THE CRYSTAL STRUCTURE ANALYSIS OF
α-CARYOPHYLLENE ALCOHOL,
ISOCALEBASSINE,
AND OTHER MOLECULES.

Being a thesis presented in part
fulfilment of the requirements
for the degree of Ph.D.

Presented by

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PREFACE

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SUMMARY

In this thesis, the structure determinations of four molecules have been carried out by the application of the heavy atom method of x-ray crystal structure analysis. The thesis is divided into five parts; part one is concerned with a brief theoretical account of some of the methods used in crystal structure analysis.

Part two describes the analysis of the sesquiterpene, α-caryophyllene alcohol, in the form of its para-bromo benzene sulphonate derivative. A considerable amount of organic degradative work had been undertaken on this compound before its analysis was attempted by x-ray methods, but very little progress had been made in determining its structure. The bromine atom was easily located, and the structure was very readily determined. Least squares refinement has reduced the agreement index, R, to 12.6%.

In part three, the determination of the structure of the calabash-curare, isocalebassine, is described. A considerable amount of information was available regarding the major portion of the chemical structure of isocalebassine when the analysis of this structure was started.

However, the crystal structure and the position of the atoms in the molecule were not known, and this analysis established the correct structure and stereochemistry of isocalebassine. Crystals of isocalebassine-O-methyl ether were studied as the di-iodide derivative. It was not possible in this analysis to obtain great accuracy in the atomic parameters, and consequently finer details of the molecular framework have been obscured. The structural parameters have been refined by the method of least squares to an agreement index, R, of 15.8%.

Several years ago, Dr. G. Ferguson of this University began the investigation of the "overcrowded" halogenobenzene derivative, 4-bromo-3-nitro benzoic acid, but abandoned the project. This analysis has been resumed, and is described in part four of this thesis. Refinement of the structural parameters to an agreement index, R, of 9.5% has been carried out, and the results obtained clearly establish that, in the solid state, the nitro group of the molecule is twisted out of the plane of the benzene ring by a significant amount.

The final chapter of this thesis describes an attempt to determine the structure of the complex, bis-tetraphenyl arsonium mercuric tetrabromide. Parameters have been evaluated for the mercury atom and the four bromine atoms. The results obtained show that the four bromine atoms form a distorted tetrahedron round the mercury atom. Refinement of these parameters has reduced the agreement index to a value of R = 28.9%.

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PART 1

SOME METHODS OF X-RAY CRYSTAL STRUCTURE ANALYSIS.

1.1 INTRODUCTION.

By the first decade of the twentieth century, a large store of knowledge had been built up concerning the external habit of crystals, and their three dimensional symmetry. However, little was known about the internal arrangement of atoms, ions, or molecules in crystalline matter. In the year 1912, it was observed that the recently discovered x-rays were diffracted by crystals, in much the same way that a beam of ordinary light was diffracted by a grating. This discovery was due to von Laue. This opened the way, not only to a greater understanding of crystals, but also to the understanding of the nature of x-radiation.

Very complex calculations are required to derive the pattern of atoms in a crystal. In the early days of crystallography, only very simple substances could be investigated with any hope of success. As more and more of these simple substances were examined by x-rays, however, it became possible to tackle inorganic structures of increasing complexity. In the case of organic chemistry, it was first of all necessary to establish the structures of the fundamental types of molecule-----

such as those of benzene and naphthalene, and different paraffin chains. Once these were known, the structure analyses of complex substances, such as phthalocyanines, terpenes, and steroids could be carried out.

Since the advent of the electronic computer, the time required for these calculations has been greatly reduced, and very large molecules, such as proteins and nucleic acids, can now be investigated by this method. The result of this is that x-ray crystallography now plays an increasingly important part in research, and the elucidation of many complex organic and inorganic structures would prove impossible without its aid.

1.2 DIFFRACTION BY A CRYSTAL.

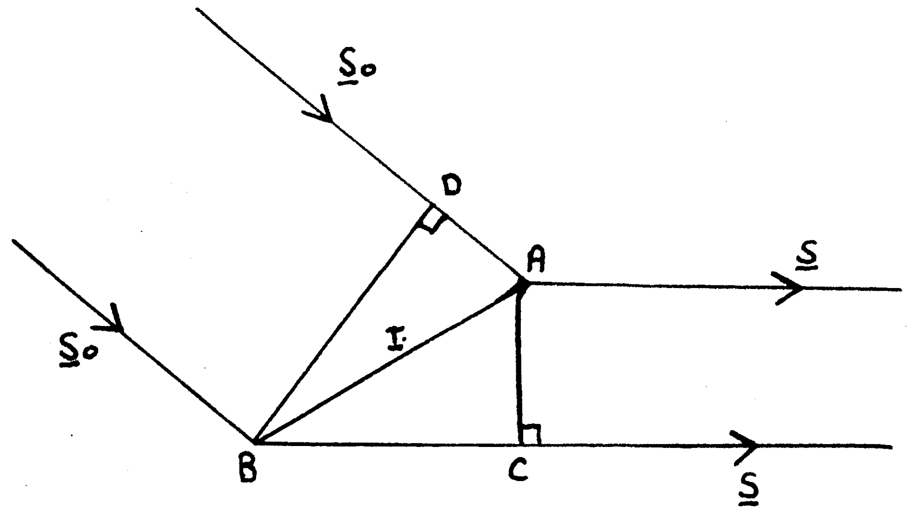
A crystal consists of groups of atoms repeated at regular intervals with the same orientation, in three dimensions. Suppose each group of atoms is replaced by a representative point; the collection of points so formed is the lattice of the crystal. The conditions for diffraction by x-rays depend solely on the lattice, irrespective of the crystal structure.

Assuming that each lattice point is the site of an electron, the positions of these electrons can be defined by the ends of vectors $\underline{r}$ such that

$$\underline{r} = u\underline{a} + v\underline{b} + w\underline{c}$$

where $\underline{a}$, $\underline{b}$, and $\underline{c}$ are the primitive translations of the lattice, and u, v, and w are integers.

When an electron is located in the path of an x-ray beam, it is forced to oscillate by the electromagnetic field of the x-rays impinging on it. Due to this, the electrons act as sources of secondary radiation, and in order to find the total effect of these secondary waves, it is necessary to consider the phase differences between the waves scattered in any particular direction.



In the diagram, A and B are two lattice points separated by a vector distance $\underline{r}$, and BD and AC are lines drawn in the incident and diffracted wave fronts respectively. A parallel beam of x-rays of wavelength λ, falling on the lattice in a direction defined by the vector $\underline{S}o$, and having magnitude $1/\lambda$, is scattered in a direction defined by the vector $\underline{S}$, also having magnitude $1/\lambda$.

The path difference between the scattered waves is

$$BC - AD = \lambda(\underline{r}.\underline{S} - \underline{r}.\underline{S}o)$$
$$= \lambda . \ \underline{r}.\underline{R}$$

where $\underline{R} = \underline{S} - \underline{S}o$.

The condition for the wave scattered at A to be in phase with the wave scattered at B is that the path difference must be a whole number of wavelengths.

Thus $(u\underline{a} + v\underline{b} + w\underline{c}).\underline{R}$ must be integral.

Since u, v, and w change by integral values, then each of the products separately must be integral. It follows that

$$\underline{a}.\underline{R} = h$$

$$\underline{b}.\underline{R} = k$$

$$\underline{c}.\underline{R} = l$$

where h, k, and l are integers.

These equations are known as the LAUE equations, and when they are simultaneously satisfied, a diffracted beam of maximum intensity will be produced.

BRAGG'S LAW.

W.L. BRAGG identified the integers h, k, and l of the Laue equations with the Miller indices of the lattice planes, and thus use could be made of these equations to interpret x-ray spectra and to determine the structure of crystals.

The Laue equations may be rewritten in the form

$\underline{a}/h.\underline{R} = 1$

$\underline{b}/k.\underline{R} = 1$

$\underline{c}/l.\underline{R} = 1$

By subtracting these equations in pairs, the following relationships are obtained

$(\underline{a}/h - \underline{b}/k).\underline{R} = 0$

$(\underline{a}/h - \underline{c}/l).\underline{R} = 0$

$(\underline{b}/k - \underline{c}/l).\underline{R} = 0$

The vector $\underline{R}$ is therefore at right angles to the vector $(\underline{a}/h - \underline{b}/k)$, and similarly is at right angles to both $(\underline{a}/h - \underline{c}/l)$, and $(\underline{b}/k - \underline{c}/l)$. These are vectors in the plane of the Miller indices hkl (fig. 1), and thus $\underline{R}$ is perpendicular to this plane.

Since $\underline{R}$ is a vector in the direction of the bisector of the incident and diffracted beams, (fig. 2), the bisector is identified with the normal to the hkl plane. This justifies the concept of each diffraction as a "reflection" of the rays from lattice planes.

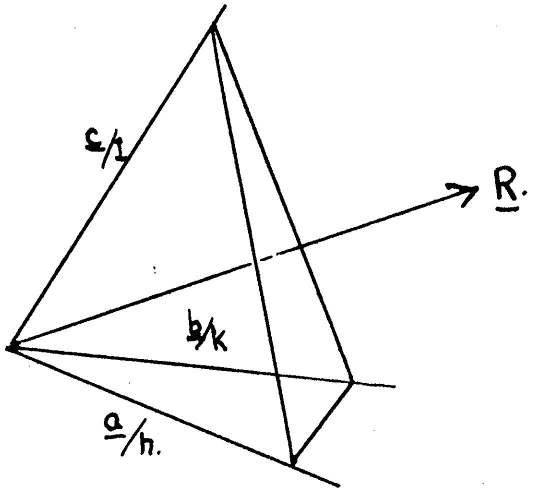


Fig. 1.

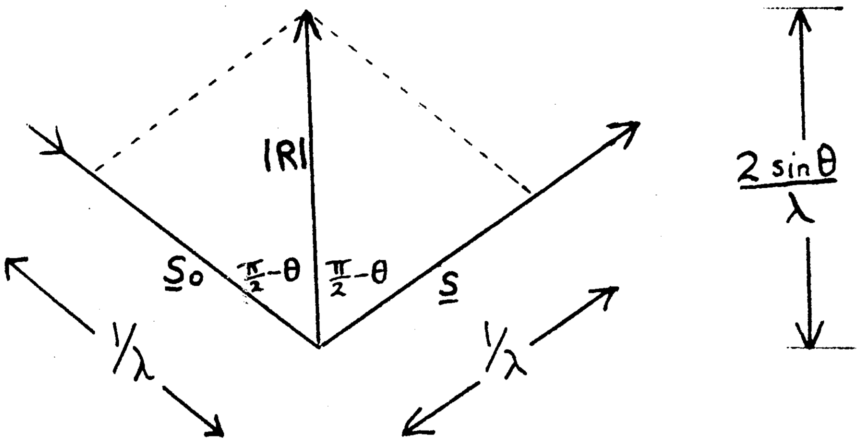


Fig. 2.

The perpendicular distance of the plane from the origin, d, is the projection of $\underline{a}/h$, $\underline{b}/k$, or $\underline{c}/l$ on the vector $\underline{R}$. That is

$$d = \frac{\underline{a}/h.\underline{R}}{|R|}$$

From the Laue equations, $\underline{a}/h.\underline{R} = 1$, and from fig. 2, $|R| = 2 \sin\theta/\lambda$. Therefore,

$$d = \lambda/2 \sin\theta \qquad \underline{\text{or}}\ \lambda = 2\ d \sin\theta.$$

This equation is known as BRAGG'S LAW.

1.3 FACTORS AFFECTING INTENSITY.

In section 1.2, the scattering units were assumed to be electrons in order that their linear dimensions could be neglected in comparison with both the space lattice dimensions and with the wavelength of the x-rays.

1.3.1 THE ATOMIC SCATTERING FACTOR.

In atoms, the electrons occupy a finite volume, and accordingly, phase differences exist between rays scattered from different points in this volume. Thus, the intensity of the resultant beam is reduced.

The scattering factor of an atom r whose electron density is ρ(uvw) is given by the expression

$$f_r(hkl) = V \iiint_{-\infty}^{\infty} \rho(uvw) \exp\left[2\pi i(hu+kv+lw)\right] dudvdw$$

where (uvw) are coordinates referred to the atomic centre.

The scattering power of the atom is a function of the angle of scattering, and of the distribution of electrons in the atom. For small angles of diffraction, the phase differences mentioned above are small, and the scattered amplitude will approach Z, the atomic number of the atom. As the angle of diffraction increases, the phase differences become larger, and thus the scattered beam becomes weaker; that is, the scattering factor becomes less than Z. The factor is called the atomic scattering factor and if the atom is assumed to have spherical symmetry, the atomic scattering factor is constant for a given angle of diffraction.

