.912 | 23.3 | -25.6 | 40,16 | 1.319 | 4.4 | + 2.6 |
| $40\overline{9}$ | 0.881 | < 2.5 | + 5.9 | 40,17 | 1.369 | 5.5 | + 6.0 |
| $40\overline{8}$ | 0.852 | 9.1 | -11.7 | 40,18 | 1.421 | 13.1 | +14.2 |

Table IX (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 40,19 | 1.471 | 5.5 | + 4.1 | $60,\overline{15}$ | 1.367 | 7.1 | − 7.5 |
| 40,20 | 1.523 | 4.4 | − 2.2 | $60,\overline{14}$ | 1.335 | 14.8 | −16.6 |
| 40,21 | 1.576 | < 3.1 | − 0.7 | $60,\overline{13}$ | 1.305 | 3.7 | − 2.6 |
| 40,22 | 1.628 | 5.1 | − 4.5 | $60,\overline{12}$ | 1.278 | 12.0 | +11.2 |
| 40,23 | 1.683 | 3.4 | + 2.1 | $60,\overline{11}$ | 1.251 | 4.9 | − 4.5 |
| 40,24 | 1.736 | 4.2 | − 3.9 | $60,\overline{10}$ | 1.229 | 3.7 | + 1.7 |
| 40,25 | 1.793 | < 2.5 | + 0.1 | $60\overline{9}$ | 1.208 | 6.4 | + 9.8 |
| 40,26 | 1.848 | 3.4 | − 3.5 | $60\overline{8}$ | 1.190 | 5.2 | + 7.1 |
| 40,27 | 1.900 | < 1.8 | + 0.7 | $60\overline{7}$ | 1.176 | 15.3 | +15.4 |
| 40,28 | 1.951 | < 1.3 | + 0.4 | $60\overline{6}$ | 1.162 | 3.9 | + 5.0 |
|  |  |  |  | $60\overline{5}$ | 1.154 | 10.1 | +10.5 |
| $60,\overline{29}$ | 1.960 | 1.2 | − 1.9 | $60\overline{4}$ | 1.149 | 8.5 | +14.6 |
| $60,\overline{28}$ | 1.910 | 2.1 | + 3.2 | $60\overline{3}$ | 1.146 | < 3.0 | + 1.7 |
| $60,\overline{27}$ | 1.863 | 2.4 | − 1.1 | $60\overline{2}$ | 1.147 | 9.6 | +15.8 |
| $60,\overline{26}$ | 1.816 | < 2.3 | + 0.4 | $60\overline{1}$ | 1.150 | 8.5 | − 8.3 |
| $60,\overline{25}$ | 1.771 | 3.0 | + 3.1 | 601 | 1.167 | 14.4 | −15.2 |
| $60,\overline{24}$ | 1.724 | 3.0 | + 2.4 | 602 | 1.180 | 5.4 | + 7.1 |
| $60,\overline{23}$ | 1.679 | 3.2 | + 2.6 | 603 | 1.196 | 10.3 | −12.1 |
| $60,\overline{22}$ | 1.635 | 3.2 | − 2.6 | 604 | 1.214 | 3.7 | − 0.1 |
| $60,\overline{21}$ | 1.592 | 3.7 | + 3.1 | 605 | 1.236 | 4.8 | + 2.3 |
| $60,\overline{20}$ | 1.550 | 5.7 | − 7.5 | 606 | 1.260 | 12.7 | +14.0 |
| $60,\overline{19}$ | 1.510 | 4.6 | + 4.0 | 607 | 1.286 | 3.7 | + 2.0 |
| $60,\overline{18}$ | 1.473 | 3.9 | + 3.9 | 608 | 1.315 | 8.8 | −10.8 |
| $60,\overline{17}$ | 1.436 | 7.1 | − 8.7 | 609 | 1.347 | 7.1 | + 6.3 |
| $60,\overline{16}$ | 1.400 | 18.8 | −21.4 | 60,10 | 1.379 | 20.5 | −25.0 |

Table IX (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 60,11 | 1.413 | 8.7 | +10.7 | 80,$\overline{15}$ | 1.676 | 11.6 | -12.2 |
| 60,12 | 1.450 | < 3.2 | + 2.1 | 80,$\overline{14}$ | 1.651 | 4.8 | + 6.3 |
| 60,13 | 1.486 | 3.8 | - 2.1 | 80,$\overline{13}$ | 1.630 | 11.3 | -14.2 |
| 60,14 | 1.528 | 4.4 | - 6.7 | 80,$\overline{12}$ | 1.610 | < 3.0 | + 0.2 |
| 60,15 | 1.567 | 3.7 | - 3.3 | 80,$\overline{11}$ | 1.592 | 4.8* | + 0.4 |
| 60,16 | 1.609 | 3.6 | - 5.8 | 80,$\overline{10}$ | 1.576 | < 3.1 | - 2.6 |
| 60,17 | 1.651 | 3.6 | - 2.4 | 80$\overline{9}$ | 1.562 | 6.4 | + 5.5 |
| 60,18 | 1.696 | 3.1 | + 2.4 | 80$\overline{8}$ | 1.551 | 4.3 | + 4.8 |
| 60,19 | 1.740 | 3.2 | - 3.9 | 80$\overline{7}$ | 1.542 | 4.7 | + 2.4 |
| 60,20 | 1.786 | < 2.5 | 0.0 | 80$\overline{6}$ | 1.534 | < 3.2 | - 3.9 |
| 60,21 | 1.832 | < 2.2 | + 0.4 | 80$\overline{5}$ | 1.530 | 5.4 | + 3.6 |
| 60,22 | 1.880 | 2.4 | + 4.0 | 80$\overline{4}$ | 1.529 | 6.6 | - 6.2 |
| 60,23 | 1.930 | 2.3 | + 1.9 | 80$\overline{3}$ | 1.529 | < 3.2 | - 2.1 |
| 60,24 | 1.978 | < 0.8 | - 0.5 | 80$\overline{2}$ | 1.531 | < 3.2 | - 5.7 |
|  |  |  |  | 80$\overline{1}$ | 1.536 | 4.7 | - 1.8 |
| 80,$\overline{24}$ | 1.962 | 2.8 | + 5.2 | 801 | 1.553 | 6.4 | - 5.4 |
| 80,$\overline{23}$ | 1.926 | 3.3 | + 4.5 | 802 | 1.564 | < 3.1 | - 1.2 |
| 80,$\overline{22}$ | 1.889 | < 1.9 | + 2.8 | 803 | 1.579 | 6.1 | - 4.8 |
| 80,$\overline{21}$ | 1.854 | < 2.1 | + 2.8 | 804 | 1.594 | < 3.0 | - 1.8 |
| 80,$\overline{20}$ | 1.820 | < 2.3 | + 0.5 | 805 | 1.613 | 6.3 | +10.9 |
| 80,$\overline{19}$ | 1.788 | < 2.5 | + 2.4 | 806 | 1.633 | 5.3 | + 7.5 |
| 80,$\overline{18}$ | 1.759 | 2.5 | + 3.2 | 807 | 1.655 | 10.8 | +14.0 |
| 80,$\overline{17}$ | 1.729 | 2.7 | - 3.4 | 808 | 1.681 | < 2.9 | - 4.0 |
| 80,$\overline{16}$ | 1.701 | 2.9 | - 4.8 | 809 | 1.706 | 4.7 | + 6.4 |

Table IX (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 80,10 | 1.733 | <2.7 | + 2.1 | 10,01 | 1.939 | < 1.5 | − 1.8 |
| 80,11 | 1.763 | <2.6 | − 1.0 | 10,02 | 1.950 | < 1.3 | − 1.7 |
| 80,12 | 1.794 | 3.4 | + 2.1 | 10,03 | 1.963 | < 1.1 | − 1.5 |
| 80,13 | 1.826 | 3.6 | − 2.4 | 10,04 | 1.978 | < 0.8 | − 0.1 |
| 80,14 | 1.861 | <2.1 | − 4.1 | 10,05 | 1.994 | < 0.3 | + 0.6 |
| 80,15 | 1.895 | 3.5 | − 2.8 | | | | |
| 80,16 | 1.932 | 2.9 | + 4.8 | 012 | 0.386 | 9.8 | + 9.7 |
| 80,17 | 1.971 | 3.3 | − 6.6 | 014 | 0.439 | 44.6 | −41.5 |
| | | | | 016 | 0.516 | 27.2 | +29.3 |
| 10,0,$\overline{14}$ | 1.995 | < 0.3 | + 0.8 | 018 | 0.606 | 36.9 | −41.5 |
| 10,0,$\overline{13}$ | 1.979 | < 0.8 | + 0.8 | 01,10 | 0.707 | 54.3 | −54.9 |
| 10,0,$\overline{12}$ | 1.963 | < 1.0 | − 1.9 | 01,12 | 0.811 | 25.2 | −28.0 |
| 10,0,$\overline{11}$ | 1.951 | < 1.3 | + 1.6 | 01,14 | 0.921 | 11.7 | −13.7 |
| 10,0,$\overline{10}$ | 1.940 | < 1.5 | + 0.5 | 01,16 | 1.032 | 6.1 | + 7.4 |
| 10;0$\overline{9}$ | 1.930 | < 1.6 | + 0.9 | 01,18 | 1.147 | 2.6 | + 3.1 |
| 10,0$\overline{8}$ | 1.922 | < 1.7 | − 0.3 | 01,20 | 1.261 | 20.2 | +18.9 |
| 10,0$\overline{7}$ | 1.918 | 4.8 | + 8.7 | 01,22 | 1.377 | 18.5 | +17.1 |
| 10,0$\overline{6}$ | 1.912 | < 1.8 | − 2.2 | 01,24 | 1.493 | 4.3 | + 3.7 |
| 10,0$\overline{5}$ | 1.911 | < 1.8 | + 2.2 | 01,26 | 1.611 | 4.8 | + 4.5 |
| 10,0$\overline{4}$ | 1.910 | < 1.8 | − 2.0 | 01,28 | 1.729 | 5.0 | − 4.7 |
| 10,0$\overline{3}$ | 1.912 | 5.1 | − 8.0 | 01,30 | 1.847 | < 2.0 | + 0.1 |
| 10,0$\overline{2}$ | 1.916 | < 1.8 | − 0.7 | 01,32 | 1.966 | < 1.1 | 0.0 |
| 10,0$\overline{1}$ | 1.921 | < 1.7 | − 1.7 | | | | |

Table IX (contd.)