1.3.2 THE TEMPERATURE FACTOR.

Atoms in crystals vibrate at ordinary temperatures with frequencies much lower than those of x-rays. Thus the electron density of any given atom will not be spherically symmetrical around the centre of the atom, but will be 'smeared' in some way. This has the effect of modifying the atomic scattering factor of the atom. Therefore, atoms which should scatter in phase, will scatter slightly out of phase; this introduces further phase differences, resulting in a reduction in intensity.

It is a very complex matter to make an accurate allowance for thermal motion.

Approximate allowance can be made by using the factor

$$f = fo \exp \left(-B \sin^2 \theta / \lambda^2 \right)$$

In this expression, θ is the Bragg angle, fo is the atomic scattering factor for atoms at rest, and B, the Debye temperature factor, is a constant.

This constant, B, is related to the mean square displacement $\bar{u}^2$, of the atoms from their mean positions; the relationship is

$$B = 8\pi^2 \bar{u}^2$$

The use of the above expression for the scattering factor implies that all atoms vibrate with equal amplitudes. This is not strictly true, and in general every crystallographically independent atom in a unit cell will have different thermal vibrations, since this depends on the surroundings of the atom, as well as on its inertia. Another assumption implied by the above expression is that the thermal vibrations are equal in all directions of the crystal. This is not necessarily true, and in many molecules the vibrations are markedly anisotropic. In the anisotropic case, the vibrations of an atom are described in such a way that the mean square amplitude of vibration in the direction of a unit vector $\underset{\sim}{l} = (l_1, l_2, l_3)$ is

$$\bar{u}^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j$$

<u>or</u>

$$\bar{u}^2 = U_{11} l_1^2 + U_{22} l_2^2 + U_{33} l_3^2$$
$$+ 2U_{23} l_2 l_3 + 2U_{31} l_3 l_1 + 2U_{12} l_1 l_2$$

(since $U_{23} = U_{32}$, etc.)

U and l are here defined with respect to the reciprocal axes a^*, b^*, c^*, so that the component of U in the (1,0,0) direction parallel to a^* is

$$\bar{u}^2 = U_{11}$$

1.4 THE RELATION BETWEEN INTENSITY AND STRUCTURE AMPLITUDE.

The total energy reflected by the volume dV in the course of a single pass of the crystal through the region of the Bragg reflection is given by

$$I = \left(\frac{I_o \lambda^3 N^2 dV}{\omega} \right) . \left(\frac{e^4}{m^2 c^4} \right) . L.p.|F|^2 \quad \text{where}$$

Io= the intensity of the incident radiation.

λ= the wavelength of the x-radiation.

N = the number of unit cells per unit volume.

dV= the volume of the crystal.

ω = the angular velocity of the crystal.

e = the charge on the electron.

m = the mass of the electron.

c = the velocity of light.

L = the "Lorentz" factor.

p = the polarisation factor.

I = the factor representing the resultant scattered by a single unit cell.

This expression should hold only for minute crystals, but it is found that it is applicable to many comparatively large crystals, the crystal in fact behaving like a mosaic of small blocks.

The Lorentz factor is a measure of the varying times crystal planes spend in the reflecting position, and varies with the type of photograph. For equatorial reflections on a normal rotation photograph it is $1/\sin 2\theta$. Expressions for equi-inclination Weissenberg photographs have been given by Tunell (1939).

In the above expression the factor p is the polarisation factor; in all the usual experimental arrangements, the x-ray beam is unpolarised, and this has the effect of reducing the intensity of the x-ray beam by the factor p, which is equal to $\frac{1 + \cos^2 2\theta}{2}$

In addition to these factors of simple geometrical origin for which allowance must be made in the conversion of intensities to structure amplitudes, there are some further factors which can arise in a less simple fashion, that is, absorption and extinction.

X-rays are absorbed by matter. For crystals completely bathed in the x-ray beam, it is possible to calculate absorption corrections, but the calculations are laborious and time consuming. Small crystals are generally used, in order to eliminate absorption as much as possible. Further corrections may be applied to account for primary and secondary extinction.

1.5 THE STRUCTURE FACTOR EXPRESSION.

The crystal lattice described so far is one in which atoms of finite size are located with their mean positions at lattice points. Most crystals, however, are much more complicated than this; a certain arrangement of atoms exists within each unit cell. We may regard any one set of corresponding atoms in the different unit cells as lying upon a lattice, and thus a crystal with N atoms in the unit cell can be regarded as based upon N congruent interpenetrating lattices, each of which will obey the Laue and Bragg conditions, but the different lattices will be, in general, out of phase. The intensities of the scattered rays will thus depend upon the atomic arrangement within the unit cell.

The position of the jth atom situated at the point (x_j, y_j, z_j), where x_j, y_j, and z_j are fractions of the unit cell vectors, can be represented by the vector $\underline{r}_j$, where

$$\underline{r}_j = x_j\underline{a} + y_j\underline{b} + z_j\underline{c} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

The path difference between the waves scattered by these atoms, and those that would be scattered by a set of atoms at the points of the lattice that define the origins of the unit cells is $\lambda \underline{r}_j.\underline{R}$. Thus the expression for the complete wave scattered by the jth lattice contains a term $f_j \exp 2\pi i \, \underline{r}_j.\underline{R}$, where f_j is the scattering factor of the jth atom.

Thus the expression for the complete wave scattered by the crystal is the summation over such terms.

$$F = \sum_{j=1}^{N} f_j \exp 2\pi i \, \underline{r}_j.\underline{R}$$

Substituting the value of $\underline{r}_j$ from (1), we have

$$F = \sum_{j=1}^{N} f_j \exp 2\pi i \, (x_j\underline{a}.\underline{R}+y_j\underline{b}.\underline{R}+z_j\underline{c}.\underline{R})$$

$$= \sum_{j=1}^{N} f_j \exp 2\pi i \, (hx_j + ky_j + lz_j)$$

The quantity F is a function of h, k, and l, and is called the <u>structure factor</u>. F is a complex quantity, which can be represented by a modulus, $|F(hkl)|$, known as the structure amplitude, and a phase constant, $\alpha(hkl)$.

The structure factor can be evaluated by means of the expression

$$|F(hkl)| = \sqrt{A^2 + B^2}$$

$$\alpha(hkl) = \tan^{-1} B/A$$

where $A = \sum_{j=1}^{N} f_j \cos 2\pi(hx_j + ky_j + lz_j)$

and $B = \sum_{j=1}^{N} f_j \sin 2\pi(hx_j + ky_j + lz_j)$

This is valid for all crystals, whatever their symmetry, but whenever there is a centre of symmetry at the origin, there is no need to calculate the sine terms, since in aggregate they must add up to zero. The resultant therefore can be obtained by summing the cosine terms only, and the possible phase angles are thus limited to 0 or π, depending upon whether the expression for A is positive or negative.

If $\rho(xyz)$ is the electron density at the point (x,y,z), the amount of scattering material in the volume element dxdydz is ρ.dxdydz. For the general case, where the crystal axes, a, b, and c, are inclined at any angles, the number of electrons in the volume element will be $\rho(xyz).V/abc.dxdydz$, where V is the volume of the unit cell.

The structure factor equation becomes

$$F(hkl) = V/abc \int_0^a\int_0^b\int_0^c \rho(xyz) \ \exp\ 2\pi i\ (h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c}).dxdydz.$$

1.6 FOURIER SERIES.

A periodic function can be represented by an appropriate sum of cosine and sine terms known as a Fourier series. Since a crystal is periodic in three dimensions, its electron density can be neatly represented by such a series in the form

$$\rho(xyz) = \sum\sum_{-\infty}^{\infty}\sum A(pqr)\ \exp\ 2\pi i(px/a+qy/b+rz/c)$$

where p, q, and r are integers, and A(pqr) is the Fourier coefficient of the general form.

In order to evaluate this series and thus obtain the electron density at any point in the crystal, it is necessary to calculate the coefficient A(pqr). This series for $\rho(xyz)$ is substituted in the general expression for the structure factor, giving

$$F(hkl) = V/abc \int_0^a\int_0^b\int_0^c \sum\sum_{-\infty}^{\infty}\sum A(pqr)\exp 2\pi i(px/a+qy/b+rz/c)\ \exp 2\pi i(hx/a+ky/b+lz/c)dxdydz$$

On integrating, every term is zero, except that for which $p = -h$, $q = -k$, and $r = -l$, which gives

$$F(hkl) = V/abc \int_0^a \int_0^b \int_0^c A(\bar{h}\bar{k}\bar{l})\, dx\, dy\, dz = VA(\bar{h}\bar{k}\bar{l})$$

Therefore, $A(\bar{h}\bar{k}\bar{l}) = F(hkl)/V$

In other words, the Fourier coefficient, A, is directly related to the corresponding structure factor. The electron density, ρ, is given by

$$\rho(xyz) = \sum\sum\sum_{h,k,l=-\infty}^{\infty} \frac{F(hkl)}{V} \exp -2\pi i(hx/a+ky/b+lz/c).$$

The zero term of the series is a constant, and is given by

$$F(000) = V/abc \int_0^a \int_0^b \int_0^c \rho(xyz)\, dx\, dy\, dz$$

$$= Z$$ (the sum of the electrons in the unit cell)

The Fourier series above can be more conveniently written

$$\rho(xyz) = \sum\sum\sum_{-\infty}^{\infty} \frac{|F(hkl)|}{V} \cos\left[2\pi hx/a+2\pi ky/b+2\pi lz/c - \alpha(hkl)\right]$$

where $\alpha(hkl)$ is the phase angle associated with each structure factor.

1.7 THE PHASE PROBLEM AND METHODS OF SOLUTION.

It has been shown that the electron density of a crystal can be obtained from structure factors. The structure factor, F(hkl) can be portrayed as a complex number characterised by a structure amplitude $|F(hkl)|$, and a phase angle, $\alpha(hkl)$. The values of the structure amplitudes can be derived from the observed intensities, but no experimental means exist for recording the phases. This constitutes the phase problem.

1.7.1 THE TRIAL AND ERROR METHOD.

To solve a crystal structure by this method, it is necessary to postulate an atomic arrangement that conforms with the space group symmetry, and to find what structure amplitudes this arrangement would give; these calculated amplitudes must then be compared with the observed values. If these amplitudes agree with each other, then the postulate is correct, but violent disagreements indicate that the postulation is wrong. This procedure is continued until the correct result is obtained.

The trial structures are arrived at by various methods. Use is made of any symmetry considerations, distribution of x-ray intensities, experience gained from other similar crystals, and so on. This method could require many calculations before the correct result is obtained. A method of circumventing these calculations is to make use of the Fourier Transform of a set of atoms. Holes representing the atomic positions in projection of the proposed structure and the atom type are punched on a mask. The diffraction pattern in parallel light represents the required Fourier Transform, and this can be compared with the corresponding weighted reciprocal lattice. In this way possible structures can be quickly tested, and the number of possibilities reduced to a manageable quantity.

1.7.2 THE PATTERSON MAP.

The vector representation of a crystal structure was developed by Patterson in 1934 and 1935. In this approach, the unknown phases of the structure factors are temporarily ignored. Instead of using the structure factors, the squares of the structure amplitudes are used as coefficients; these are directly related to the observed intensities.

The Patterson function can be expressed as

$$A(uvw) = \frac{1}{V}\int_0^1\int_0^1\int_0^1 \rho(xyz).\rho(x+u,\ y+v,\ z+w)dxdydz$$

In this expression, $\rho(x+u,\ y+v,\ z+w)$ represents the distribution of scattering matter about the point (xyz) expressed in terms of u, v, and w. It is similar to $\rho(xyz)$ but displaced from the point (xyz) by a vector whose components are u, v, and w respectively. V is the volume of the unit cell.

If the two functions $\rho(xyz)$ and $\rho(x+u,\ y+v,\ z+w)$ are expanded by expressing them in terms of the corresponding Fourier series we have

$$A(uvw) = 1/V^2\sum_{-\infty}^{\infty}\sum\sum|F(hkl)|^2\exp 2\pi i(hu+kv+lw).$$

Since the Patterson function is centrosymmetrical, this equation simplifies to

$$A(uvw) = 1/V^2\sum_{-\infty}^{\infty}\sum\sum|F(hkl)|^2 \cos 2\pi(hu+kv+lw).$$

A(uvw) will only be large when both the electron density distributions are large, and this is the situation which arises if an atom is situated at both (xyz) and (x+u, y+v, z+w).

Consequently, every pair of atoms in the unit cell will give rise to a "peak" in the Patterson map, and the function thus shows a superposition of all the interatomic vectors.