| hkl | $2\sin\theta$ | Fo | Fc | hkl | $2\sin\theta$ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 022 | 0.742 | 6.6 | -11.1 | 03,18 | 1.513 | 6.9 | - 7.6 |
| 024 | 0.771 | 39.4 | -39.5 | 03,20 | 1.631 | < 2.6 | - 0.4 |
| 026 | 0.817 | 7.8 | - 4.0 | 03,22 | 1.722 | < 2.4 | - 0.4 |
| 028 | 0.877 | < 2.2 | + 1.0 | 03,24 | 1.817 | < 2.1 | - 0.3 |
| 02,10 | 0.949 | 3.2 | - 4.4 | 03,26 | 1.915 | < 1.6 | + 0.1 |
| 02,12 | 1.030 | 24.5 | +23.2 | | | | |
| 02,14 | 1.117 | 11.8 | +10.4 | 042 | 1.471 | < 2.9 | - 1.3 |
| 02,16 | 1.210 | 11.1 | + 9.8 | 044 | 1.484 | < 2.9 | + 0.8 |
| 02,18 | 1.309 | 10.1 | +12.0 | 046 | 1.509 | < 2.9 | + 1.7 |
| 02,20 | 1.411 | 11.2 | - 8.8 | 048 | 1.541 | < 2.8 | + 1.0 |
| 02,22 | 1.514 | 6.1 | + 3.4 | 04,10 | 1.582 | < 2.8 | + 0.1 |
| 02,24 | 1.621 | < 2.7 | + 0.5 | 04,12 | 1.634 | < 2.7 | + 1.7 |
| 02,26 | 1.729 | < 2.4 | - 0.2 | 04,14 | 1.690 | < 2.5 | - 0.2 |
| 02,28 | 1.839 | < 2.0 | - 0.3 | 04,16 | 1.754 | < 2.3 | - 1.1 |
| 02,30 | 1.948 | < 1.4 | 0.0 | 04,18 | 1.821 | < 2.0 | - 0.2 |
| | | | | 04,20 | 1.897 | < 1.7 | - 0.3 |
| 032 | 1.105 | < 2.5 | - 0.5 | 04,22 | 1.977 | < 1.0 | + 0.2 |
| 034 | 1.123 | 3.3 | - 1.9 | | | | |
| 036 | 1.155 | 10.3 | +14.1 | 052 | 1.836 | 2.3 | - 3.3 |
| 038 | 1.200 | 11.7 | +13.5 | 054 | 1.849 | 3.4 | - 4.5 |
| 03,10 | 1.252 | 6.4 | - 8.3 | 056 | 1.868 | < 1.9 | - 3.3 |
| 03,12 | 1.313 | < 2.9 | 0.0 | 058 | 1.893 | 1.7 | + 5.6 |
| 03,14 | 1.384 | 7.6 | + 9.1 | 05,10 | 1.929 | < 1.5 | - 0.5 |
| 03,16 | 1.460 | 6.6 | - 6.0 | 05,12 | 1.969 | < 1.1 | - 0.8 |

Table IX (contd.)

| hkl | 2sinθ | Fo | Fc |
|---|---|---|---|
| 110 | 0.415 | 30.2 | +20.4 |
| 210 | 0.533 | 53.3 | +49.4 |
| 310 | 0.685 | 23.3 | +23.3 |
| 410 | 0.856 | 27.0 | +28.0 |
| 510 | 1.033 | 8.4 | − 8.6 |
| 610 | 1.215 | 4.3 | − 8.3 |
| 710 | 1.399 | 4.5 | − 3.4 |
| | | | |
| 120 | 0.758 | 28.7 | +32.8 |
| 220 | 0.829 | 6.5 | + 8.3 |
| 320 | 0.934 | 9.3 | +16.4 |
| 420 | 1.067 | 4.9 | + 4.8 |
| 520 | 1.212 | 4.3 | + 3.5 |
| 620 | 1.371 | 4.0 | − 2.1 |
| | | | |
| 130 | 1.116 | 4.0 | + 1.4 |
| 230 | 1.166 | 4.5 | + 6.6 |
| 330 | 1.243 | 7.7 | +11.0 |
| 430 | 1.344 | 4.9 | + 5.3 |
| 530 | 1.463 | 7.5 | +10.4 |

## Part II The Crystal and Molecular Structure of n-Hexatriacontane.

### (a) Historical

The aliphatic paraffins have long been studied by X-ray diffraction methods since they comprise the simplest homologous series of compounds in organic chemistry and their hydrocarbon chains occur in many other types of compounds. This work however has been hampered by the large size of the unit cells, the polymorphism of these compounds and the difficulties of obtaining suitable single crystals.

A number of polymorphic forms of the n-paraffins are known. The ones which exist at room temperature are the "orthorhombic", monoclinic and triclinic forms. In addition, the early members of the series behave differently and there is a hexagonal form at temperatures just under the melting-point due to rotation of the molecular chains about their long axes.

The "orthorhombic" form is the most common and has the approximate dimensions, the perameters varying slightly with the chain length:

$$a = 7.45,\ b = 4.96,\ c = 2.54n + 4.0\ \text{A}.$$

where n is the number of carbon atoms in the molecule. The paraffin chains lie perpendicular to (001) and this form occurs only for the higher members of the series. It is also known as the normal or high temperature or A form.

The monoclinic form can be regarded as having the same packing of the chains as the orthorhombic form but the ab plane is tilted with respect to the c axis so that approximately:

$$a = 5.60, \quad b = 7.45 Å, \quad \beta = 62°.$$

It has been observed only for the higher members of the series when n is even.

The triclinic form has been found only for the lower members of the series. Two other forms have been observed at liquid air temperatures for members of the series when n is very small.

### The Orthorhombic Form.

This appears to be the most commonly occurring form of the n-paraffins and is the one on which most of the work of structure determination has been carried out.

It was first described by Muller[38] who obtained good single crystals of n-monacosane ($n\text{-}C_{29}H_{60}$) as thin diamond shaped plates with an interfacial angle of 65–66°. Rotation and oscillation photographs gave the dimensions of the unit cell as

$$a = 7.46 \quad b = 4.98, \quad c = 77.4 \text{ A.}, \quad \text{all within } \pm 0.5\%.$$

This cell was shown to be orthorhombic within ± 1° and to contain four molecules. Muller derived the space group $V_h^{16}$ which in modern parlance corresponds to $D_{2h}^{16}$ – Pnam with the origin transferred to 00¼. Taking the origin in the mirror plane as chosen by Muller, the eight equivalent positions are:

$$x, y, \pm nz; \quad \tfrac{1}{2}+x, \tfrac{1}{2}-y, \pm nz; \quad \bar{x}, \bar{y}, \tfrac{1}{2} \pm nz; \quad \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}\pm nz.$$

where $n = 0 - 14$ for the atoms in the chain numbered outwards from the central atom which lies in the mirror plane. The coordinates $x$ and $y$ of the atoms with $n$ even differ from those, $x'$ and $y'$, of the atoms with $n$ odd so that five parameters have to be determined.

The reflectionswith $l = 0, 1, 30, 31, 60, 61$ and $62$ are strong indicating the repetitive nature of the chain and from the intense (00,60) and (00,62) planes Muller obtained z = 0.03286 ± 0.00002 in fractional coordinates giving the value of 2.542A as the periodicity along the chain with a high degree of accuracy. The other parameters were determined with less accuracy. Taking $y = -y' = 0.063$, $x = 0.269 \pm 0.014$, $x' = 0.098 \pm 0.014$ in fractional coordinates, the carbon-carbon bond length along the chain was found to be 1.9 ± 0.1A and the valence angle as 84 ± 8° which may be compared with the value of 1.54A for diamond and the tetrahedral angle of 109.5°. Muller suggested that the scattering centres chosen above represented methylene groups and that the presence of the hydrogen atoms would shift the rows of centres further apart. The introduction of the tetrahedral angle into the chain altered the carbon-carbon bond length to 1.55A and Muller suggested that the paraffin chain was in fact tetrahedral. The distance of nearest approach of two methylene groups was 3.75A and between the end groups of two molecules across the centre of symmetry 4.0A.

This work, although based on only a few of the reflections, did establish the essentially planar structure of the molecule and the regular zig-zag nature of the chain.

Hengstenberg[39] arrived at similar conclusions as a result of his work on n-hexacontane (n - $C_{60}H_{122}$). The length of the long spacing was found to be 78.4A but in addition a pseudo-cell or sub-cell was postulated of the dimensions

$$a = 7.45, \quad b = 4.96, \quad c = 2.55A.$$

This cell is orthorhombic of space group $V_h^{16}$ ($D_{2h}^{16}$ - Pnam) and contains four methylene groups which lie on the mirror planes. From an examination of the (hk0) series of reflections Henhstenberg found the carbon-carbon bond distance to be 1.52A, the angle of the zig-zag 114° and the distances between neighbouring atoms in different molecules about 4.1A.

In a further paper Muller[40] discussed the consequences of his previous results when applied to other paraffins with this crystal form, He argued that those with an odd number of carbon atoms will be truly orthorhombic with two molecules lying along the c axis so that c is equal to twice the long spacing, whilst the even numbered members will really be monoclinic with c equal to the long spacing and the angle β very nearly rectangular but determined in magnitude by the relative displacements of consecutive molecules along the $a$ axis.

The paraffins with an odd number of carbon atoms are packed parallel to one another so that the plane of symmetry, passing through the central carbon atom of each molecule, becomes a mirror plane of the unit cell. The packing also produces centres of symmetry between the layers of molecules and these, together with the mirror plane and the glide plane parallel to the (010), cause the space group to be $D_{2h}^{16}$ - Pnam.

Muller thought that the paraffins with an even number of carbon atoms would have centres of symmetry between the layers as well as at the mid-point of the molecules. These, together with the glide plane, would give rise to the space group $C_{2h}^{5}$ - $P2_1/a$.

This idea was contradicted by the work of Kohlhaus and Soremba[41] who examined n-triacontane ($n\text{-}C_{30}H_{62}$) by means of rotation, oscillation and Schiebold-Souter moving film photographs. The cell constants were found to be

$$a = 7.46, \quad b = 4.97, \quad c = 81.8A.$$

The space group was chosen as $D_{2h}^{16}$ - Pnam with four molecules per unit cell and the repeat distance along the c axis was found to be 2.53A. An examination of the (hk0) series of reflections gave, in fractional coordinates,

$$x = 0.056 \pm 0.006, \quad y = 0.046 \pm 0.004,$$

from which the carbon-carbon bond length was found to be 1.57 ± 0.05A and the zig-zag angle of the chain 106 ± 4°. The nearest distance of approach between neighbouring molecules was found to be 3A and between molecules in different layers 4.2A.

For this structure the mirror planes are again perpendicular to the molecular chains but lie midway between the layers. The centres of symmetry in the molecules then coincide with the centres of symmetry in the unit cell. However there appear to be discrepancies in this work regarding the choice of space group and the structure quoted above cannot be regarded as definitely settled.

C. W. Bunn[42] showed that the X-ray diffraction patterns of long chain paraffins remained almost unaltered once the chain contained more than 130 carbon atoms. Thus these molecules can be regarded as infinitely long and the end to end packing of the chains, which has to be taken into account with chains of 30 carbons, can be safely ignored.

For samples of polythene which contains chains of about 1000 carbon atoms he found:

$$a = 7.41, \quad b = 4.94, \quad c = 2.539A.$$

The compound is orthorhombic with space group $D_{2h}^{16}$ - Pnam as found by Hengstenberg and the atoms lie in the special positions:

$$x, \bar{y}, \tfrac{1}{4}; \quad \bar{x}, y, \tfrac{3}{4}; \quad \bar{x} + \tfrac{1}{2}, \bar{y} + \tfrac{1}{2}, \tfrac{3}{4}; \quad x + \tfrac{1}{2}, y + \tfrac{1}{2}, \tfrac{1}{4}.$$

By means of a three-dimensional Fourier analysis, Bunn found that

$$x = 0.038, \quad y = 0.065,$$

in fractional coordinates.

This gave the carbon-carbon bond length as 1.53A and the zig-zag angle of the chain as 112°.

The nearest distance of approach between carbon atoms in different molecules was 4.13A.

The electron density maps, in sections through the molecular chain, revealed that the methylene groups were considerably elongated in the planes of the three atoms. Some of this distortion may be due to the anisotropic motions of the atoms and to a real distortion of the methylene groups but it may also arise from the impurity content of polythene. It has been shown by infra-red spectroscopy[43] that polythene contains a number of methyl side chains and it has been estimated that one methyl group is present per 50 methylene groups[44]. It therefore seems possible that some of the discrepancies encountered by Bunn may be due to this.

Vǎinshtein and Pinsker[45] studied n-paraffin of m.p. 53.5°C by means of electron diffraction and obtained for the sub-cell

$$a = 7.41, \quad b = 4.96, \quad c = 2.54\text{A}.$$

The space group was $D_{2h}^{16}$ - Pnam as before.

Electron diffraction reveals the electrostatic potentials around the atoms so that it is suitable for revealing the hydrogens. Fourier projections obtained from the electron diffraction data show the carbon and hydrogen atoms resolved and sections through $\frac{1}{4}c$ reveal the carbon-hydrogen peak ratio as about 3.5:1 and not 6:1 (the ratio of nuclear charges). This may be due to the screening effects of the electrons.

The paper appears to contain a number of errors but the atomic parameters measured directly from the Fourier projection (private communication: V.Vand) are given by:

| | $\frac{x}{a}$ | $\frac{y}{b}$ | x | y |
|---|---|---|---|---|
| C | 0.039 | 0.063 | 0.29 | 0.31 |
| $H_1$ | 0.197 | 0.040 | 1.46 | 0.20 |
| $H_2$ | 0.014 | 0.290 | 0.10 | 1.44 |

The interatomic distances then are:

C-C 1.53, C-H, 1.17, C-$H_2$ 1.15, $H_1$-$H_2$ 1.84 and 2.64A.

and the intermolecular distances are given by:

C ... C 4.18, 4.20, $H_1$ ... $H_2$ 2.50, 2.74, $H_2$ ... $H_2$ 2.49A.

The angle C-C-C is 112.5° and the angle $H_1$-C-$H_2$ is 105°.

The interatomic distances are said to be accurate to ± 0.02A but the C-H distances are considerably greater than the values found for methane, ethane etc. by electron diffraction and spectroscopic methods.

## The Monoclinic Form

Piper and Malkin[46] in 1930 found that n-tetratriacontane ($n$-$C_{34}H_{80}$) and n-hexacosane ($n$-$C_{60}H_{122}$) existed at room temperature in two stable forms and postulated the existence of a monoclinic form, which they named the C form, to account for the second of these.

It was first described by Schoon[47] in an electron diffraction investigation of n-triacontane ($n$-$C_{30}H_{62}$) and the dimensions of the unit cell of the monoclinic form were compared with those of the orthorhombic form of the same compounds as determined by X-ray methods.

| | a | b | $c\sin\beta$ | $\beta$ |
|---|---|---|---|---|
| Orthorhombic Form. | 4.97A. | 7.53A. | 40.02A. | 90° |
| Monoclinic Form. | 5.59 | 7.49 | 35.27 | 61.9° |

Schoon then showed how a number of monoclinic forms could be derived from the orthorhombic form by the displacement of the long c axis with relation to either the a or b axis by an amount equivalent to a whole number of zig-zag units. For the form above he obtained theoretically:

$$a = 5.59, \quad b = 7.48A. \quad \beta = 62.9^\circ$$

on assuming a value of 2.54A as the repeat distance along the c axis.

The interfacial angle of the crystal then calculates as 73.5° compared with 67° for the orthorhombic form.

## The Triclinic Form

Muller[48] in 1930 observed that n-paraffins with 18,20 and 22 carbon atoms existed near the melting point in the normal or orthorhombic form but that at lower temperatures there appeared another form which he named the B form and suggested was triclinic.

The fullest account of a paraffin of this form was given by Muller and Lonsdale[49] for n-octadecane ($n-C_{18}H_{38}$) but as yet no detailed work has been done on this.

## The Hexagonal Form.

In 1932, Muller[50] found that n-paraffins containing between 21 and 29 carbon atoms adopted hexagonal packing on approaching their melting points. Outside this range the paraffins approach this state of packing but melt before reaching it. To account for this increase in symmetry, Muller suggested that the molecular chains were rotating about their long axes in a manner similar to that found for a number of primary alkylammonium halides by Hendricks[51].

## Occurrence of the Different Forms.

Piper et alia[52] examined the forms in which a range of n-paraffins crystallised and, from this and other works, it appears that:

1. the odd-membered n-paraffins containing 11 or more carbon atoms crystallise in the orthorhombic form, as do the even members of the series with 18 or more carbons near their melting points.

2. the even-membered n-paraffins containing 26 or more carbon atoms normally adopt the monoclinic form but on heating they pass into the orthorhombic form at a temperature about 5° below their melting points and do not usually revert to the monoclinic form on cooling. Thus if these paraffins have previously been molten they tend to appear as the orthorhombic form but crystallise from solution as the monoclinic.

3. The even members of the series containing up to 24 carbon atoms and the odd members with 9 or less carbons crystallise in the triclinic form. At temperatures near their melting points they change to the orthorhombic form but revert to the triclinic on cooling.

4. The hexagonal form, obtained on heating to just below the melting point, occurs only for those paraffins with between 21 and 29 carbon atoms.

(b) Sub-cell Theory

The previous investigations of the structure of the n-paraffins have demonstrated the essentially repetitive nature of the molecular chain and such a representation has been used, since the beginning of this work, as a means of simplifying the problem of structure analysis. The theory of this has recently been more fully worked out by Vand[53].

The repetitive nature of the molecular chain means that, in a crystal of a n-paraffin, the electron density also tends to repeat itself within the unit cell. The repeat unit is known as the sub-cell and this sub-cell (axes $s^j$) will be much smaller in volume than the main cell (axes $a^j$). The sub-cells will repeat themselves only over a part of the main cell and this part is known as the sub-cell region. The unit cell may contain more than one of these regions. If the centre of each sub-cell is chosen as its origin then the centre of the sub-cell region will be found at the centre of gravity of the sub-cell origins.

The number of sub-cells in the sub-cell region is finite and this gives rise to an interference function of the form

$$I_o = \prod_j \frac{\sin \pi N^j H^j}{\sin \pi H^j}$$

where $N^j$ represents three integers describing the number of sub-cells in the sub-cell axial directions and $H^j$ are the Miller sub-cell indices. This oscillating function extends throughout the reciprocal space but its maxima coincide with the sub-cell reciprocal lattice points.

The centre of the sub-cell region need not coincide with the origin of the main cell. The structure factors of the atoms in the sub-cell region will be referred to the main cell origin by including in their equations the expression $\exp(2\pi i x_m h)$ where h is the order vector (equivalent to the Miller indices) of the main cell and $x_m$ are the coordinates of the centre of the sub-cell region referred to the main cell origin.

The structure factor $F_h$ of the main cell is then given by

$$F_h = \overset{o}{F}_h + \prod_j \frac{\sin \pi N^j H^j}{\sin \pi H^j} F_H \exp(2\pi i x_m h)$$

where $\overset{o}{F}_h$ is the contribution of the atoms outside the sub-cell region and $F_H$ is the structure factor of the sub-cell.

The primitive translations ($s^i$) of the sub-cell may be referred to those ($a^k$) of the main cell by the transformation matrix

$$s^i = g^i_k a^k$$

The same matrix then describes the relationship between the Miller indices ($H^i$) of the sub-cell and those ($h^k$) of the main cell.

$$H^i = g^i_k h^k$$

(There is an error in Vand's paper, the matrices being reversed).

Similarly the (small) crystal reciprocal cell can be expressed in terms of the (large) reciprocal sub-cell by a matrix which is the same as $g_k^i$ on reading from top to bottom instead of from left to right.

## (c) n-Hexatriacontane.

As has been seen a great deal of work has been carried out on the structures of the n-paraffins but the information available is far from complete. In some cases the molecular packing is still uncertain and most of the structures have been obtained by a study of a few reflecting planes. In addition no electron density map of a member of this series apart from polythene has yet been obtained.

An examination of certain substituted members of this series, such as the dicarboxylic acids with an even number of carbon atoms[54] and hexamethylene diamine[55], has indicated an alternation of the carbon-carbon bond lengths along the chain. This effect is thought to be related to the presence of the substituents at the ends of the chains and should therefore occur to a much lesser extent, if at all, in an n-paraffin but no information about this is available.

An electron microscope investigation of the crystal growth of n-hexatriacontane[56] was recently carried out in this Department and it was felt that a more detailed investigation of this compound by X-ray methods would be of interest.

## (d) Crystal Data.

n-hexatriacontane, $C_{36}H_{74}$; M = 507.0; m.p. 75.5°C; d calc 0.964, found 0.961. Monoclinic prismatic, a = 5.57 ± 0.01, b = 7.42 ± 0.01, c = 48.35 ± 0.08A. $\beta = 119°6' \pm 4'$. Absent spectra, (h0l) when h is odd, (0k0) when k is odd. Space group $C_{2h}^5 - P2_1/a$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell, 1746A$^3$. Absorption coefficient for X-rays ($\lambda = 1.542$), u = 4.52 cm$^{-1}$. Total number of electrons per unit cell, F(000) = 580.

## (e) Determination of the Sub-cell.

On marking the observed values of the structure factors against the points of the reciprocal lattice it was found that a three-dimensional reciprocal sub-lattice could be drawn up with the sub-lattice points in the regions of the large structure factors. The sub-cell axes were designated $a_s$, $b_s$ and $c_s$ and it was seen that the $b_s^*$ and $b^*$ axes coincided in magnitude and direction, the $c_s^*$ and $c_s$ axes coincided in direction whilst the $a_s^*$ axis was displaced from the $a^*$. The symmetry of this monoclinic cell requires that the $a_s$ and a axes are identical and also the $b_s$ and b axes but permits the $c_s$ axis to be inclined to the c axis. Transformation of these into reciprocal space gives the relationships found above.

An examination of the sub-cell system in n-hexatriacontane revealed that $N^j$ - the number of sub-cells - is 18 in the $c_s$ axial direction and unity in the direction of the other two axes. The value of the interference function then became $I_o = \frac{\sin \pi 18 L}{\sin \pi L}$ when the Miller indices HKL were assigned to the sub-cell planes. This interference function extends over the three dimensions in space but is a function only of L.

The centre of gravity of the sub-cell region coincides with the origin of the main cell so that $x_m = 0$. All the atoms in the molecular chain are included in these 18 sub-cells except for one hydrogen atom of each of the methyl groups at the ends of the chain. If the diffraction effect of these two hydrogen atoms is ignored the structure factor equation of the main cell becomes

$$F_h = \frac{\sin 18 \pi L}{\sin \pi L} \cdot F_H$$

From this equation it is seen that for two planes differing in their indices only in l by unity, the term which will cause the greatest change in the magnitude of their structure factors will be the interference function Io. The length of $c_s^*$ was found approximately from the observed values of the structure factors of the (00l) planes and a graph of Io against $c_s^*$ constructed. The variation in the magnitudes of the observed values of the structure factors for planes of the type mentioned above were taken as due solely to the changes in Io. Using this graph and the approximate length of $c_s^*$, coordinates were assigned to the sub-cell reciprocal lattice points in the (hk0) and 0kl) zones and the dimensions of the reciprocal sub-cell obtained by graphical methods. The dimensions of the sub-cell were then calculated and found to be

$a_s$ = 5.57 A.
$b_s$ = 7.42 A.
$c_s$ = 2.548 A. $\beta_s = 117°26'$

Values of Io were then given to the strong main cell planes and the magnitudes of the "observed" values of the sub-cell planes obtained.