This would appear to be the solution of the phase problem; however, the number of interatomic vectors obtained even for a very small structure may be quite considerable, and for large structures, the number becomes very large indeed, and the vector map becomes correspondingly complex, resulting in overlap of peaks. It can easily be shown that, for a structure containing N atoms in the unit cell, there will be N peaks superimposed at the origin, and a further N(N-1)/2 peaks in the Patterson function. The chance of so many peaks being resolved is very slim indeed.

There are certain special sections, known as Harker sections (1936), which may be useful in solving the Patterson distribution. Provided the crystal has certain elements of symmetry, then specific vector peaks may arise on definite line or plane sections through the unit cell.

For example, in the space group $P2_12_12_1$, special vectors arise on the planes (u, v, $\frac{1}{2}$), (u, $\frac{1}{2}$, w) and ($\frac{1}{2}$, v, w). Thus, a full three dimensional computation may not be necessary.

1.7.3 THE HEAVY ATOM METHOD.

The "height" of the peaks on the Patterson map is proportional to the product of the atomic numbers of the two atoms involved in each peak. Therefore, if the crystal contains a relatively small number of atoms with a high atomic number, the height of the peaks produced by interatomic vectors between these atoms will be large, and the peaks will "stand out" against a background of smaller overlapping peaks, produced by interatomic vectors between the lighter atoms. If the heavy atom positions are simply related because of the symmetry of the crystal, it now becomes a relatively easy task to evaluate the coordinates of these atoms.

From the coordinates of the heavy atoms, it is possible to calculate phase angles for each reflection. Since the contribution of the heavy atoms to the phases outweigh the contribution of the lighter atoms then these phase angles (α_H) will be close approximations to the correct phase angles for the molecule as a whole.

It is now possible to compute a Fourier summation, using the observed values of the structure amplitudes, and the heavy atom phase angles. Sim (1957, 1961) has shown that it is possible to predict what percentage of the structure factors have almost correct phase angles based on the heavy atom phase angles alone. This percentage is dependent on r, where

$$\underline{r}^2 = (\sum f_H^{\ 2})/(\sum f^2_{\ L})$$

When r is equal to 1, for example, then in the centrosymmetrical case, about 80% of the phase angles have been correctly determined, while in the non-centrosymmetrical case, 38% of the phase angles lie within ± 20° of the correct phase angle and this becomes 67% when r increases to 2.

From the Fourier synthesis carried out using the heavy atom phases, it should be possible to "pick out" some or all of the features of the structure. New phase angles can now be calculated, and these should be a closer approximation to the correct phase angles. These new phase angles are now used in the calculation of another Fourier summation. This process is repeated until the structure analysis is complete.

The determination of the structures of the phthalocyanines (Robertson, 1935, 1936, Robertson and Woodward, 1937 and 1940) present classical examples of the power of the heavy atom method.

However, there are drawbacks to this method. Since most of the structure amplitudes are derived from the heavy atom contribution, the remainder of the molecule, the part which usually is the most interesting, must be derived from the smaller fraction of the structure amplitudes. Addition of a heavy atom to a structure may also lead to high absorption errors, which can also reduce the accuracy of the data.

1.7.4 THE ISOMORPHOUS REPLACEMENT METHOD.

These drawbacks to the heavy atom method can be overcome if two different heavy atoms can be substituted successively in the molecule without altering the overall crystal structure. In this case, it is not necessary for the contribution of the heavy atom to outweigh the contribution of the rest of the molecule. This method of phase determination was first extensively applied to organic structures in the case of the phthalocyanines (Robertson, 1935 and 1936).

This method is most easily applicable to centrosymmetrical crystals, although it is possible to use it in non-centrosymmetrical cases. Two isomorphous derivatives of the type (A+B) and (A+C) are prepared, so that only part of the structures are different. B and C are usually heavy atoms, whose positions can be found by application of Patterson syntheses in the normal manner. The observed values of the structure amplitudes must be placed on the same absolute scale. Assuming exact isomorphism, we have

$$F(A+B) = F(A) + F(B)$$

$$F(A+C) = F(A) + F(C)$$

Structure factors F(B) and F(C) can be calculated. Therefore, by comparing the differences in F(B) and F(C) with the differences in F(A+B) and F(A+C), it becomes possible to assign phases to both F(A+B) and F(A+C).

In the non-centrosymmetrical case it is possible to assign phases to the various derivatives by using a graphical method, and by making use of three isomorphous derivatives.

1.7.5 INEQUALITIES.

This method of overcoming the phase problem makes use of relationships between structure factors, and was first discovered by Harker and Kasper, (1948). It is convenient in examining these relationships to make use of the 'Unitary Structure Factor', U(h), which is defined by

$$U(h) = F(h)/\sum_{j=1}^{N} f_j$$

Thus, U(h) gives the structure factor as a fraction of its possible value.

To derive the inequalities of Harker and Kasper, use is made of Cauchy's inequality, which states that

$$\left|\sum_{j=1}^{N} a_j b_j\right|^2 \leqslant \left(\sum_{j=1}^{N} |a_j|^2\right)\left(\sum_{j=1}^{N} |b_j|^2\right)$$

where a_j and b_j are any real or complex numbers. By application of this inequality relationship to the unitary structure factor, the result shown below is obtained.

$$|U(h)|^2 \leqslant 1.$$

This applies to the most general case where the crystal has no symmetry, and merely defines the unitary structure factor.

When there is a centre of symmetry present, the unitary structure factor may be written

$$U(h) = \sum_{1}^{N} n_j \cos 2\pi(hx_j/a+ky_j/b+lz_j/c)$$

where n_j is simply the fraction of the total electrons present in any particular atom 'j'. Application of Cauchy's inequality to this expression gives

$$|U(h)|^2 \leqslant \tfrac{1}{2} + \tfrac{1}{2}U(2h)$$

where U(h) is U(hkl), and U(2h) is U(2h, 2k, 2l).

These relationships can be used to derive phase information. For example, suppose that a value for a particular reflection U(h) is measured. If this value turns out to be greater than $\frac{1}{2}$ then the inequality is only satisfied if U(2h) is positive. A large number of other inequalities can be derived, and thus direct phase determination can be accomplished.

1.8 METHODS OF REFINEMENT.

Once a structure has been completely determined, an effort is generally made to obtain the best possible agreement between the observed and calculated structure amplitudes, and at the same time improve the phase angles. In order to do this, it is necessary to make adjustments to the positional and thermal parameters already obtained for the structure. This process is known as refinement.

1.8.1 FOURIER METHODS.

The simplest method of refinement is that of successive Fourier syntheses. An electron density map is calculated, and from this new map improved coordinates for the atoms may be calculated. These new coordinates are now used to calculate a cycle of structure factors, and the structure factors obtained are used to calculate another Fourier map. This process can be repeated many times if necessary.

The true electron density is represented by an infinite series, while, in practice, the number of terms which are included in such a summation is limited in number, this being mainly due to the wavelength of the incident radiation.

This results in diffraction ripples surrounding true peaks on the Fourier map, and causes the peaks to be displaced from their correct positions. This is called the termination of series error.

A method of overcoming this difficulty was suggested by Booth (1946). Two Fourier series using the same terms are computed, one using observed structure amplitudes as coefficients (Fo), and the other using calculated structure amplitudes as coefficients (Fc). Both these Fourier syntheses will be subject to series termination errors, and both will have the atomic coordinates shifted by some distance from their true positions. However, in the case of the Fc Fourier synthesis, specific coordinates have been inserted into it, and the same coordinates should be deduced from it. On account of the series termination errors, these two sets of coordinates will be found to differ, and if the difference between them is subtracted from the coordinates obtained in the case of the Fo Fourier synthesis, approximately the correct atomic coordinates should be obtained. This correction is known as a "back-shift" correction.

A second way in which Fourier syntheses may be used for refinement is the "difference synthesis". This approach, which uses (Fo-Fc) as Fourier coefficients, was first suggested by Booth (1948a), and has been discussed by Cochran (1951). If a proposed structure is correct in every way, then a flat featureless map is produced with only slight undulations caused by random errors in the original data. If the structure is not correct, then large undulations will appear. If the known atomic positions are superimposed on the map, then the direction in which they must be moved in order to attain their true position is that of the steepest contour ascent. Errors in temperature factors are also indicated by large positive or negative peaks at an atomic site, and the temperature factor can be adjusted to compensate for this.

1.8.2 THE METHOD OF LEAST SQUARES.

When the structure parameters differ by small amounts from their true values, it is possible systematically to vary the parameters in such a way that the discrepancy between the observed and calculated structure factors is minimised. This method of refinement, first introduced by Hughes in 1941, is known as the "least squares" refinement of atomic parameters.

The function which is minimised is

$$R = \sum_{q} w.(hkl)(\ |Fo(hkl)| - |Fc(hkl)|\ )^2 ....(1)$$

where 'q' is the number of independent observations. 'w' is the weighting factor for each term, and is used because the |Fo| values of each term cannot be determined with the same accuracy. Various weighting schemes have been developed, all of which attempt to make 'w' inversely proportional to the variance of |Fo| . When the value of R is close to a minimum, then the above function is minimised in the following way.

Let p_1, p_2,........, p_n be the $\underline{n}$ parameters on which |Fc| is dependent. These may be coordinates, thermal parameters or scale factors. Then, for R to be a minimum, we must have

$$\partial R/\partial p_j = 0 \quad (j = 1,\ 2,\ ......,n).......(2)$$

$$\text{i.e. } \sum_{q} w.(hkl).\Delta.\ \partial|Fc|/\partial p_j = 0.............(3)$$

where $\Delta = |Fo| - |Fc|$.

For a set of p_j close to the correct values, Δ may be expanded as a function of the parameters

$$\Delta(\underline{p} + \underline{e}) = \Delta(\underline{p}) - \sum_{i=1}^{n} e_i \partial|Fc|/\partial p_i .....(4)$$

where $\underline{e}$ is the error which, when added to the parameters, gives the correct value.

Substituting equation (4) in equation (3), we have

$$\sum_{i=1}^{n} \left\{ \sum_{hkl} w\partial|Fc|/\partial p_i . \partial|Fc|/\partial p_j \right\} e_i = \sum_{hkl} w.\Delta.\partial|Fc|/\partial p_j$$

for $j = 1, \ldots\ldots n$.

i.e. $\sum_{i=1}^{n} a_{ij}.e_i = b_j$

where $a_{ij} = \sum_{hkl} w\partial|Fc|/\partial p_i . \partial|Fc|/\partial p_j$

and $b_j = \sum_{hkl} w.\Delta.\partial|Fc|/\partial p_j$.

These <u>n</u> equations are known as the "normal equations", and it is these normal equations which must be solved in order to refine a structure. Successive applications of this procedure lead to the best possible atomic coordinates and thermal parameters for the structure, compatible with the accuracy of the original data. The main advantage which the least squares procedure has over the Fourier method of refinement is that it is free from series termination errors.

1.9 ACCURACY OF X-RAY STRUCTURE ANALYSIS.

The process of refinement is the attempt to make the calculated structure amplitudes approach as closely as possible to the observed structure amplitudes. It is therefore convenient to have some means by which the measure of agreement between $|Fo|$ and $|Fc|$ can be indicated. Such an expression is known as the agreement index, and is obtained from

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

Thus during the process of structure analysis and the early stages of refinement, the value of R should always be decreasing.

When the final atomic coordinates of a molecular structure have been attained, then their accuracy can be assessed by calculating standard deviations (σ). If the standard deviation is small, then the position of the atom has been determined accurately. The standard deviations can be derived from the least squares residuals by application of the equation

$$\sigma^2(U_j) = \sum w.\Delta^2. \; / \; (m-n)\sum w(\partial\Delta/\partial U_j)^2$$

where m is the number of independent observations and n is the number of parameters to be determined.

Having obtained the best possible atomic coordinates, the normal procedure is to calculate various molecular parameters, such as bond lengths and angles, using standard trigonometric formulae. Measurements obtained for these parameters will almost inevitably deviate from standard accepted values, and it is now essential to discover whether any differences from standard values are due to experimental error, or whether they are significant.

The standard deviation of a bond length between two atoms is given by the equation

$$\sigma^2(AB) = (\sigma^2(A) + \sigma^2(B))$$

where $\sigma(A)$ and $\sigma(B)$ are the standard deviations of the positions of atoms A and B.

The standard deviation of the angle (β) in radians for an angle formed at B between the bonds AB and BC is given by (Cruickshank, 1953).

$$\sigma^2(\beta) = \frac{\sigma^2(A)}{AB^2} + \sigma^2(B)\left[\frac{1}{AB^2} - \frac{2\cos\beta}{AB.BC} + \frac{1}{BC^2}\right] + \frac{\sigma^2(C)}{BC^2}$$

Any errors which occur may be expected to be random, and therefore may be expected to show a normal Gaussian distribution.

The probability, P, that any observed difference from the expected value of the bond length or angle is due to chance only is given in terms of σ by

$P = 5\%$ $\Delta = 1.645\sigma$
$P = 1\%$ $\Delta = 2.327\sigma$
$P = 0.1\%$ $\Delta = 3.090\sigma$

That is a difference of 3σ and over may be taken as being significant (Cruickshank, 1949).

A final method of checking on the accuracy of a structure is to calculate series of planes through atoms which might be expected to be planar. The significance of deviations from a plane calculated in this way is assessed by application of the χ^2 test (Fisher and Yates, 1957). In this, the value of χ^2 is found from the expression $\chi^2 = \sum\Delta^2/\sigma^2$ where Δ is the deviation in Å of an atom from the calculated plane, and σ is the mean standard deviation in Å of the atomic positions. By calculating χ^2 from the above equation, the probability that no atom deviates significantly from the calculated plane can be found. If the probability is less than 1%, then it is likely that one or more of the atoms included in the mean plane calculation does deviate from the plane.

PART 2.

THE STRUCTURE OF α-CARYOPHYLLENE ALCOHOL:

X-RAY ANALYSIS OF α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

2.1 INTRODUCTION.

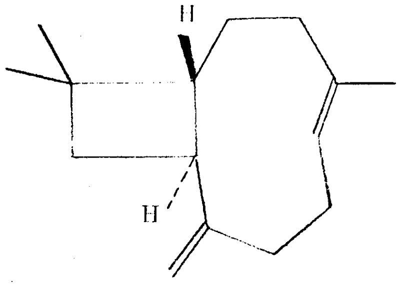
The emergence of the name α-caryophyllene alcohol was due to the original work in 1922 by the Japanese workers, Asahina and Tsukamoto on the sulphuric acid treatment of caryophyllene (1), which is the major sesquiterpene constituent of oil of cloves. From this reaction, three rearrangement products were isolated; these were, the unsaturated hydrocarbon, clovene (2), and the two isomeric alcohols, which they designated α-caryophyllene alcohol and β-caryophyllene alcohol (3). α-caryophyllene alcohol is the minor product of this rearrangement of caryophyllene yielding about 4% of the total reaction product.

Not until 1930 did Bell and Henderson attempt to carry out a more systematic investigation of the chemistry of α-caryophyllene alcohol. They found that on dehydration, α-caryophyllene alcohol yielded an unsaturated hydrocarbon. Investigation of the properties of this hydrocarbon led these workers to the conclusion that it was clovene.

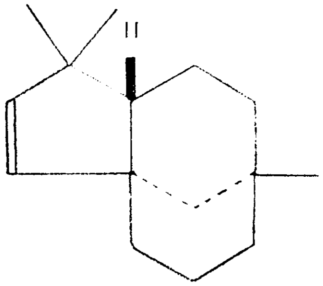
When the structure of clovene had been firmly established, it was possible, on the basis of the results of Bell and Henderson, to postulate either structures (4) or (5) for α-caryophyllene alcohol. In 1954, however, in the course of work on caryophyllene, Barton and Nickon prepared the clovan-2-ol (4), and it was found that this compound was not identical with α-caryophyllene alcohol. Structure (5) could also be rejected.

In 1951, Dev reported that the sesquiterpene humulene (6), which is biogenetically related to caryophyllene, under identical conditions of rearrangement gave a crystalline, tricyclic, fully saturated alcohol, apparently identical with α-caryophyllene alcohol.

Roberts (1965) found by gas-liquid chromatography that commercial caryophyllene contained about 10% humulene. He therefore subjected pure samples of caryophyllene and humulene to treatment with concentrated sulphuric acid in ether. Isolation of the rearrangement products from each reaction showed that humulene yielded α-caryophyllene alcohol, whereas no trace was observed in the case of caryophyllene.



(1)



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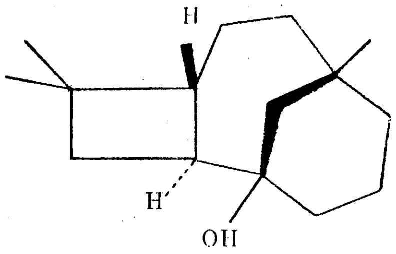

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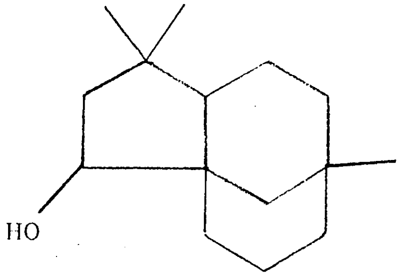
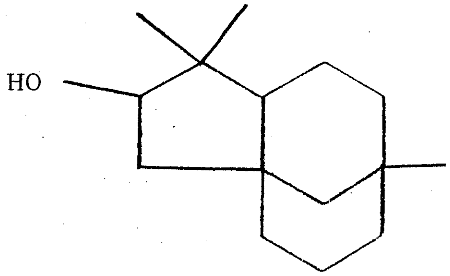
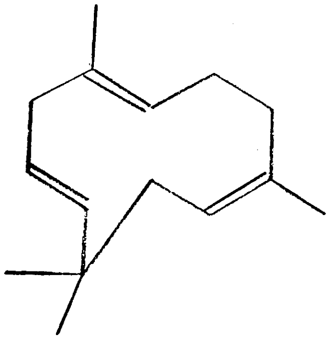


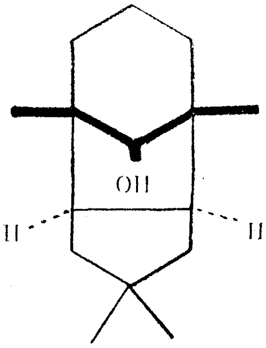
(4)



(5)



(6)



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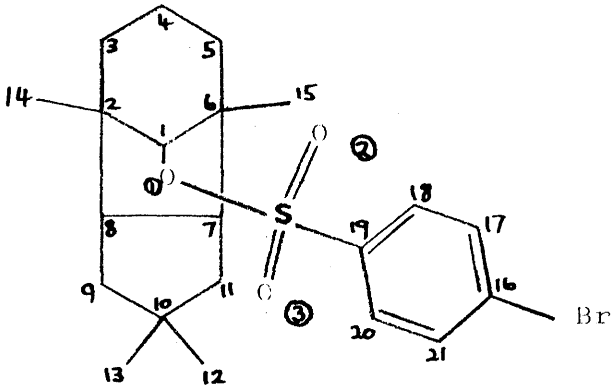


(8)

Hence, the structure of α-caryophyllene alcohol has to be explained in terms of a molecular rearrangement of humulene, and not caryophyllene, as previously assumed.

What has been detailed up to now was the sum total of the reported work on α-caryophyllene alcohol, when the x-ray analysis of the para-bromo benzene sulphonate derivative (8) was undertaken.

The results of the x-ray investigation established the constitution and stereochemistry (7) for α-caryophyllene alcohol. Classical degradative procedures allowed Nickon et.al. (1964) to arrive almost simultaneously at an identical result.

2.2 EXPERIMENTAL.

α-caryophyllene alcohol para-bromo benzene sulphonate has molecular formula $C_{21}H_{29}O_3S\ Br$. The molecular weight is 441.4, and the crystal melts sharply at 147-148°C.

Rotation, oscillation, Weissenberg, and precession photographs were taken with copper K-α (λ=1.542 Å) and molybdenum K-α (λ= 0.7107 Å) radiation. The cell dimensions were determined from rotation and precession photographs and from these the following values were obtained;

$a = 12.65 \pm 0.05$ Å

$b = 10.82 \pm 0.03$ Å

$c = 16.43 \pm 0.04$ Å

$\beta = 109^\circ\ 13'$

The volume of the unit cell was calculated using the expression

$$V = abc \sin\beta$$

and was found to be 2124 Å^3.

Inspection of the Weissenberg photographs showed that the absent spectra are h0l when l is odd, and 0k0 when k is odd. Consequently, the space group is uniquely determined to be $P2_1/c$.

The density is 1.40 g/ml., and consequently the number of molecules in the unit cell, given by

$$n = d\,V/1.66\,M$$

is four. This number of molecules leads to a calculated density of 1.38 g/ml.

The calculated linear absorption coefficient for copper K-α radiation is 39.2 cm^{-1}. The total number of electrons per unit cell, F(000), is 900. The value obtained for "$\sum f^2$" for the 'heavy' bromine atom is 1225, while that obtained for "$\sum f^2$" for the 'light' atoms is 1233. Hence, the value of r, which can be found from the expression

$$\underline{r}^2 = "\sum f_H^2"/"\sum f_L^2"$$

was found to be 0.99.

Intensity data, which were recorded using small crystals, completely bathed in a uniform x-ray beam, were obtained from equatorial and equi-inclination upper layer Weissenberg photographs, taken from crystals rotated about the needle axis (b-crystal axis); in this way, the reciprocal lattice nets h0l, ...,h8l were recorded. The multiple film technique (Robertson, 1943) was employed.

The intensities were estimated visually by comparison with a calibrated intensity strip, and were corrected for Lorentz, polarisation and rotation factors appropriate to the upper layers (Tunell, 1939). Thus, this procedure leads to a set of $|F|$ values on a relative scale. In all the total number of independent observed structure amplitudes was 2021.

Since small crystals were used, no corrections for absorption were applied. Various layers were placed on the same absolute scale by comparison of the observed and calculated structure amplitudes obtained from the Patterson function. Throughout the refinement, the scale was adjusted by correlation with the observed and calculated structure amplitudes, to ensure that $\sum|Fo| = \sum|Fc|$.

2.3 STRUCTURE DETERMINATION AND REFINEMENT.

The equivalent positions of the space group $P2_1/c$ are

$x, \quad y, \quad z;$

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

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

$-x, \quad -y, \quad -z.$

The vectors to be expected between bromine atoms with one molecule in the asymmetric unit are

$-2x_{Br}, \quad -2y_{Br}, \quad -2z_{Br};$

$-2x_{Br}, \quad \frac{1}{2}, \quad \frac{1}{2}-2z_{Br};$

$0, \quad \frac{1}{2}-2y_{Br}, \quad \frac{1}{2}.$

In addition, the vectors expected between bromine and sulphur atoms are

$x_S-x_{Br}, \quad y_S-y_{Br}, \quad z_S-z_{Br};$

$x_S-x_{Br}, \frac{1}{2}+y_S+y_{Br}, \frac{1}{2}+z_S-z_{Br};$

$x_S+x_{Br}, \frac{1}{2}+y_S-y_{Br}, \frac{1}{2}+z_S+z_{Br};$

$x_S+x_{Br}, \quad y_S+y_{Br}, \quad z_S+z_{Br}.$

By examination of the Harker sections at $(U,\frac{1}{2},W)$ and $(0,V,\frac{1}{2})$ it was possible to determine the coordinates of the bromine atom.

It was also possible, by making use of the coordinates already obtained for the bromine atom, and also the interatomic vectors detailed on page 43, to determine the coordinates of the sulphur atom. The Harker section at $V=\frac{1}{2}$ is shown in fig. 1. The peak marked A on this map was chosen as representing the bromine-bromine vector. The coordinates of the bromine and sulphur atoms were confirmed by consultation of the appropriate sections of the three dimensional Patterson function.