The sub-cell also possessed the space group $C_{2h}^{5}$-$P2_1/a$ and contained four methylene groups i.e. one methylene group in the asymmetric unit. The carbon chains were taken to lie along the $c_s$ axis with the points midway between the carbon atoms lying on the centres of symmetry of the cell at (000) and ($00\frac{1}{2}$). This, together with the strong (201) and ($20\overline{2}$) sub-cell planes in the projection on the (010) and the very strong (020) plane in the projection on the (100), was sufficient to allow a trial structure to be postulated. After some degree of refinement by trial and error methods the discrepancies for the (HOL) and (OKL) reflections were respectively 16.4% and 12.0%. The scattering curve was obtained from the theoretical curve derived by McWeeny[29] for the valence state of carbon by applying to it a temperature factor of $B = 3.0 \times 10^{-16}$.

Fourier synthesis F1 and F2 were carried out in the projections along the $b_s$ and $a_s$ axes and are shown in Fig. 1. All the "observed" reflections - the 14 (HOL) and 17 (OKL) - were included in these. New coordinates for the carbon atom were obtained and on recalculation of the structure factors the discrepancies were found to have risen to 19.1% and 13.5% respectively for the (HOL) and (OKL) reflections. The electron density maps showed strong

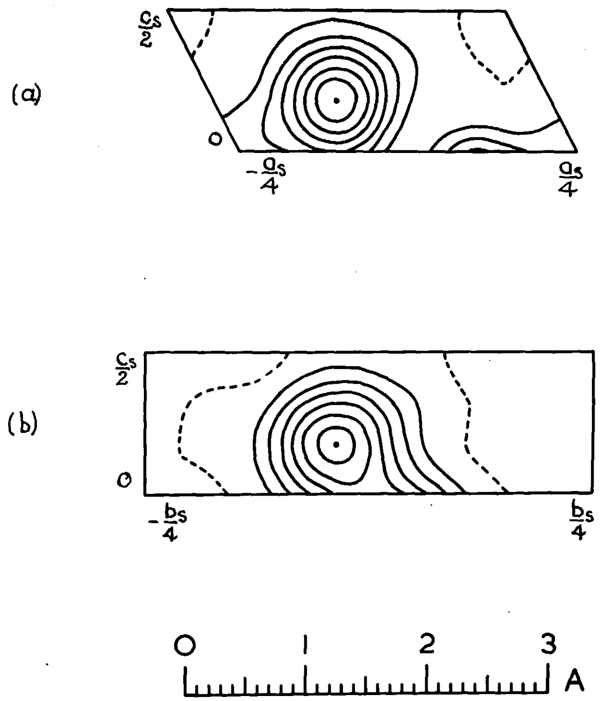


Fig. 1. Electron-density projections of the sub-cell (a) F1 along the $b_s$ axis, (b) F2 along the $a_s$ axis. Each contour line represents a density increment of one electron per A$^2$, the one electron line being dotted.

indications of the presence of the hydrogen atoms and accordingly the positions of these two atoms in the methylene group were calculated assuming a carbon-hydrogen bond length of 1.09A and the normal valence angles. The inclusion of the contributions of these atoms to the structure factors of the planes with a value of $2\sin\theta \leqslant 1.2$ reduced the values of the discrepancies for the (HOL) and (OKL) reflections to 12.7% and 9.3% respectively. None of the planes were found to have changed signs.

The atomic coordinates referred to the sub-cell axes and with the sub-cell centre as origin are shown in Table I.

Table I.

Coordinates of the Sub-cell Atoms, referred to the sub-cell axes and centre.

| | $\frac{X}{a_s}$ | $\frac{Y}{b_s}$ | $\frac{Z}{c_s}$ | X | Y | Z |
|---|---|---|---|---|---|---|
| $C_1$ | 0.068 | 0.036 | -0.181 | 0.38 | 0.27 | -0.46 |
| $H_1$ | 0.061 | 0.183 | -0.188 | 0.34 | 1.36 | -0.48 |
| $H_2$ | 0.280 | 0.000 | 0.012 | 1.56 | 0.00 | 0.03 |

## (f) Analysis of the Structure of the Main Cell.

Values of Io were assigned to all the observed reflections and their structure factors calculated, the indices of the planes being suitably transformed by a matrix derived from the known relationships between the crystal reciprocal cell and the reciprocal sub-cell. The matrix was

$$g_k^i = \boxed{\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0.01526 & 0 & 0.05352 \end{array}}$$

The discrepancies for the (h0l) and (0kl) reflections were found to be 28.7% and 21.5% respectively but the agreement between the observed and calculated values of the structure factors was best for the planes with values of L - the sub-cell index - approaching whole numbers and the calculated values of the structure factors of the planes with increasing fractional values of L sometimes became very small whilst the observed values did not and vice versa.

On studying the previous step it became apparent that the sub-cell contained two centres of symmetry at (000) and (00½), either of which could be taken as the origin when the sub-cell was considered on its own. Only one of these however will coincide with the sub-cell centre which must be taken as the origin on building up the molecule. The choice of the second sub-cell centre as the origin will give a different structure to the hydrocarbon chain but will change only slightly the magnitude of the structure factors of the planes with sub-cell indices approaching whole numbers. As these planes include all the strongly reflecting ones, it will be seen that reasonable agreement between the observed and calculated structure factors may still be obtained.

The sub-cell centre was transferred to the centre of symmetry previously at ($00\frac{1}{2}$) and the atomic coordinates shown in Table I are referred to this centre as origin. The structure factors of the main cell planes were recalculated with these new coordinates. The discrepancies fell to 19.1% and 14.9% respectively indicating that this choice of the origin was correct.

Signs were now given to all the observed reflections and Fourier syntheses F3 and F4 were carried out in the projections on the (010) and (100) respectively. These are shown in Figs. 2 and 4 respectively and the numbering of the atoms in Figs. 3 and 5. The (001), (002), and (003) planes were not observed being obscured by the beam trap and they, together with the (021) plane which was obscured by the very intense (020) , were included at their calculated values. The resulting electron density maps show all the carbon atoms resolved and give some indications of the positions of the hydrogen atoms. The electron density at the centre of the peaks, which

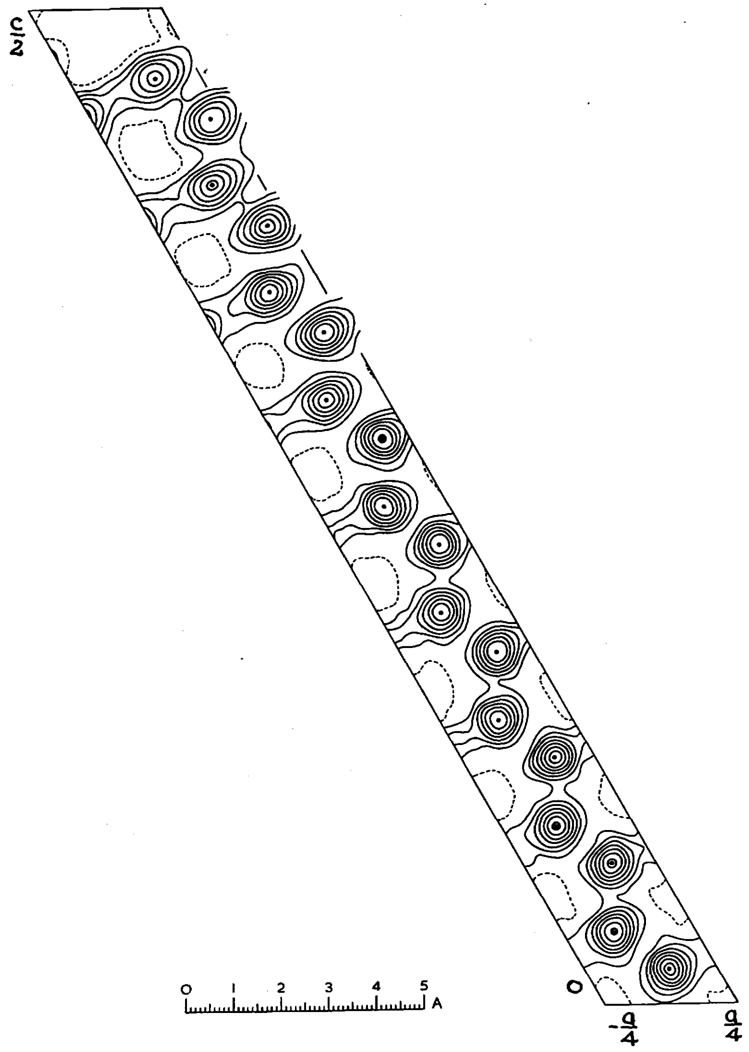


Fig. 2. F3. Electron-density projection of the main cell along the b axis on the (010). Each contour line represents a density increment of one electron per $A^2$, the one electron line being dotted.

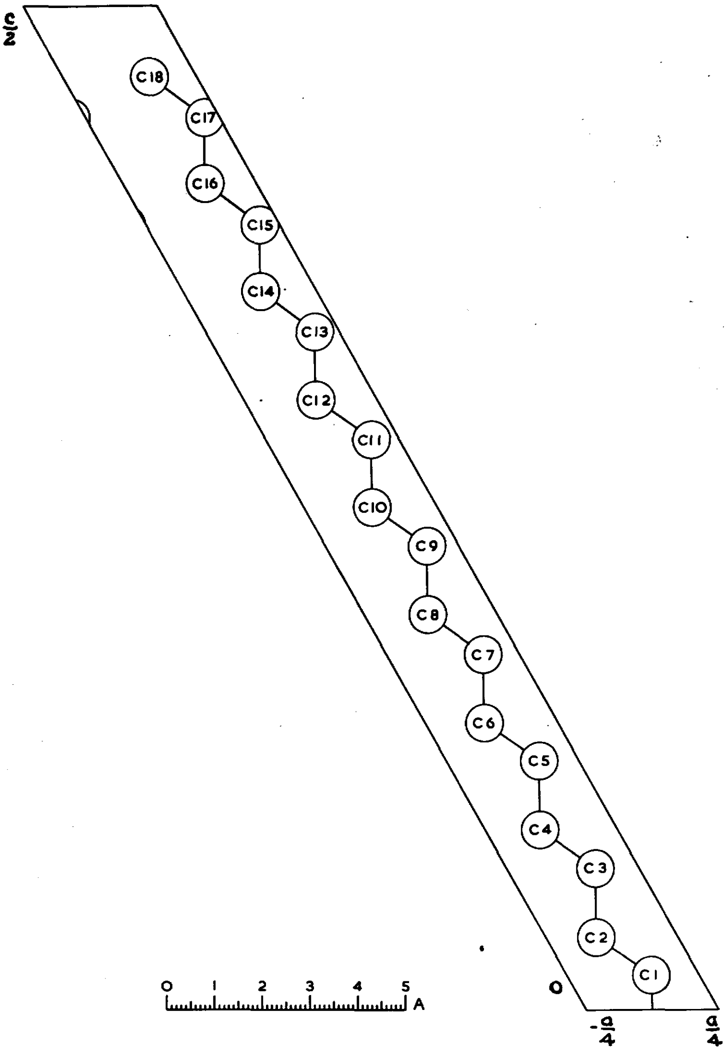


Fig. 3. Numbering of the atoms in the projection of the main cell along the b axis on the (010).