Since the bromine and sulphur atoms were known to be para-related across the benzene ring, it was possible, using standard values for valency bond lengths and trigonometric formulae, to calculate approximate coordinates for the two carbon atoms directly bonded to the heavy atoms. Therefore, the atomic coordinates determine from the three dimensional Patterson function were

	x/a	y/b	z/c
C(16)	0.18250	0.17382	0.09875
C(19)	0.40000	0.15464	0.21250
S(1)	0.53975	0.14181	0.28980
Br(1)	0.03723	0.18637	0.02537

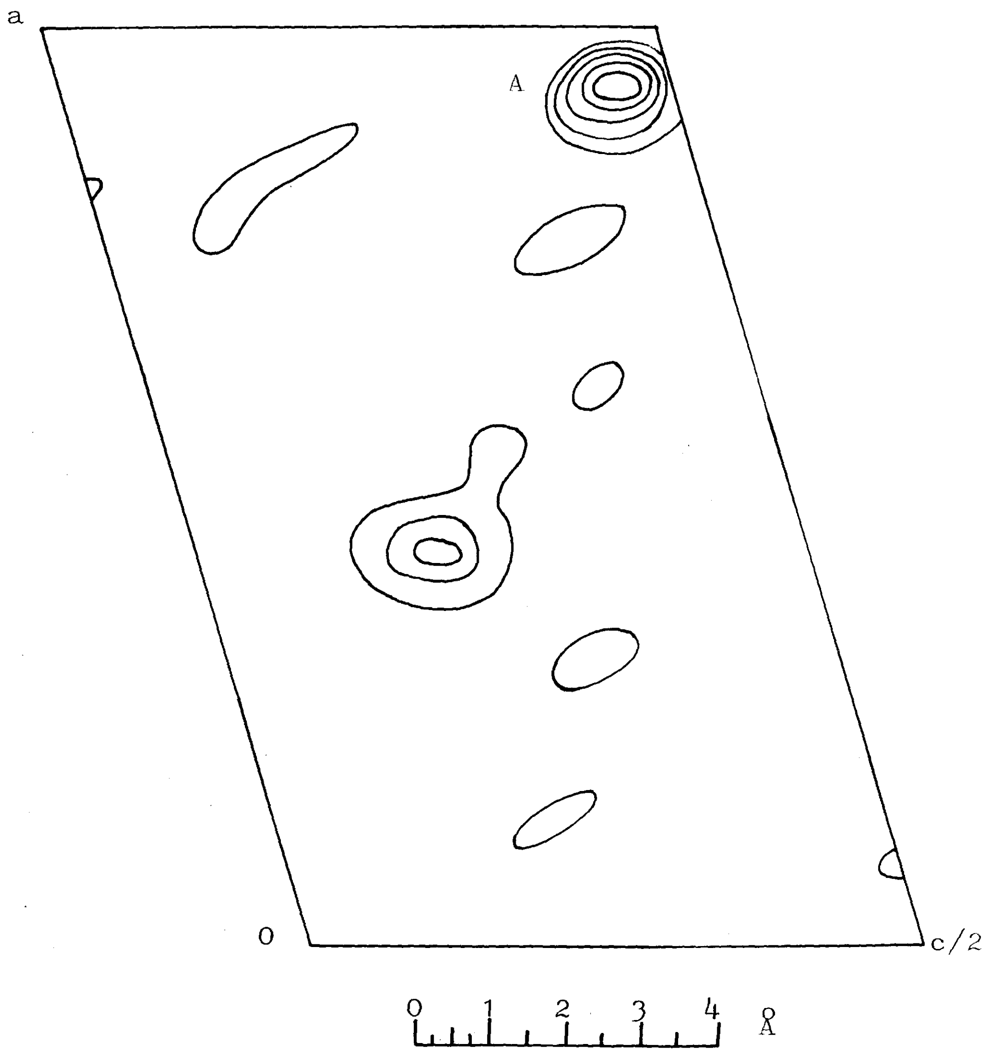


Fig. 1. The Harker Section at $V = \frac{1}{2}$.

Structure factors were calculated using these coordinates, employing isotropic temperature factors of $U = 0.05$ Å^2 (where $U = \bar{u}^2$, the mean square amplitude of vibration). This led to an agreement index, R, of 46.0%, over all observed structure amplitudes. The criterion adopted for selecting structure factors whose phases were approximately correct was to reject all those for which $|Fo| > 2|Fc|$. Thus, of the 2021 independent structure amplitudes, 1794 (or approximately 88%) were deemed to have been safely sign determined in the structure factor calculation.

From the first three dimensional Fourier calculation, it was possible to distinguish all the atoms in the structure. C(12), C(14), and C(15) were poorly resolved, and it was therefore decided to exclude them from the second structure factor and phasing calculations. Since the nature of all the atoms was clearly defined, twenty-three light atoms were included as their appropriate chemical type in the evaluation of a second set of structure factors. The isotropic temperature factors employed were once again $U = 0.05$ Å^2, and this led to an overall agreement index, R, of 34.4%; i.e. an overall decrease in R of 11.4% or 0.5% per extra atom included.

1839 of these reflections were regarded as safely sign determined, and were used in the computation of a new Fourier synthesis.

This three dimensional Fourier synthesis showed all the atoms (with the exception of hydrogens) clearly resolved. Including all the atoms as their appropriate chemical type, and once again employing an overall isotropic temperature factor of $U = 0.05\ \text{Å}^2$, a further set of structure factors was calculated, and this led to an agreement index of 26.3%. The subsequent electron density distribution was calculated using the observed structure amplitudes and the improved phase constants. Corrections for series termination errors were applied to the atomic coordinates by calculating "back-shift" corrections from a three dimensional $|Fc|$ Fourier synthesis computed using the same phase constants (Booth, 1946). By comparison of the peak heights of both these Fourier syntheses, adjustments were made to the individual isotropic thermal parameters. Refinement of the coordinates and the isotropic thermal parameters was continued by this method for another two cycles, and resulted in a reduction of the agreement index to 22.6%.

Anisotropic temperature factors were calculated and refinement of these parameters and the atomic coordinates was continued by the method of least squares. After four cycles, the $|Fo|$ values were rescaled, and a further one cycle of least squares terminated the refinement at R = 12.6%. A diagrammatic representation of the course of the analysis is provided in Table 1.

Theoretical atomic scattering factors were employed for the structure factor calculations; those of Berghuis et.al. (1955) for carbon, oxygen, and sulphur, and the Thomas-Fermi (1935) values for bromine. The weighting scheme used in the least squares refinement was

if $|Fo| \leqslant 16.00$ $\sqrt{w}(hkl) = 1$

if $|Fo| > 16.00$ $\sqrt{w}(hkl) = 16.00/|Fo(hkl)|$.

TABLE 1

COURSE OF THE ANALYSIS

OPERATION	ATOMS INCLUDED	R(%)
3D Patterson synthesis	-	-
1st 3D Fourier synthesis	Br + S + 2(C)	46.0
2nd 3D " "	Br + S + 18(C) + 3(O)	34.4
3rd 3D " "	Br + S + 21(C) + 3(O)	26.3
4th 3D " "	"	23.1
5th 3D " "	"	22.4
1st Least Squares Cycle	"	18.7
2nd " "	"	15.7
3rd " "	"	14.8
4th " "	"	14.0
|Fo| Values Rescaled	"	12.8
5th Least Squares Cycle	"	12.6

2.4 RESULTS OF THE ANALYSIS.

The final atomic coordinates for one molecule are listed in Table 3. The final anisotropic temperature factors given by the least squares refinement are listed in Table 4. These are the individual values of U_{ij} which are given by the equation

$$q(hkl) = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{31}lhc^*a^* + 2U_{23}klb^*c^* + 2U_{12}hka^*b^*)\right]$$

The standard deviations of the atomic coordinates, which are listed in Table 5, were calculated from the least squares residuals as explained in section 1.9.

Table 6 lists the interatomic bond lengths, while the interbond angles are given in Table 7.

Some of the more important intramolecular non-bonded contacts are given in Table 8, while the shorter intermolecular contacts, that is, those contacts less than or equal to four Angstroms, are listed in Table 9. In Table 10, deviations of individual atoms from a series of best planes through the various ring systems are listed.

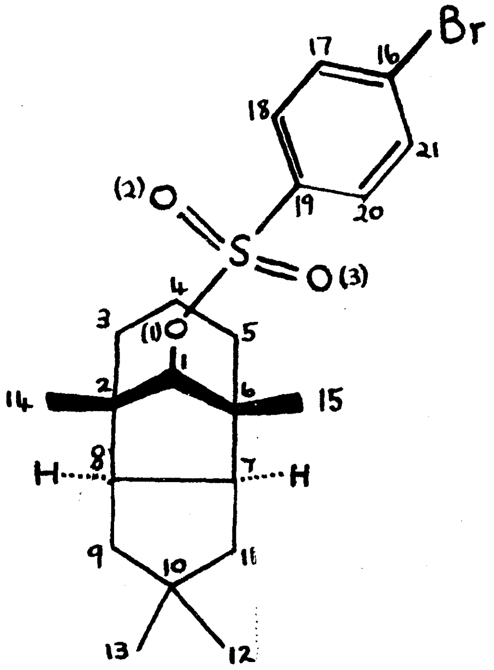
Table 11 lists the observed and calculated structure factors, which are obtained from the final least squares cycle. The final agreement index over 2021 observed structure amplitudes is 12.6%. No unobserved structure amplitudes are included in this table.

The final three dimensional electron density distribution over one molecule was calculated from the observed structure amplitudes and phase constants obtained from the last least squares cycle. This is shown in fig. 2 by means of superimposed contour sections drawn parallel to (001). The atomic arrangement corresponding to this is shown in fig.3 and the packing of the molecules in the crystal as viewed along the b-axis is illustrated in fig. 4.

Using the formulae given in section 1.9, the standard deviations for the bond lengths and the bond angles can be calculated. The average estimated standard deviation for a carbon-carbon single bond is 0.02 Å, and for a typical tetrahedral angle it is 1°.

2.5 DISCUSSION OF RESULTS.

The constitution and relative stereochemistry of the para-bromo benzene sulphonate derivative of α-caryophyllene alcohol as determined by this analysis are shown in (9). As already stated (section 2.1), Nickon et.al (1964) have derived the constitution and stereochemistry of the alcohol alone by classical degradative procedures, a result which has been confirmed by an unambiguous synthesis of the alcohol carried out by Corey and Nozoe (1964).



The molecular parameters obtained are not very accurate. This could be due to several reasons. The presence of both a bromine and a sulphur atom in the molecule means that absorption effects may be quite high, thus cutting down the accuracy of the atomic coordinates. The presence of the two heavy atoms also impedes the refinement of the coordinates and temperature factors of the light atoms, since these light atoms make a smaller contribution to each structure factor.

The average carbon-carbon bond length in the benzene ring is 1.39 Å and this is in excellent agreement with the accepted distance of 1.396 Å for benzene. The average sp^3-carbon-sp^3-carbon single bond distance is 1.55 Å, in good agreement with the standard value of 1.545 Å for diamond.

The length of the sp^3-carbon-oxygen single bond is 1.48 Å. This is in agreement with values of 1.46 Å for 5-bromo griseofulvin (Brown and Sim, 1963), 1.47 Å for bromogeigerin acetate (Hamilton, McPhail and Sim, 1962), 1.47 Å for bromodihydroisophotosantonic lactone (Asher, 1963), and 1.47 Å in L-serine phosphate (McCallum, Robertson and Sim, 1959).

Using Pauling's (1960) covalent bond radii and electronegativity data, the reference value for such a bond is 1.43 Å. Experimental values close to this have been found; for example, 1.427 Å for methanol (Venkateswarlu and Gordy, 1955), and Swallen (1955), and also 1.425 Å for DL-serine (Shoemaker, Barieau, Donohue, and Chia-Si Lu, 1953).

The length of the aromatic carbon-bromine bond is 1.87 Å. In International Tables for X-Ray Crystallography, Volume III (1962), this bond length is quoted as 1.85 Å, but values considerably higher than this have been found, and the generally accepted figure is about 1.90 Å. In morellin para-bromo benzene sulphonate (Kartha, 1963), the value found was 1.92 Å, in β -1:2 - 4:5 - tetrabromo benzene (Gafner and Herbstein, 1960) the length found was 1.90 Å, and Brown (1964) found a bond length of 1.87 Å in the analysis of 1-p-bromo benzene sulphonyl-oxymethyl-5-methyl bicyclo (3,3,1) nonan-9-ol. Since the position of C(16), being bonded directly to the bromine atom, is inaccurate due to diffraction effects of the bromine, this bond length is, in any case, a difficult one to assess.

The aromatic carbon-sulphur bond length is 1.73 Å, which is in close agreement with the value of 1.74 Å in zinc para-toluene sulphonate hexahydrate (Hargreaves, 1957), and 1.72 Å found by Brown (1964). It is rather shorter than the value of 1.765 Å found by Sime and Abrahams (1960) in 4,4' dichloro diphenyl sulphone, and the value of 1.76 Å given by Kartha (1964).

The mean sulphur to oxygen double bond distance is 1.45 Å and the sulphur to oxygen single bond distance is 1.58 Å. This is in good agreement with the values of 1.46 Å and 1.60 Å respectively which were found by Truter (1958) in potassium ethyl sulphate. The theoretical length for a sulphur-oxygen single bond is 1.69 Å, and therefore a contraction of about 0.1 Å has taken place. This can be explained by the formation of partial double bond character in the formal single bond between the oxygen and sulphur atoms. These two atoms have different electronegativities, since the sulphur atom can form π bonds using its d-orbitals.