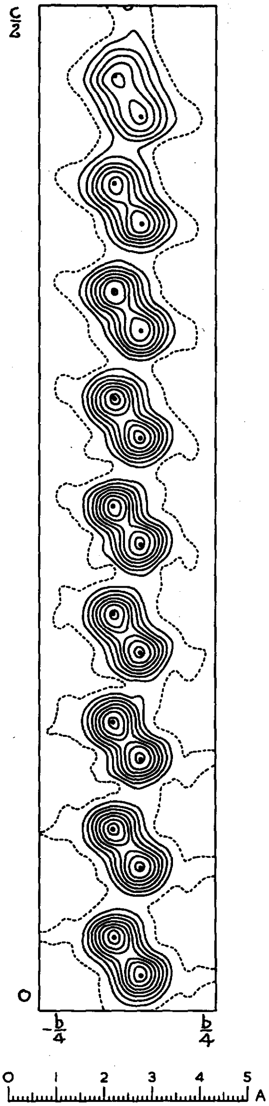


Fig. 4. F4. Electron-density projection of the main cell along the a axis on the (100). Each contour line represents a density increment of one electron per $A^2$, the one electron line being dotted.

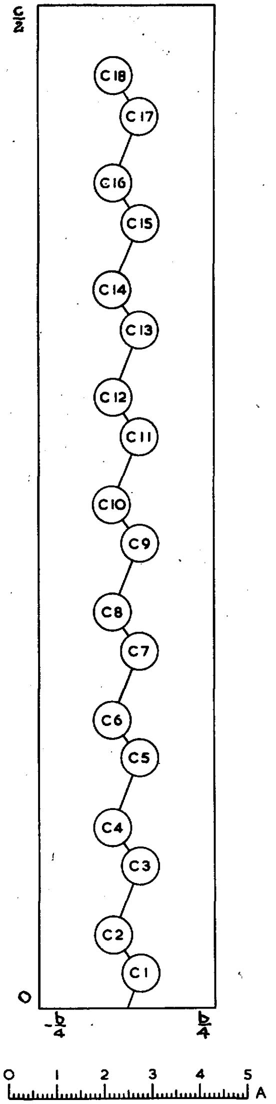


Fig. 5. Numbering of the atoms in the projection of the main cell along the a axis on the (100).

is due to a carbon and a superimposed hydrogen atom, falls fairly regularly from over 8e.$A^{-2}$. at the centre of the chain to over 6e$A^{-2}$. at the ends and this decline in electron density can be explained by the increasing thermal motion of the atoms towards the end of the chain. Coordinates were assigned to the carbon atoms, and are shown in Table II where x, y and z are referred to the monoclinic crystal axes with a centre of symmetry as the origin and x′, y and z′ are referred to the orthogonal axes a, b and c′. The molecular dimensions are shown in Table III and it will be seen that the carbon-carbon bond lengths vary considerably amongst themselves but not in a systematic manner along the chain.

### (g) Redetermination of the Structure of the Sub-cell.

In a compound of this nature, it is of interest to determine accurately the structure of the sub-cell, especially as this may lead to more precise values of the molecular parameters.

If a regular structure is assumed for the paraffin chain, the positions of the carbon atoms will lie on a straight line on transposing those with an even index across the centre of symmetry at (000). The atomic coordinates, in each of the axial directions, can then be expressed by the equation

$$u = mv + w$$

## Table II

## Atomic Coordinates

Centre of symmetry as origin, x, y, z, $x'$ and $z'$ in A.

| Atom | $\frac{x}{a}$ | $\frac{y}{b}$ | $\frac{3}{c}$ | x | y | z | $x'$ | $z'$ |
|---|---|---|---|---|---|---|---|---|
| $C_1$ | 0.0700 | 0.0384 | 0.0173 | 0.39 | 0.28 | 0.84 | – 0.02 | 0.73 |
| $C_2$ | –0.0557 | –0.0384 | 0.0364 | –0.31 | –0.29 | 1.76 | – 1.17 | 1.54 |
| $C_3$ | 0.0844 | 0.0371 | 0.0705 | 0.47 | 0.28 | 3.41 | – 1.19 | 2.98 |
| $C_4$ | –0.0413 | –0.0404 | 0.0898 | –0.23 | –0.30 | 4.34 | – 2.34 | 3.79 |
| $C_5$ | 0.1023 | 0.0377 | 0.1243 | 0.57 | 0.28 | 6.01 | – 2.35 | 5.25 |
| $C_6$ | –0.0251 | –0.0404 | 0.1432 | –0.14 | –0.30 | 6.92 | – 3.51 | 6.05 |
| $C_7$ | 0.1149 | 0.0364 | 0.1775 | 0.64 | 0.27 | 8.58 | – 3.53 | 7.50 |
| $C_8$ | –0.0090 | –0.0404 | 0.1970 | –0.05 | –0.30 | 9.52 | – 4.68 | 8.32 |
| $C_9$ | 0.1311 | 0.0377 | 0.2312 | 0.73 | 0.28 | 11.18 | – 4.71 | 9.77 |
| $C_{10}$ | 0.0054 | –0.0404 | 0.2506 | 0.03 | –0.30 | 12.12 | – 5.86 | 10.59 |
| $C_{11}$ | 0.1454 | 0.0364 | 0.2843 | 0.81 | 0.27 | 13.75 | – 5.87 | 12.01 |
| $C_{12}$ | 0.0197 | –0.0377 | 0.3040 | 0.11 | –0.28 | 14.70 | – 7.04 | 12.84 |
| $C_{13}$ | 0.1598 | 0.0384 | 0.3377 | 0.89 | 0.28 | 16.33 | – 7.05 | 14.27 |
| $C_{14}$ | 0.0395 | –0.0391 | 0.3580 | 0.22 | –0.29 | 17.31 | – 8.20 | 15.12 |
| $C_{15}$ | 0.1777 | 0.0391 | 0.3911 | 0.99 | 0.29 | 18.91 | – 8.21 | 16.52 |
| $C_{16}$ | 0.0574 | –0.0364 | 0.4114 | 0.32 | –0.27 | 19.89 | – 9.35 | 17.38 |
| $C_{17}$ | 0.1957 | 0.0377 | 0.4444 | 1.09 | 0.28 | 21.49 | – 9.36 | 18.77 |
| $C_{18}$ | 0.0736 | –0.0337 | 0.4647 | 0.41 | –0.25 | 22.47 | –10.52 | 19.63 |

## Table III

### Dimensions of the Molecules

| | | | |
|---|---|---|---|
| $C_1' - C_1$ | 1.57 A | $C_1' - C_1 - C_2$ | 112.3° |
| $C_1 - C_2$ | 1.52 | $C_1 - C_2 - C_3$ | 111.7 |
| $C_2 - C_3$ | 1.55 | $C_2 - C_3 - C_4$ | 111.8 |
| $C_3 - C_4$ | 1.52 | $C_3 - C_4 - C_5$ | 111.3 |
| $C_4 - C_5$ | 1.57 | $C_4 - C_5 - C_6$ | 110.6 |
| $C_5 - C_6$ | 1.52 | $C_5 - C_6 - C_7$ | 111.0 |
| $C_6 - C_7$ | 1.56 | $C_6 - C_7 - C_8$ | 112.1 |
| $C_7 - C_8$ | 1.52 | $C_7 - C_8 - C_9$ | 112.1 |
| $C_8 - C_9$ | 1.56 | $C_8 - C_9 - C_{10}$ | 111.7 |
| $C_9 - C_{10}$ | 1.53 | $C_9 - C_{10} - C_{11}$ | 110.9 |
| $C_{10} - C_{11}$ | 1.53 | $C_{10} - C_{11} - C_{12}$ | 111.6 |
| $C_{11} - C_{12}$ | 1.55 | $C_{11} - C_{12} - C_{13}$ | 111.7 |
| $C_{12} - C_{13}$ | 1.53 | $C_{12} - C_{13} - C_{14}$ | 112.5 |
| $C_{13} - C_{14}$ | 1.55 | $C_{13} - C_{14} - C_{15}$ | 112.0 |
| $C_{14} - C_{15}$ | 1.51 | $C_{14} - C_{15} - C_{16}$ | 112.5 |
| $C_{15} - C_{16}$ | 1.53 | $C_{15} - C_{16} - C_{17}$ | 113.1 |
| $C_{16} - C_{17}$ | 1.50 | $C_{16} - C_{17} - C_{18}$ | 113.3 |
| $C_{17} - C_{18}$ | 1.54 | | |

where u is the observed value of the coordinate in that axial direction, m is the displacement of each succeeding sub-cell in that direction, v is the sub-cell index ranging in value from -9 to +8 and w is the coordinate of the atom within the sub-cell.

The coordinates obtained from the electron density contour maps were expressed as fractional values of the cell edges and the values along the c axis were obtained by averaging over the two projections.

The eighteen equations in each of the axial directions, were then solved by the least squares method later described during the evaluation of the β angle and the following values of m and w were obtained.

| | | | |
|---|---|---|---|
| $m_x$ | $0.01549 \pm 0.00010$ | $w_x$ | $0.06978 \pm 0.00053$ |
| $m_y$ | $0.00001 \pm 0.00005$ | $w_y$ | $0.03811 \pm 0.00044$ |
| $m_z$ | $0.053496 \pm 0.000014$ | $w_z$ | $0.016926 \pm 0.000077$ |

These values were expressed in Angstrom units by multiplying by the axial lengths, so that

$$x = a.m_x$$

where a is the axial length. The standard deviation of x is given by

$$\sigma(x) = \left\{a^2 \cdot \sigma^2(m_x) + m_x^2 \cdot \sigma^2(a)\right\}^{\frac{1}{2}}$$

where σ(a) is the standard deviation of the a axis. This gave

| | | | |
|---|---|---|---|
| $x_1$ | 0.08630 ± 0.00058 | $x_2$ | 0.3887 ± 0.0030 |
| $y_1$ | 0.00008 ± 0.00039 | $y_2$ | 0.2828 ± 0.0033 |
| $z_1$ | 2.5865 ± 0.0044 | $z_2$ | 0.8184 ± 0.0040 |
| $x_1^1$ | −1.1715 ± 0.0034 | $x_2^1$ | −0.0093 ± 0.0037 |
| $z_1^1$ | 2.2601 ± 0.0041 | $z_2^1$ | 0.7151 ± 0.0035 |

where ($x_1$ $y_1$ $z_1$) are the coordinates of the sub-cell point (001) and ($x_2$ $y_2$ $z_2$) the coordinates of the carbon atom in the asymmetric unit of the sub-cell, both being referred to the main cell axes and origin. These points were then referred to the orthogonal axes a, b and $c^1$, where $c^1$ is perpendicular to a and b, by means of the transformation

$$x^1 = x + z\cos\beta \;, \qquad \sigma(x^1) = \left\{\sigma^2(x) + \cos^2\beta \cdot \sigma^2(z) + (z\sin\beta)^2 \cdot \sigma^2(\beta)\right\}^{\frac{1}{2}} \;,$$

$$z^1 = z\sin\beta \;, \qquad \sigma(z^1) = \left\{\sin^2\beta \cdot \sigma^2(z) + (z\cos\beta)^2 \cdot \sigma^2(\beta)\right\}^{\frac{1}{2}} .$$

The positions of all the carbon atoms were then calculated by means of this data and thus assuming a regular structure for the chain. A comparison with the observed values revealed that the average distance between the two sets of atomic coördinates was 0.02A and the greatest discrepancy was of 0.04A for $C_{18}$. These differences would appear to within the limits of experimental error so no attempt was made to fit the observed coordinates into a higher order curve which would be required for a bent or drawn out chain.

With the aid of the formulae given earlier[18] the dimensions of the sub-cell were found to be

$a_s = 5.57 \pm 0.01$ A

$b_s = 7.42 \pm 0.01$ A

$c_s = 2.546 \pm 0.004$ A $\qquad \beta_s = 117°24' \pm 5'$.

The carbon atoms in the sub-cell in the molecular chain passing through the origin were called $C_1$ and $C_2$, in agreement with the notation previously used. The error in the length of the bond $C_1^7 - C_1$ was taken as twice that of the distance of $C_1$ from the centre of symmetry at the main cell origin and gave

$$C_1^7 - C_1 = 1.538 \pm 0.007 \text{ A.}$$

Similarly $C_1 - C_2 = 1.529 \pm 0.010$ A.

for the interatomic distances within the sub-cell. The zig-zag angle of the chain was found to be 112°1′ ± 21′.

The positions of the hydrogen atoms were recalculated assuming the same dimensions as previously and the coordinates of the atoms of the methylene group in the asymmetric unit of the sub-cell, but referred to the main cell axes and origin, are shown in Table IV.

Table IV.

Coordinates of the Sub-cell Atoms, referred to the main cell axes and origin.

| | $\frac{x}{a}$ | $\frac{y}{b}$ | $\frac{z}{c}$ | x | y | z |
|---|---|---|---|---|---|---|
| C | 0.0698 | 0.0381 | 0.0169 | 0.389 | 0.283 | 0.818 |
| $H_1$ | 0.053 | 0.179 | 0.0160 | 0.30 | 1.33 | 0.78 |
| $H_2$ | 0.281 | 0.010 | 0.0281 | 1.57 | 0.07 | 1.36 |

These positions were then referred to the sub-cell axes and to sub-cell centre as origin and the coordinates obtained are shown in Table V.

## Table V

Coordinates of the Sub-cell Atoms, referred to the sub-cell axes and centre.

| | $\frac{X}{a_s}$ | $\frac{Y}{b_s}$ | $\frac{Z}{c_s}$ | X | Y | Z |
|---|---|---|---|---|---|---|
| C | 0.0649 | 0.0381 | −0.1836 | 0.361 | 0.283 | −0.467 |
| $H_1$ | 0.049 | 0.179 | −0.200 | 0.27 | 1.33 | −0.51 |
| $H_2$ | 0.273 | 0.010 | 0.026 | 1.52 | 0.07 | 0.07 |

The arrangement of these sub-cell atoms in the projections along the $b_s$ and $a_s$ axes are shown in Fig. 6. In the projection along the $a_s$ axis alternate carbon-carbon bonds are omitted for the sake of clarity.

The matrix $g^i_k$ for expressing the diffraction orders $H^i$ of the sub-cell in terms of $h^k$ of the main cell is the same as that for expressing the sub-cell translations $s^i$ in terms of the crystal translations $a^k$. The matrix then is

$$g^i_k = \boxed{\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0.015494 & 0 & 0.053496 \end{matrix}}$$

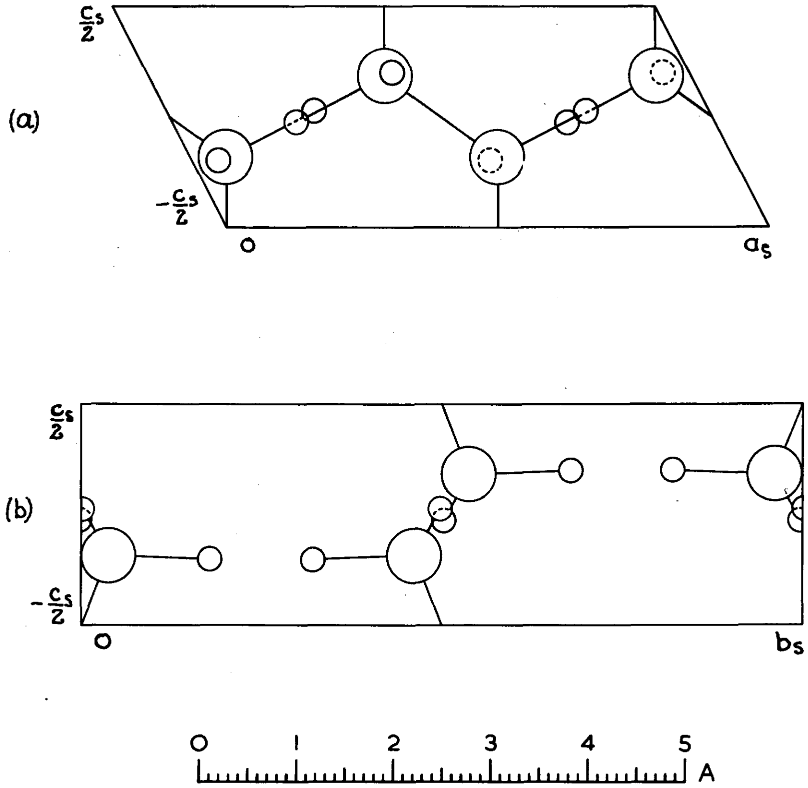


Fig. 6. Arrangement of the atoms in the projections of the sub-cell (a) along the $b_s$ axis, (b) along the $a_s$ axis. In latter case alternate C-C bonds are omitted.

The structure factors were recalculated and the discrepancies were found to have fallen to 16.7% and 13.8% for the (h0l) and (0kl) reflections. None of the planes was found to have changed signs. For the two zones the best value of B, the temperature factor, was found to be $3.0\times10^{-16}$ and this value was also taken for the hydrogen atoms.

The standard molecule at the origin of the main cell was called A and the reflected molecule at ($\frac{1}{2}$ $\frac{1}{2}$ 0) B, and the shortest distances of approach between non-bonded atoms assuming the positions calculated for the regular structure were found to be

| | | |
|---|---|---|
| $C_1$ (A) | ...... $C_2$ (B) | 4.14 A. |
| $C_1$ (A) | ...... $C_1$ (B) | 4.20 |
| $C_1$ (A) | ...... $C_3$ (B) | 4.20 |

The hydrogen atoms attached to $C_1$ were designated $H_{11}$ and $H_{12}$ and the shortest hydrogen-hydrogen distances were calculated as

| | | |
|---|---|---|
| $H_{11}$ (A) | ...... $H_{22}$ (B) | 2.61 A |
| $H_{12}$ (A) | ...... $H_{31}$ (B) | 2.96 |
| $H_{11}$ (A) | ...... $H_{31}$ (B) | 2.97 |
| $H_{12}$ (A) | ...... $H_{11}$ (B) | 2.97 |
| $H_{11}$ (A) | ...... $H_{11}$ (B) | 2.98 |

The distance between the observed positions of the carbon atoms of the methyl groups across the centre of symmetry at $(00\frac{1}{2})$ was found to be 4.19A.

### (h) Comparison with the Orthorhombic Form.

The $a_s$ axis of the sub-cell was displaced in the direction of the $c_s$ axis by an amount equivalent to one zig-zag unit of the chain. This operation produced a sub-cell, which however is not a true sub-cell of the structure, of the dimensions

$a_o = 4.945 \pm 0.01$ A

$b_o = 7.42 \pm 0.01$ A

$c_o = 2.546 \pm 0.004$A $\qquad \beta_o = 90^\circ 11' \pm 7'$

The sides of this sub-cell agree closely with those found for a number of n-paraffins of the orthorhombic form and the angle $\beta_o$ does not differ significantly from one right angle.

The coordinates of the atoms of the methylene group in the asymmetric unit of the sub-cell were referred to the orthogonal axes $a_s'$, $b_s$ and $c_s$ where $a_s'$ was perpendicular to $b_s$ and $c_s$. These atoms will then be expressed in terms of the sub-cell given above if the departure of $\beta_o$ from orthogonality is ignored and their coordinates are given in Table VI.

Table VI

Coordinates of the Sub-cell Atoms, referred to the orthogonal axes $a_s'$, $b_s$ and $c_s$ where $a_s'$ is perpendicular to $b_s$ and $c_s$.

| | $\frac{X'}{a_o}$ | $\frac{Y}{b_o}$ | $\frac{Z'}{c_o}$ | $X'$ | $Y$ | $Z'$ |
|---|---|---|---|---|---|---|
| C | 0.0649 | 0.0381 | −0.2489 | 0.321 | 0.283 | −0.634 |
| $H_1$ | 0.049 | 0.179 | −0.249 | 0.24 | 1.33 | −0.63 |
| $H_2$ | 0.273 | 0.010 | −0.249 | 1.35 | 0.07 | −0.63 |

The above values correspond very closely with those, found by Bunn and also by Vaĭnstein and Pinsker, previously quoted for the orthorhombic form. It would appear that the sideways packing of the chains is the same in the orthorhombic and monoclinic forms. Schoon's contention as to the way in which the monoclinic unit cell can be derived from the orthorhombic is thus very nearly true since the $\beta_s$ angle of the sub-cell is very nearly equal to the $\beta$ angle of the monoclinic crystal cell.

The plane containing the carbon atoms of the chain passes through the main cell origin, the sub-cell origin and the point $C_1$ and its equation, referred to the orthogonal axes a′, b and c is given by

$$X' - 1.347Y = 0.$$

The plane then makes an angle of 41.4° with the b axis.

## (i) Discussion

The results of this work are in general agreement with the conclusions of the earlier investigators. The sideways packing of the molecular chains was found to be very similar to that shown for the orthorhombic form. Schoon's contention as to the way in which the monoclinic form of the n-paraffin's is derived from the orthorhombic form is very nearly true but the value of the monoclinic angle depends not only on the length of the zig-zag unit but on the end to end packing of the molecules and hence the length of the hydrocarbon chain.

In the case of n-hexatriacontane the considerable length of the molecule prevents the accurate determination of the perameters of individual atoms but the values obtained show that the chain is regular within the limits of experimental error with perhaps some slight distortion at the ends where the effects of the end to end packing will be greatest. This regularity of the chain permits more accurate values of the atomic perameters to be obtained and gives the length of the zig-zag of the chain as 2.546 ± 0.004 A, the carbon-carbon bond lengths as alternatively 1.538 ± 0.007 and 1.529 ± 0.010 A and the angle of the zig-zag as 112°12′ ± 21′. These results do not differ significantly from the values obtained by Bunn for polythene. The values of the carbon-carbon bond lengths are not significantly different from one another or the value of 1.54 A found for the carbon-carbon single bond length in diamond, although some deviation in bond length along the chain might be expected.

The zig-zag angle of the chain is increased over the tetrahedral angle of 109°28′ and it would appear that the mutual repulsion between alternate carbon atoms is sufficient to force them further apart.

## (j) Experimental

### 1. Preparation of the crystals.

Crystals of n-hexatriacontane were grown from a solution in light petroleum by slow evaporation at room temperature, the temperature being maintained constant by immersing the vessel in water inside a Dewar flask.

The crystals were obtained as flat diamond shaped plates with an interfacial angle of about 75°. The a and b axes lay in the plane of the plate along the bisectors of the interfacial angles with the (001) and (110) faces well developed. Most of the crystals were twinned about the (001) but a number of untwinned ones were selected with the aid of the polarising microscope.

### 2. Determination of the unit cell.

Rotation, oscillation and zero- and first-layer Weissenberg photographs were taken about the a and b axes using nickel-filtered copper $K\alpha$ radiation ($\lambda = 1.542$ A). The a and b axial lengths were measured from the rotation photographs on which copper powder lines, of known spacing, had been superimposed to give an accurate value of the camera radius.