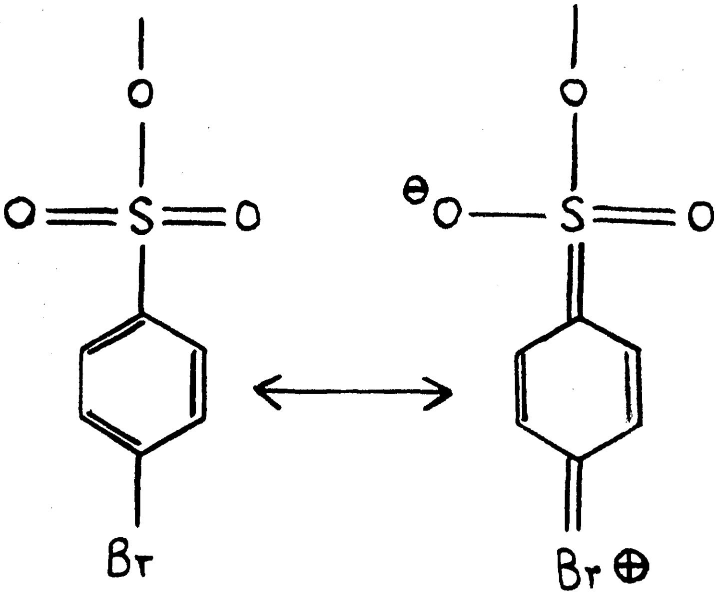
Cruickshank (1961) has shown that the π bond order of the sulphur-oxygen single bond in potassium ethyl sulphate is 0.25.

This should give a bond length of about 1.58 Å-1.60 Å. In addition to this, in the case of potassium ethyl sulphate, the other three sulphur-oxygen bond distances should contract from the double bond value of 1.49 Å to 1.46 Å since the other π bonding orbital of sulphur is shared with only three of the four oxygens, giving these bonds an order of 0.25 + 0.33 = 0.58. He suggests an empirical rule that the average sulphur-oxygen bond length in the sulphate and related groups is 1.49 Å, but that any sulphur-oxygen bonds which involve a linkage of oxygen to another atom may lengthen by amounts up to 0.15 Å with a corresponding contraction of the other sulphur-oxygen bonds in order that the average might be preserved.

In the case of α-caryophyllene alcohol p-bromo benzene sulphonate, the average bond length is 1.49 Å, and individual bonds are expanded to 1.58 Å and contracted to 1.45 Å in accordance with this theory.

Since the S(1)-C(19) and the Br(1)-C(16) bonds have lengths which are slightly shorter than the accepted standard values, it is perhaps possible that some sort of quinonoid electronic structure might be present in the para-bromo benzene sulphonate part of the molecule.

This perhaps suggests resonance of the form:-



Since the bond distance between the sulphur and bromine atoms has the smallest estimated standard deviation (less than 0.01 Å), this was considered to be the safest to examine in pursuing this theory. The calculated value for this distance is 6.44 Å based on standard valency bond lengths. If some sort of quinonoid structure does exist, then the experimental value for the sulphur to bromine distance should be significantly less than 6.44 Å. This bond distance was found to be 6.36 Å -- a contraction of 0.08 Å.

There is no sign of this phenomenon in the results of Kartha (1963), but Brown (1964) obtained a contraction of 0.13 Å. It also appears to be present to a lesser extent in the molecule of 4,4'-dichloro-diphenyl sulphone (Sime and Abrahams, 1960).

The average internal valency bond angle in the six-membered ring system C(1), C(2), C(3), C(4), C(5) and C(6) is 109.9°. This is in good agreement with the expected value of 109°28' for the tetrahedral angle. The average interbond angle in the benzene ring is 120.0°, which is in excellent agreement the expected value (Tables of Interatomic Distances, 1958). The average valency bond angle in the five-membered ring system C(1), C(2), C(6), C(7) and C(8) is 103.1°, and in the ring system C(7), C(8), C(9), C(10) and C(11) it is 104.0°. Both these values are significantly less than tetrahedral, but the average bond angle in five-membered rings is frequently found to be less than 109°. Some of these angles are depicted in Table 2.

These values indicate that the ring systems are non-planar, with consequent bond angle deformation. This is indeed what has happened in the case of α-caryophyllene alcohol, and the non-planarity of these rings is discussed later in this section.

TABLE 2.

NAME OF COMPOUND.	AUTHOR.	ANGLE.
Epilimonol Iodoacetate	Arnott et.al.	104°
Isoclovene Hydrobromide	Clunie et.al.	105°
Bromogeigerin Acetate	Hamilton et.al.	106°
Clerodin Bromolactone	Paul et.al.	106°
Methanol solvate of Echitamine Bromide	Hamilton et.al.	106°
Himbacine Hydrobromide	Fridrichsons and Mathieson	105°

The C(1)-C(6)-C(7) bond angle of 99.5° is significantly less than the other valency bond angles in this ring system. This effect, namely that of a five-membered ring with a small average bond angle and having one angle significantly less than the others, has been observed by Miller (1966) in 9-α-bromocortisol acetate, which contains a five-membered ring whose average bond angle is 103°, but which has one angle of 98°. It has also been observed by Macaulay (1966) in the 17-β-iodo acetoxy derivative of 3-keto-4,4 dimethyl androstane, for which the mean value is 104° and the small angle is 97°. It is difficult to account for this, but in the case of both these compounds, and also in the case of α-caryophyllene alcohol, the small angle occurs at a carbon which is fully substituted by other carbon atoms.

Both the C(6)-C(7)-C(11) bond angle of 117.6° and the C(2)-C(8)-C(9) bond angle of 116.7° are significantly greater than tetrahedral. This perhaps indicates that there is some repulsion between the gem-dimethyl group and the "bridgehead" atoms, that is to say C(1) and O(1), with the result that one half of the molecule is "bending away" from the other half.

The six-membered ring is in the expected "chair" conformation. The equation of the best plane through the atoms C(2), C(3), C(5) and C(6), calculated using the method of Schomaker et.al.(1959) is

$$0.7840\ x + 0.3591\ y - 0.5064\ z - 5.8845 = 0$$

The individual deviations of these atoms from the plane are listed in Table 10; no deviation is significant.

The equation of the best plane through the six carbon atoms of the benzene ring is

$$0.6346\ x + 0.2210\ y - 0.7406\ z - 0.3717 = 0$$

Application of the χ^2 test (Fisher and Yates, 1957) indicates that there are no significant deviations from this plane, and that these six atoms are coplanar.

The individual deviations are again listed in Table 10. The deviations of the sulphur and bromine atoms from this plane, although very small, are never the less significant.

In the five-membered ring made up by C(1), C(2), C(6), C(7) and C(8), the last four atoms are found to be coplanar, whereas C(1) is found to deviate from the plane by 0.7 Å. The equation of the best plane through these four atoms is

$$0.5133\ x - 0.7668\ y - 0.3854\ z - 1.5810 = 0$$

The deviations of these four atoms from the plane, and also the deviations of C(1), C(14) and C(15) are once again listed in Table 10.

In the other five-membered ring, this effect is also apparent. C(7), C(8), C(9), and C(11) were found to lie on a plane, while C(10) was found to deviate from this plane by 0.65 Å. The equation of the best plane through these atoms is

$$0.8234\ x + 0.1075\ y - 0.5572\ z - 6.8233 = 0$$

The individual displacements of all the atoms from this plane are again listed in Table 10. The two atoms of the gem-dimethyl group are found to deviate by quite a considerable extent from this plane, in particular C(12), which was found to lie 2.22 Å away.

The dihedral angle between the plane of the six-membered ring and the plane of the first five-membered ring is 71.2° and the dihedral angle between the planes of the two five-membered rings is 123.7°. The molecule thus adopts a "zig-zag" conformation.

As mentioned earlier in this section, the fact that the two five-membered rings are non-planar may be used to explain why the bond angles are so much less than tetrahedral.

Examination of the non-bonded intramolecular distances offers further proof that there is some non-bonded interaction between the "bridgehead" atoms, and the gem-dimethyl group, with consequent distortion of the molecule. If a Dreiding model of the molecule is constructed, it can be seen that the five-membered ring containing the gem-dimethyl group ought to be almost coplanar, and the other five-membered ring only slightly distorted. Measurement of the distance apart of C(1) and C(12) shows that these two atoms should be 3.7 Å apart, but this in fact is found to have lengthened to 5.0 Å, and measurement of the distance apart of C(4) and C(12) shows that these atoms should be 6.0 Å apart, but in fact they are found to be only 5.3 Å apart.

When the Dreiding model is adjusted to give these distances, considerable strain and distortion immediately becomes apparent. Slight increases and decreases in other non-bonded distances to compensate for this distortion can also be seen.

The arrangement of α-caryophyllene alcohol molecules as viewed along the b - axis is shown in fig. 4. In the crystal, the molecules are held together by Van der Waals' forces. None of the intermolecular contacts listed in Table 9 are significantly shorter than the sum of the Van der Waals' radii of the atoms involved.

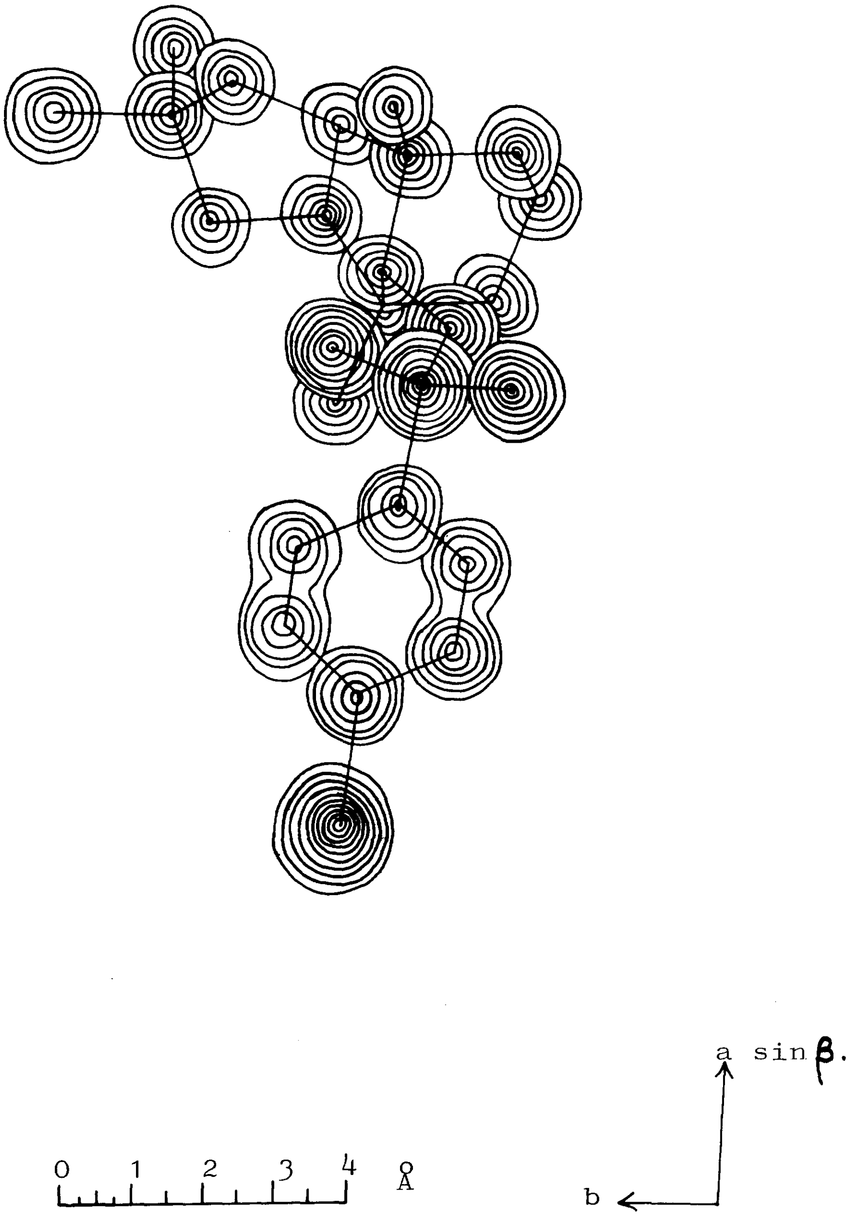


Fig. 2. The final three dimensional electron density distribution over one molecule of α-caryophyllene alcohol p-bromo benzene sulphonate. The superimposed contour sections are drawn parallel to (001).