On the b axis Weissenberg photograph, sodium chloride powder lines were superimposed at the two ends of traverse. The values of the Bragg angles $\theta$ are accurately known for these lines and a graph was drawn relating P, the displacement from the centre of the film, to θ. In practice the second powder line was taken as an arbitrary zero and the displacement measured from this. This curve is very nearly a straight line and allows for any non-circularity of the camera. For any reflection the value of P was measured from the film, θ found from the graph and its $D^*$ value determined with a high degree of accuracy. $D^*_{hkl}$ is the distance of the point having Miller indices hkl from the origin of the reciprocal lattice.

The axial planes (0018) and (0019) were indexed by inspection and an approximate value found for $c^*$. The higher order planes were then indexed and a more accurate value of $c^*$ determined using the formula

$$c^* = \frac{2 \sum \sin\theta}{\sum l}$$

This formula gives a weight l to each reflection i.e. greater weight to the high order reflections.

The standard deviation of $c^*$ is given by

$$\sigma(c^*) = \left\{ \frac{\sum l \delta^2}{(n-1)\sum l} \right\}^{\frac{1}{2}}$$

where $\delta$ is the difference between the observed and calculated values of $D^*$ for each plane.

Thus $c^* = 0.03650 \pm 0.00006$

and $c\sin\beta = 42.25 \pm 0.07$ A.

where $$c\sin\beta = \frac{\lambda}{c^*} \quad \text{and} \quad \sigma(c\sin\beta) = \frac{\lambda\sigma(c^*)}{c^{*2}}$$

The (h0l) series of reflections were indexed to give small l numerals to the intense reflections and the strongest plane was called the (20$\bar{1}$) and not the (200) by comparison with the (h1l) reflections. The value of the monoclinic angle β was determined by a method due to Vand[57] and summarised below.

For a monoclinic cell,

$$D^{*2}_{hkl} = H^{*2}_{hk} + K^{*2}_{hk} + 2K^*_{hk}\,lc^* + l^2c^{*2}$$

where $D^*_{hkl}$ is the distance of the point having Miller indices hkl from the origin of the reciprocal lattice,

$$H^*_{hk} = ha^*\sin\beta^*$$

and $$K^*_{hk} = ha^*\cos\beta^*.$$

$H^*_{hk}$ and $K^*_{hk}$ are constant for a band of reflections of given indices h and k.

By writing $(D^*_{hkl}/c^*)^2 - l^2 = y_i$ , $l = x_i$,

$$(H^*_{hk}/c^*)^2 + (K^*_{hk}/c^*)^2 = q \text{ and } 2K^*_{hk}/c^* = p,$$

n linear equations are obtained of the form

$$y_i = px_i + q \,, \qquad i = 1, 2 \,\ldots\ldots\, n.$$

where $x_i$ are whole numbers and $y_i$ are known from measurement.

To determine p and q with the greatest accuracy, a Gaussian method of least squares was used, assuming that all the equations have equal weight.

Then
$$p = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{n\sum x_i^2 - (\sum x_i)^2}$$

and
$$q = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i}{n\sum x_i^2 - (\sum x_i)^2}$$

and the standard deviations of p and q are given by

$$\sigma(p) = \left\{ \frac{n \sum \delta_i^2}{(n-2)\left[ n \sum x_i^2 - \left(\sum x_i\right)^2 \right]} \right\}^{\frac{1}{2}}$$

and $$\sigma(q) = \left\{ \frac{\sum x_i^2 \sum \delta_i^2}{(n-2)\left[ n \sum x_i^2 - \left(\sum x_i\right)^2 \right]} \right\}^{\frac{1}{2}}$$

where $\delta_i = y_i' - y_i$

and where $y_i'$ are the values calculated using the above values of p and q.

Then

$$H_{hk}^* = c^*\left(q - \tfrac{1}{4}p^2\right)^{\frac{1}{2}} ,$$

$$\sigma(H_{hk}^*) = \left\{ \left(q - \tfrac{1}{4}p^2\right)\sigma^2(c^*) + \frac{c^{*2}}{4\left(q - \frac{1}{4}p^2\right)}\sigma^2(q) + \frac{p^2 c^{*2}}{16\left(q - \frac{1}{4}p^2\right)}\sigma^2(p) \right\}^{\frac{1}{2}},$$

and $$a = \frac{h\lambda}{H_{hk}^*} ,$$

$$\sigma(a) = \frac{h\lambda}{H_{hk}^{*2}}\,\sigma(H_{hk}^*)$$

which gives a = 5.572 ± 0.011 A.

Also $K^*_{hk} = \frac{1}{2}pc^*$,

$$\cot \beta^* = \frac{K^*_{hk}}{H^*_{hk}} = \frac{p}{2(q-\frac{1}{4}p^2)^{\frac{1}{2}}},$$

and $$\sigma(\beta^*) = \sin^2\beta^* \left\{ \frac{4q^2\sigma^2(p) + p^2\sigma^2(q)}{16(q-\frac{1}{4}p^2)} \right\}^{\frac{1}{2}}$$

whence $\beta^* = 60°54' \pm 4'$

$\beta = 119°6' \pm 4'$.

$$c = \frac{c \sin \beta}{\sin \beta},$$

and $$\sigma(c) = \left\{ \frac{1}{\sin^2\beta} \sigma^2(c \sin \beta) + \frac{c^2}{\tan^2\beta} \sigma^2(\beta) \right\}^{\frac{1}{2}}$$

whence c = 48.35 ± 0.08 A.

3. Density determination.

The density of n-hexatriacontane was found by extrapolation from the data given by Paterson[58].

4. Intensity measurements and corrections.

The (0kl) and (h0l) reflections were obtained by Weissenberg films of the zero-layer lines of crystals rotated about the a and b axis. The intensities were measured on a relative scale by visual estimation using the multiple film technique[36].

Table VII

| Reflections | Cross-section of crystal in mm. | No. of reflections observed | % of theoretical | Range of intensities |
|---|---|---|---|---|
| h0l | 0.24 x 0.09 | 88 | 27.2 | 800:1 |
| 0kl | 0.30 x 0.09 | 90 | 20.5 | 9,500:1 |

Table VII shows that the crystals used were far from uniform but in view of the low absorption coefficient no attempt was made to correct for the absorption of the X-ray beam in the crystal. The intensities were corrected by the usual Lorentz and polarisation factors and the observed values of the structure factors were later placed on an absolute scale by comparison with the calculated values.

5. Fourier analysis.

For the sub-cell projection along the $b_s$ axis the electron density was computed at 225 points on the asymmetric unit, the $a_s$ and $c_s$ axes being subdivided into 30 parts of 0.186 and 0.085A. respectively. The summations were carried out by three figure methods[37] and the results were plotted on a scale of 5 cm. per A. by graphical interpolation from the summation totals. The electron density, in the projection along the $a_s$ axis, was computed at 300 points, the summation intervals being $b_s/60 = 0.124$A and $C_s \sin\beta_s/20 = 0.113$A.

For the main cell projection along the b axis the electron density was computed at 900 points on the asymmetric unit, the a axis being subdivided into 30 parts of 0.186A and the c axis into 120 parts of 0.403A. The results were plotted on a scale of 4cm. per A. by graphical interpolation from the summation totals. The electron density in the projection along the a axis was computed at 1,800 points, the summation intervals being $b/60 = 0.124$A and $c\sin\beta/120 = 0.352$A.

## Table VIII

Observed and Calculated Values of the Structure Factors.

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 200 | 0.633 | 77 | +84 | 00,20 | 0.730 | 14 | +17 |
| 400 | 1.264 | < 6 | 0 | 00,21 | 0.767 | 7 | − 7 |
| 600 | 1.897 | < 4 | + 4 | 00,22 | 0.803 | < 5 | + 3 |
| | | | | 00,23 | 0.840 | < 5 | − 2 |
| 001 | 0.037 | (?) | 21 | 00,24 | 0.876 | < 5 | + 1 |
| 002 | 0.073 | (?) | −22 | 00,25 | 0.913 | < 5 | 0 |
| 003 | 0.110 | (?) | +22 | 00,26 | 0.949 | < 5 | 0 |
| 004 | 0.146 | 18 | −22 | 00,27 | 0.986 | < 6 | 0 |
| 005 | 0.183 | 18 | +21 | 00,28 | 1.022 | < 6 | 0 |
| 006 | 0.219 | 17 | −21 | 00,29 | 1.059 | < 6 | 0 |
| 007 | 0.256 | 17 | +21 | 00,30 | 1.095 | < 6 | + 1 |
| 008 | 0.292 | 17 | −20 | 00,31 | 1.132 | < 6 | − 1 |
| 009 | 0.329 | 16 | +20 | 00,32 | 1.168 | < 6 | + 1 |
| 00,10 | 0.365 | 16 | −19 | 00,33 | 1.205 | < 6 | − 2 |
| 00,11 | 0.402 | 16 | +18 | 00,34 | 1.241 | < 6 | + 3 |
| 00,12 | 0.438 | 14 | −18 | 00,35 | 1.278 | 9 | − 5 |
| 00,13 | 0.475 | 15 | +18 | 00,36 | 1.314 | 13 | + 9 |
| 00,14 | 0.511 | 16 | −19 | 00,37 | 1.351 | 43 | −37 |
| 00,15 | 0.548 | 18 | +21 | 00,38 | 1.387 | 25 | −24 |
| 00,16 | 0.584 | 24 | −22 | 00,39 | 1.424 | 10 | +10 |
| 00,17 | 0.621 | 31 | +28 | 00,40 | 1.460 | 8 | − 7 |
| 00,18 | 0.657 | 57 | −55 | | | | |
| 00,19 | 0.694 | 100 | −96 | 020 | 0.415 | 324 | +300 |

Table VIII (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 040 | 0.830 | 110 | +104 | 20,$\overline{36}$ | 1.150 | 11 | + 7 |
| 060 | 1.245 | 20 | + 23 | 20,$\overline{35}$ | 1.117 | 8 | - 6 |
| 080 | 1.660 | 13 | - 16 | 20,$\overline{34}$ | 1.085 | 8 | + 6 |
|  |  |  |  | 20,$\overline{33}$ | 1.054 | 7 | - 6 |
| 20,$\overline{57}$ | 1.859 | 12 | + 11 | 20,$\overline{32}$ | 1.023 | 8 | + 6 |
| 20,$\overline{56}$ | 1.823 | 12 | + 7 | 20,$\overline{31}$ | 0.993 | 9 | - 7 |
| 20,$\overline{55}$ | 1.788 | 8 | - 4 | 20,$\overline{30}$ | 0.964 | 10 | + 7 |
| 20,$\overline{54}$ | 1.754 | < 5 | + 3 | 20,$\overline{29}$ | 0.934 | 10 | - 7 |
| 20,$\overline{53}$ | 1.720 | < 6 | - 3 | 20,$\overline{28}$ | 0.905 | 11 | + 8 |
| 20,$\overline{52}$ | 1.685 | < 6 | + 2 | 20,$\overline{27}$ | 0.876 | 11 | - 8 |
| 20,$\overline{51}$ | 1.652 | < 6 | - 2 | 20,$\overline{26}$ | 0.848 | 12 | + 9 |
| 20,$\overline{50}$ | 1.618 | < 6 | + 2 | 20,$\overline{25}$ | 0.821 | 13 | - 10 |
| 20,$\overline{49}$ | 1.583 | < 7 | - 2 | 20,$\overline{24}$ | 0.793 | 15 | + 11 |
| 20,$\overline{48}$ | 1.549 | < 7 | + 2 | 20,$\overline{23}$ | 0.769 | 16 | - 14 |
| 20,$\overline{47}$ | 1.515 | < 7 | - 2 | 20,$\overline{22}$ | 0.744 | 21 | + 16 |
| 20,$\overline{46}$ | 1.480 | < 7 | + 2 | 20,$\overline{21}$ | 0.720 | 25 | - 23 |
| 20,$\overline{45}$ | 1.447 | < 7 | - 2 | 20,$\overline{20}$ | 0.698 | 44 | + 48 |
| 20,$\overline{44}$ | 1.413 | < 7 | + 2 | 20,$\overline{19}$ | 0.675 | 110 | +108 |
| 20,$\overline{43}$ | 1.378 | < 7 | - 3 | 20,$\overline{18}$ | 0.656 | 17 | - 19 |
| 20,$\overline{42}$ | 1.344 | < 7 | + 3 | 20,$\overline{17}$ | 0.636 | 8 | + 9 |
| 20,$\overline{41}$ | 1.311 | < 7 | - 2 | 20,$\overline{16}$ | 0.620 | 7 | - 4 |
| 20,$\overline{40}$ | 1.278 | < 7 | + 2 | 20,$\overline{15}$ | 0.603 | 5 | + 2 |
| 20,$\overline{39}$ | 1.247 | < 7 | 0 | 20,$\overline{14}$ | 0.589 | < 4 | - 1 |
| 20,$\overline{38}$ | 1.213 | 110 | - 99 | 20,$\overline{13}$ | 0.577 | < 4 | 0 |
| 20,$\overline{37}$ | 1.182 | 16 | - 9 | 20,$\overline{12}$ | 0.568 | < 4 | 0 |