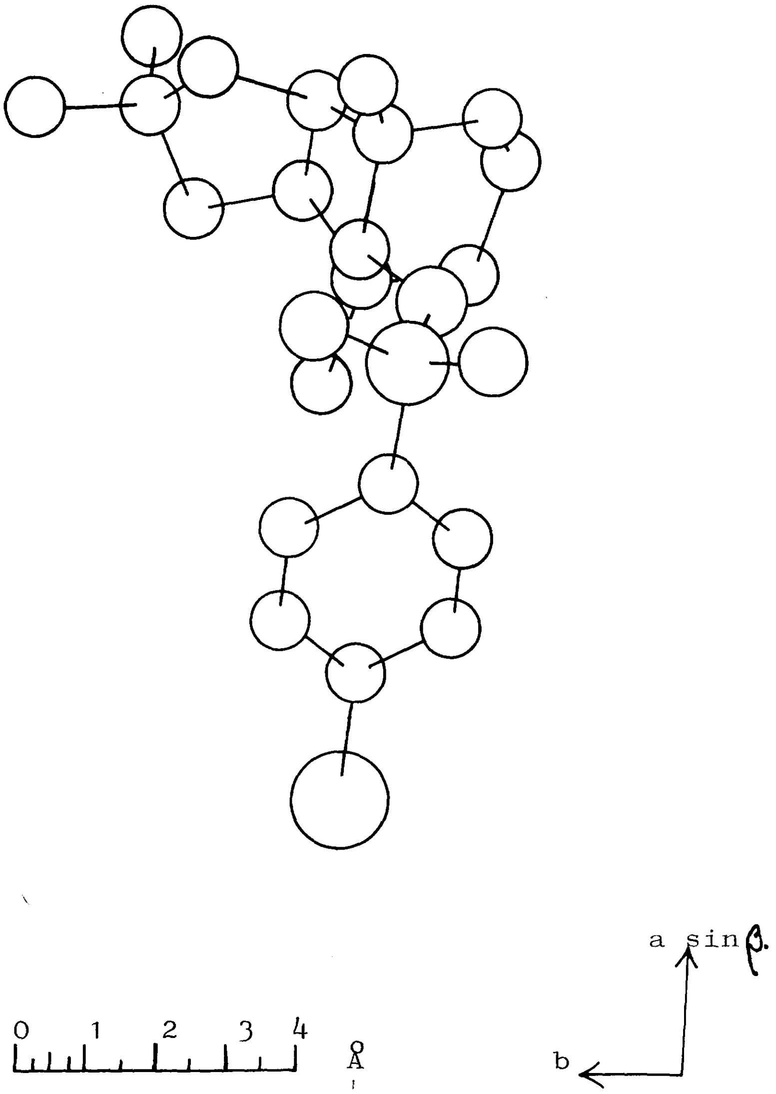


Fig. 3. The atomic arrangement corresponding to Fig. 2.

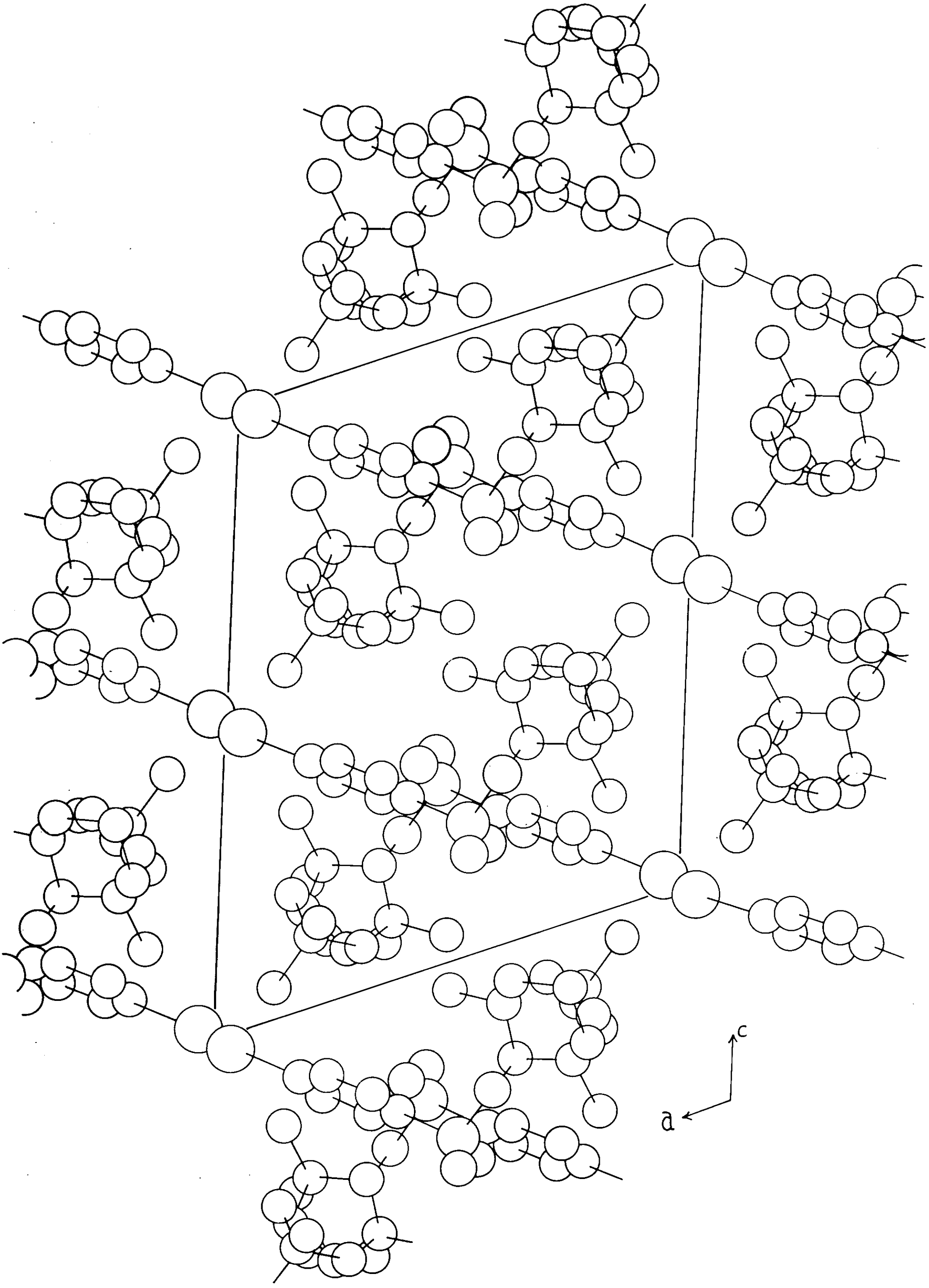


Fig. 4. The arrangement of the molecules in the crystal as viewed along the b-axis.

TABLE 3.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

FINAL ATOMIC COORDINATES.

ATOM.	x/a	y/b	z/c
C(1)	0.6616	0.2114	0.1903
C(2)	0.7860	0.1931	0.2197
C(3)	0.8141	0.0585	0.2000
C(4)	0.7682	0.0281	0.1010
C(5)	0.6433	0.0708	0.0635
C(6)	0.6255	0.2021	0.0915
C(7)	0.7160	0.2919	0.0744
C(8)	0.8229	0.2853	0.1588
C(9)	0.8473	0.4178	0.1899
C(10)	0.7976	0.4951	0.1081
C(11)	0.6887	0.4320	0.0651
C(12)	0.8768	0.4880	0.0499
C(13)	0.7838	0.6365	0.1287
C(14)	0.8439	0.2165	0.3167
C(15)	0.5060	0.2440	0.0445
C(16)	0.1861	0.1728	0.1019
C(17)	0.2406	0.0599	0.1143

TABLE 3 (Cont.).

ATOM.	x/a	y/b	z/c
C(18)	0.3488	0.0511	0.1719
C(19)	0.4025	0.1530	0.2149
C(20)	0.3440	0.2698	0.2037
C(21)	0.2368	0.2960	0.1474
O(1)	0.6064	0.1127	0.2242
O(2)	0.5450	0.0292	0.3355
O(3)	0.5733	0.2584	0.3293
S(1)	0.5375	0.1418	0.2862
Br(1)	0.0406	0.1821	0.0236

TABLE 4.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

FINAL ANISOTROPIC TEMPERATURE FACTORS. (Å^2)

ATOM.	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	0.0478	0.0394	0.0414	0.0179	0.0333	-0.0151
C(2)	0.0469	0.0581	0.0489	0.0240	0.0311	0.0126
C(3)	0.0740	0.0696	0.0764	0.0132	0.0233	0.0500
C(4)	0.0674	0.0840	0.0751	-0.0285	0.0628	0.0152
C(5)	0.0718	0.0524	0.0632	-0.0264	0.0560	0.0043
C(6)	0.0390	0.0550	0.0391	-0.0284	0.0338	-0.0132
C(7)	0.0412	0.0646	0.0407	0.0117	0.0411	-0.0017
C(8)	0.0458	0.0619	0.0511	-0.0055	0.0376	-0.0180
C(9)	0.0673	0.0553	0.0688	-0.0191	0.0453	-0.0403
C(10)	0.0649	0.0658	0.0711	0.0056	0.0747	-0.0100
C(11)	0.0642	0.0395	0.0684	0.0116	0.0430	0.0041
C(12)	0.0957	0.0773	0.0934	-0.0116	0.1298	-0.0202
C(13)	0.1176	0.0382	0.1372	-0.0377	0.1382	-0.0299
C(14)	0.0639	0.1025	0.0454	0.0154	-0.0004	0.0021
C(15)	0.0323	0.0800	0.0502	0.0037	-0.0036	-0.0038
C(16)	0.0541	0.0558	0.0723	0.0048	0.0648	0.0073
C(17)	0.0773	0.0515	0.0648	-0.0118	0.0780	-0.0213

TABLE 4 (Cont.).

ATOM.	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(18)	0.0739	0.0529	0.0680	-0.0065	0.0820	-0.0053
C(19)	0.0672	0.0375	0.0547	0.0140	0.0556	-0.0114
C(20)	0.0851	0.0586	0.0553	0.0108	0.0547	-0.0061
C(21)	0.0701	0.0556	0.0690	0.0193	0.0578	0.0207
O(1)	0.0608	0.0361	0.0616	-0.0037	0.0653	-0.0046
O(2)	0.0835	0.0574	0.0626	0.0381	0.0572	0.0067
O(3)	0.0768	0.0590	0.0617	-0.0224	0.0643	-0.0165
S(1)	0.0624	0.0470	0.0442	0.0037	0.0517	-0.0079
Br(1)	0.0611	0.0914	0.1071	0.0078	0.0381	0.0091

TABLE 5.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

STANDARD DEVIATIONS OF FINAL ATOMIC COORDINATES (Å).

ATOM.	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0.011	0.011	0.011
C(2)	0.013	0.013	0.013
C(3)	0.016	0.016	0.016
C(4)	0.015	0.016	0.016
C(5)	0.015	0.014	0.014
C(6)	0.011	0.012	0.011
C(7)	0.011	0.012	0.011
C(8)	0.012	0.013	0.012
C(9)	0.015	0.014	0.015
C(10)	0.014	0.014	0.014
C(11)	0.014	0.013	0.014
C(12)	0.017	0.016	0.017
C(13)	0.020	0.015	0.022
C(14)	0.015	0.017	0.014
C(15)	0.011	0.015	0.013
C(16)	0.013	0.013	0.015
C(17)	0.015	0.014	0.014

TABLE 5 (Cont.).

ATOM.	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(18)	0.015	0.014	0.014
C(19)	0.013	0.012	0.013
C(20)	0.015	0.015	0.014
C(21)	0.015	0.014	0.015
O(1)	0.008	0.008	0.008
O(2)	0.010	0.009	0.009
O(3)	0.009	0.009	0.009
S(1)	0.003	0.003	0.003
Br(1)	0.002	0.002	0.002

TABLE 6.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

BOND LENGTHS (Å)

C(1)	-	C(2)	1.50	C(10)	-	C(11)	1.49
C(1)	-	C(6)	1.54	C(10)	-	C(12)	1.60
C(1)	-	O(1)	1.48	C(10)	-	C(13)	1.59
C(2)	-	C(3)	1.56	C(16)	-	C(17)	1.39
C(2)	-	C(8)	1.59	C(16)	-	C(21)	1.38
C(2)	-	C(14)	1.54	C(16)	-	Br(1)	1.87
C(3)	-	C(4)	1.57	C(17)	-	C(18)	1.39
C(4)	-	C(5)	1.56	C(18)	-	C(19)	1.36
C(5)	-	C(6)	1.53	C(19)	-	C(20)	1.45
C(6)	-	C(7)	1.60	C(19)	-	S(1)	1.73
C(6)	-	C(15)	1.52	C(20)	-	C(21)	1.37
C(7)	-	C(8)	1.59	O(1)	-	S(1)	1.58
C(7)	-	C(11)	1.55	O(2)	-	S(1)	1.45
C(8)	-	C(9)	1.52	O(3)	-	S(1)	1.44
C(9)	-	C(10)	1.53				

TABLE 7.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

BOND ANGLES (°).