Table VIII (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| $20,\overline{11}$ | 0.561 | < 4 | 0 | 20,14 | 0.987 | < 6 | + 1 |
| $20,\overline{10}$ | 0.556 | < 4 | 0 | 20,15 | 1.016 | < 6 | + 1 |
| $20\overline{9}$ | 0.553 | < 4 | + 1 | 20,16 | 1.049 | < 6 | − 2 |
| $20\overline{8}$ | 0.552 | < 4 | − 1 | 20,17 | 1.079 | < 6 | + 7 |
| $20\overline{7}$ | 0.555 | < 4 | + 2 | 20,18 | 1.110 | 74 | − 95 |
| $20\overline{6}$ | 0.559 | 5 | − 4 | 20,19 | 1.142 | 18 | − 16 |
| $20\overline{5}$ | 0.567 | 7 | + 6 | 20,20 | 1.175 | 8 | 9 |
| $20\overline{4}$ | 0.576 | 12 | − 9 | | | | |
| $20\overline{3}$ | 0.587 | 20 | + 15 | $40,\overline{57}$ | 1.837 | 17 | − 15 |
| $20\overline{2}$ | 0.600 | 36 | − 28 | $40,\overline{56}$ | 1.809 | < 5 | + 2 |
| $20\overline{1}$ | 0.615 | 114 | +107 | $40,\overline{55}$ | 1.779 | < 5 | − 1 |
| 201 | 0.651 | 24 | − 33 | $40,\overline{43}$ | 1.461 | < 7 | − 2 |
| 202 | 0.670 | 15 | + 21 | $40,\overline{42}$ | 1.439 | < 7 | + 3 |
| 203 | 0.691 | 12 | − 16 | $40,\overline{41}$ | 1.416 | 9 | − 4 |
| 204 | 0.714 | 11 | + 13 | $40,\overline{40}$ | 1.394 | 11 | + 8 |
| 205 | 0.738 | 9 | − 10 | $40,\overline{39}$ | 1.373 | 37 | − 30 |
| 206 | 0.762 | 8 | + 9 | $40,\overline{38}$ | 1.352 | 34 | − 28 |
| 207 | 0.788 | 7 | − 7 | $40,\overline{37}$ | 1.330 | 10 | + 11 |
| 208 | 0.814 | 6 | + 6 | $40,\overline{36}$ | 1.310 | 8 | − 7 |
| 209 | 0.842 | 5 | − 6 | $40,\overline{35}$ | 1.290 | < 7 | + 6 |
| 20,10 | 0.869 | < 5 | + 4 | $40,\overline{34}$ | 1.271 | < 7 | − 5 |
| 20,11 | 0.898 | < 5 | − 4 | $40,\overline{22}$ | 1.121 | < 6 | + 3 |
| 20,12 | 0.928 | < 5 | + 3 | $40,\overline{21}$ | 1.115 | < 6 | − 6 |
| 20,13 | 0.957 | < 6 | − 2 | $40,\overline{20}$ | 1.113 | 79 | + 94 |

Table VIII (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 40,$\overline{19}$ | 1.109 | 23 | + 21 | 019 | 0.389 | < 3 | + 3 |
| 40,$\overline{18}$ | 1.107 | < 6 | - 11 | 01,10 | 0.419 | < 3 | - 4 |
| 40,$\overline{17}$ | 1.105 | < 6 | + 8 | 01,11 | 0.452 | 4 | + 4 |
| 40$\overline{3}$ | 1.214 | < 6 | + 2 | 01,12 | 0.485 | 4 | - 5 |
| 40$\overline{2}$ | 1.231 | < 6 | - 3 | 01,13 | 0.518 | 5 | + 5 |
| 40$\overline{1}$ | 1.246 | 16 | - 7 | 01,14 | 0.552 | 6 | - 6 |
| 401 | 1.282 | < 7 | 0 | 01,15 | 0.587 | 9 | + 7 |
| 40,14 | 1.578 | < 7 | + 2 | 01,16 | 0.621 | 12 | - 9 |
| 40,15 | 1.602 | < 6 | - 3 | 01,17 | 0.654 | 17 | +12 |
| 40,16 | 1.628 | 10 | + 9 | 01,18 | 0.689 | 34 | -28 |
| 40,17 | 1.655 | 21 | - 24 | 01,19 | 0.724 | 62 | -54 |
| 40,18 | 1.682 | 22 | - 28 | 01,20 | 0.759 | 11 | +11 |
| 40,19 | 1.708 | 8 | + 9 | 01,21 | 0.793 | 7 | - 6 |
| | | | | 01,22 | 0.829 | 5 | + 3 |
| 60,$\overline{21}$ | 1.665 | 27 | + 22 | 01,23 | 0.865 | < 5 | - 2 |
| 60,$\overline{20}$ | 1.669 | 27 | + 29 | 01,24 | 0.899 | < 5 | + 1 |
| 60,$\overline{19}$ | 1.671 | < 6 | - 9 | 01,35 | 1.294 | < 7 | + 2 |
| 60,$\overline{18}$ | 1.678 | < 6 | + 5 | 01,36 | 1.331 | < 7 | - 3 |
| 60$\overline{4}$ | 1.828 | < 5 | - 3 | 01,37 | 1.367 | 13 | +11 |
| 60$\overline{3}$ | 1.843 | < 5 | + 5 | 01,38 | 1.402 | 11 | + 7 |
| 60$\overline{2}$ | 1.862 | 14 | - 28 | | | | |
| 60$\overline{1}$ | 1.878 | 8 | - 10 | 021 | 0,418 | (?) | +11 |
| | | | | 022 | 0.421 | 9 | -12 |
| 018 | 0.359 | < 3 | - 3 | 023 | 0.430 | 9 | +12 |

Table VIII (contd.)

| hkl | 2sinθ | Fo | Fc | hkl | 2sinθ | Fo | Fc |
|---|---|---|---|---|---|---|---|
| 024 | 0.440 | 8 | -11 | 02,39 | 1.483 | 8 | + 8 |
| 025 | 0.453 | 8 | +11 | | | | |
| 026 | 0.470 | 8 | -11 | 03,12 | 0.761 | < 5 | - 5 |
| 027 | 0.487 | 7 | +11 | 03,13 | 0.783 | < 5 | + 5 |
| 028 | 0.507 | 7 | -11 | 03,14 | 0.806 | 6 | - 6 |
| 029 | 0.530 | 7 | +11 | 03,15 | 0.830 | 8 | + 8 |
| 02,10 | 0.552 | 7 | -10 | 03,16 | 0.854 | 12 | - 10 |
| 02,11 | 0.578 | 6 | +10 | 03,17 | 0.879 | 17 | + 15 |
| 02,12 | 0.603 | 6 | -11 | 03,18 | 0.904 | 37 | - 33 |
| 02,13 | 0.630 | 7 | +10 | 03,19 | 0.931 | 77 | - 68 |
| 02,14 | 0.659 | 9 | -11 | 03,20 | 0.959 | 12 | + 15 |
| 02,15 | 0.688 | 10 | +12 | 03,21 | 0.988 | 7 | - 7 |
| 02,16 | 0.718 | 14 | -13 | 03,22 | 1.016 | < 6 | + 4 |
| 02,17 | 0.746 | 20 | +18 | 03,23 | 1.044 | < 6 | - 3 |
| 02,18 | 0.777 | 39 | -35 | 03,35 | 1.421 | < 7 | + 4 |
| 02,19 | 0.809 | 64 | -63 | 03,36 | 1.454 | < 7 | - 7 |
| 02,20 | 0.839 | 7 | +11 | 03,37 | 1.488 | 22 | + 24 |
| 02,21 | 0.871 | < 5 | - 5 | 03,38 | 1.521 | 15 | + 14 |
| 02,22 | 0.903 | < 5 | + 2 | 03,39 | 1.554 | 9 | - 5 |
| 02,34 | 1.309 | < 7 | + 2 | | | | |
| 02,35 | 1.343 | < 7 | - 4 | 04,15 | 0.994 | < 6 | + 5 |
| 02,36 | 1.378 | 7 | + 6 | 04,16 | 1.015 | < 6 | - 6 |
| 02,37 | 1.413 | 31 | -27 | 04,17 | 1.034 | 7 | + 8 |
| 02,38 | 1.447 | 20 | -17 | 04,18 | 1.058 | 15 | - 15 |

Table VIII (contd.)

| hkl | 2sinθ | Fo | Fc |
|---|---|---|---|
| 04,19 | 1.081 | 24 | - 27 |
| 04,20 | 1.103 | < 6 | + 5 |
| 04,21 | 1.129 | < 6 | - 2 |
| 04,35 | 1.524 | < 7 | - 2 |
| 04,36 | 1.555 | < 7 | + 4 |
| 04,37 | 1.585 | 14 | - 16 |
| 04,38 | 1.616 | 8 | - 10 |
| 05,14 | 1.155 | < 6 | - 5 |
| 05,15 | 1.172 | < 6 | + 6 |
| 05,16 | 1.189 | 7 | - 8 |
| 05,17 | 1.206 | 11 | + 12 |
| 05,18 | 1.225 | 28 | - 28 |
| 05,19 | 1.247 | 55 | - 59 |
| 05,20 | 1.266 | < 7 | + 13 |
| 05,21 | 1.289 | < 7 | - 7 |
| 05,35 | 1.644 | < 6 | + 4 |
| 05,36 | 1.673 | < 6 | - 7 |
| 05,37 | 1.701 | 18 | + 25 |
| 05,38 | 1.730 | 12 | + 15 |
| 07,15 | 1.552 | < 7 | + 4 |
| 07,16 | 1.563 | < 7 | - 6 |
| 07,17 | 1.577 | 8 | + 9 |
| 07,18 | 1.592 | 12 | - 19 |
| 07,19 | 1.608 | 29 | - 40 |

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