C(2) -C(1) -C(6)	104.3	C(6) -C(7) -C(8)	105.8
C(2) -C(1) -O(1)	111.0	C(6) -C(7) -C(11)	117.6
C(6) -C(1) -O(1)	109.7	C(8) -C(7) -C(11)	103.1
C(1) -C(2) -C(3)	110.1	C(2) -C(8) -C(7)	103.7
C(1) -C(2) -C(8)	102.1	C(2) -C(8) -C(9)	116.8
C(1) -C(2) -C(14)	113.8	C(7) -C(8) -C(9)	105.8
C(3) -C(2) -C(8)	108.8	C(8) -C(9) -C(10)	103.9
C(3) -C(2) -C(14)	107.8	C(9) -C(10)-C(11)	102.3
C(8) -C(2) -C(14)	114.2	C(9) -C(10)-C(12)	110.0
C(2) -C(3) -C(4)	112.3	C(9) -C(10)-C(13)	112.4
C(3) -C(4) -C(5)	109.1	C(11)-C(10)-C(12)	111.0
C(4) -C(5) -C(6)	112.6	C(11)-C(10)-C(13)	113.1
C(1) -C(6) -C(5)	110.8	C(12)-C(10)-C(13)	108.0
C(1) -C(6) -C(7)	99.5	C(7) -C(11)-C(10)	105.1
C(1) -C(6) -C(15)	114.6	C(17)-C(16)-C(21)	120.9
C(5) -C(6) -C(7)	109.1	C(17)-C(16)-Br(1)	120.5
C(5) -C(6) -C(15)	110.1	C(21)-C(16)-Br(1)	118.6
C(7) -C(6) -C(15)	112.3	C(16)-C(17)-C(18)	119.5

TABLE 7 (Cont.).

C(17)-C(18)-C(19)	120.6	C(19)-S(1) -O(1)	102.1
C(18)-C(19)-C(20)	119.6	C(19)-S(1) -O(2)	107.8
C(18)-C(19)-S(1)	120.4	C(19)-S(1) -O(3)	110.6
C(20)-C(19)-S(1)	119.9	O(1) -S(1) -O(2)	104.2
C(19)-C(20)-C(21)	118.7	O(1) -S(1) -O(3)	109.9
C(16)-C(21)-C(20)	120.5	O(2) -S(1) -O(3)	120.6
C(1) -O(1) -S(1)	121.9		

TABLE 8.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

SOME INTRAMOLECULAR NON-BONDED DISTANCES (Å)

C(1)......C(3)	2.51	C(5)......C(15)	2.50
C(1)......C(4)	3.03	C(6)......C(8)	2.54
C(1)......C(5)	2.53	C(6)......O(1)	2.47
C(1)......C(14)	2.55	C(6)......S(1)	3.78
C(1)......C(15)	2.58	C(7)......C(9)	2.48
C(1)......C(19)	3.49	C(7)......C(10)	2.41
C(1)......S(1)	2.67	C(8)......C(10)	2.40
C(2)......C(5)	2.92	C(8)......C(11)	2.46
C(2)......C(6)	2.40	C(9)......C(11)	2.35
C(2)......C(7)	2.50	C(9)......C(12)	2.57
C(2)......C(4)	2.60	C(9)......C(13)	2.59
C(2)......O(1)	2.46	C(11).....C(12)	2.55
C(3)......C(5)	2.55	C(11).....C(13)	2.57
C(3)......C(6)	2.91	C(12).....C(13)	2.58
C(3)......C(14)	2.50	C(16).....C(19)	2.76
C(4)......C(6)	2.58	C(17).....C(20)	2.79
C(4)......C(14)	3.92	C(17).....Br(1)	2.81
C(4)......C(15)	3.91	C(18).....C(21)	2.78

TABLE 8 (Cont.).

C(18).....O(2)	3.01	C(20).....O(3)	2.96
C(18).....O(3)	3.87	C(20).....S(1)	2.75
C(18).....S(1)	2.69	C(21).....Br(1)	2.83
C(19).....O(1)	2.57	O(1)......O(2)	2.39
C(19).....O(2)	2.57	O(1)......O(3)	2.47
C(19).....O(3)	2.61	O(2)......O(3)	2.51
C(20).....O(2)	3.78	S(1)......Br(1)	6.36

TABLE 9.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

INTERMOLECULAR CONTACTS LESS THAN 4 Å.

C(20)......O(2)$_{\mathrm{III}}$	3.30	C(7).......O(3)$_{\mathrm{II}}$	3.87
C(18)......O(3)$_{\mathrm{V}}$	3.32	C(20)......O(1)$_{\mathrm{III}}$	3.88
C(4)......C(17)$_{\mathrm{I}}$	3.63	C(15)......O(3)$_{\mathrm{II}}$	3.90
C(11)......O(2)$_{\mathrm{II}}$	3.63	C(13)......C(20)$_{\mathrm{III}}$	3.90
C(14)......Br(1)$_{\mathrm{IV}}$	3.66	C(5)......C(17)$_{\mathrm{I}}$	3.94
C(15)......O(2)$_{\mathrm{III}}$	3.83	O(2)......O(3)$_{\mathrm{V}}$	3.95
C(21)......O(2)$_{\mathrm{III}}$	3.83	C(17)......O(3)$_{\mathrm{V}}$	3.95
C(5)......C(5)$_{\mathrm{I}}$	3.86	C(11)......O(2)$_{\mathrm{III}}$	3.96

The subscripts refer to the following positions:-

I	$1-x$,	$-y$,	$-z$;
II	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$;
III	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$;
IV	$1+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$;
V	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$.

TABLE 10.

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

DEVIATIONS FROM THE BEST PLANES THROUGH SETS OF ATOMS (Å).

(a). PLANE DEFINED BY C(2), C(3), C(5), AND C(6).

ATOM.	DEVIATION.	ATOM.	DEVIATION.
C(2)	0.003	C(1)	-0.804
C(3)	-0.002	C(4)	0.621
C(5)	0.002	C(14)	-0.506
C(6)	-0.003	C(15)	-0.456

(b). PLANE DEFINED BY C(2), C(6), C(7), AND C(8).

ATOM.	DEVIATION.	ATOM.	DEVIATION.
C(2)	-0.003	C(1)	-0.705
C(6)	0.003	C(14)	-0.671
C(7)	-0.005	C(15)	-0.710
C(8)	0.005		

TABLE 10 (Cont.).

(c). PLANE DEFINED BY C(7), C(8), C(9), AND C(11).

ATOM.	DEVIATION.	ATOM.	DEVIATION.
C(7)	0.000	C(10)	0.645
C(8)	-0.000	C(12)	2.224
C(9)	0.000	C(13)	0.395
C(11)	-0.000		

(d). PLANE DEFINED BY C(16),C(17),C(18),C(19),C(20),AND C(21).

ATOM.	DEVIATION.	ATOM.	DEVIATION.
C(16)	0.014	O(1)	1.420
C(17)	-0.002	O(2)	-0.933
C(18)	-0.014	O(3)	-0.066
C(19)	0.018	S(1)	0.011
C(20)	-0.005	Br(1)	0.038
C(21)	-0.011		

TABLE 11 (Overleaf).

α-CARYOPHYLLENE ALCOHOL p-BROMO BENZENE SULPHONATE.

THE OBSERVED AND CALCULATED STRUCTURE AMPLITUDES.

H	K	L	Fo	Fc
0	0	2	29.2	-30.3
0	0	4	46.2	38.4
0	0	6	47.9	50.7
0	0	8	58.0	-52.2
0	0	10	41.9	34.8
0	0	12	16.5	-20.0
0	0	14	9.7	4.5
0	0	16	16.7	-19.7
1	0	2	151.6	250.2
1	0	4	90.8	94.6
1	0	6	62.0	61.3
1	0	8	7.1	11.6
1	0	10	21.4	-17.8
1	0	12	9.3	-7.6
1	0	14	24.9	-23.9
1	0	16	8.9	9.6
1	0	-2	105.3	148.6
1	0	-4	36.6	-20.9
1	0	-6	28.6	34.5
1	0	-8	102.2	105.9
1	0	-10	14.2	13.2
1	0	-12	19.9	20.5
1	0	-14	27.7	-21.6
1	0	-16	9.4	8.7
1	0	-18	11.1	-14.6
2	0	0	20.1	5.3
2	0	2	74.1	89.9
2	0	4	21.5	26.5
2	0	6	60.7	56.3
2	0	10	12.2	-13.7
2	0	12	24.5	-24.9
2	0	-2	34.2	38.9
2	0	-4	196.6	336.7
2	0	-6	84.3	82.9
2	0	-14	11.7	11.0
2	0	-16	17.8	-15.9
2	0	-18	14.1	14.1
3	0	0	37.2	-15.3
3	0	2	31.0	42.7
3	0	4	61.3	83.8
3	0	6	58.7	-58.0
3	0	8	8.0	-9.9
3	0	10	16.4	-19.8
3	0	-2	158.9	213.8
3	0	-4	40.7	44.5
3	0	-6	71.7	78.4
3	0	-8	26.8	27.1
3	0	-10	19.8	14.5
3	0	-12	41.0	33.7
3	0	-14	16.6	12.9
3	0	-16	21.3	18.5
3	0	-18	11.8	-15.6
4	0	0	31.9	42.7
4	0	2	64.4	80.5
4	0	4	26.5	-25.4
4	0	6	10.6	-9.6
4	0	10	29.6	-36.2
4	0	12	30.4	-28.3
4	0	-2	77.1	69.2
4	0	-4	39.1	46.9
4	0	-6	22.9	27.6
4	0	-8	91.4	106.3
4	0	-10	66.3	55.3
4	0	-12	12.5	13.1
4	0	-14	15.1	15.4
4	0	-16	11.7	-11.0
5	0	0	102.3	88.4
5	0	2	122.1	-96.2
5	0	4	12.5	-10.0
5	0	6	46.5	-46.0
5	0	8	9.0	-7.0
5	0	10	9.6	-10.7
5	0	14	11.6	-10.5
5	0	-2	54.3	52.8
5	0	-4	21.4	-16.0
5	0	-6	89.8	103.0
5	0	-8	79.9	91.6
5	0	-10	59.1	63.6
5	0	-12	14.1	12.2
6	0	0	49.3	32.3
6	0	2	18.6	15.1
6	0	4	58.4	-60.2
6	0	6	8.8	-5.0
6	0	8	69.4	-60.1
6	0	12	18.0	-14.9
6	0	14	7.3	-5.4
6	0	-2	16.6	-14.9
6	0	-4	[illegible]	114.5
6	0	-6	58.6	49.8
6	0	-8	43.0	40.5
6	0	-10	18.6	[illegible]
6	0	-12	26.1	24.2
6	0	-16	17.8	14.6
7	0	0	71.0	[illegible]
7	0	2	49.3	-41.0
7	0	4	22.2	-20.2
7	0	6	33.8	-30.7
7	0	8	13.7	-12.1
7	0	10	27.0	-23.1
7	0	-2	15.3	8.5
7	0	-4	29.2	28.4
7	0	-6	84.1	83.8
7	0	-8	23.0	-20.1
7	0	-10	36.8	32.6
7	0	-12	33.8	29.0
7	0	-14	32.9	29.6
7	0	-16	11.5	10.6
8	0	0	43.1	-30.9
8	0	2	8.7	-7.9
8	0	4	52.8	-43.2
8	0	6	35.0	-29.3
8	0	8	24.6	-20.3
8	0	10	12.4	-12.2
8	0	12	15.8	-12.9
8	0	-4	49.0	40.4
8	0	-6	23.3	-22.3
8	0	-8	56.2	43.9
8	0	-10	18.0	11.5
8	0	-12	27.3	26.8
9	0	0	28.2	-20.3
9	0	2	68.8	-52.7
9	0	4	17.5	-14.0
9	0	6	32.8	-24.9
9	0	8	9.1	-7.7
9	0	10	12.3	-7.9
9	0	-2	22.4	-18.5
9	0	-4	56.9	-41.3
9	0	-6	33.7	29.9
9	0	-10	43.8	37.6
9	0	-14	11.7	10.4
9	0	-16	16.7	12.7
10	0	0	38.4	-36.2
10	0	2	24.8	-18.9
10	0	4	30.3	-25.6
10	0	6	26.4	-22.8
10	0	8	12.9	-11.9
10	0	10	6.3	-4.7
10	0	-2	9.3	-3.7
10	0	-6	43.3	-37.4
10	0	-8	38.2	35.9
10	0	-10	13.6	-14.0
10	0	-12	9.7	8.4
10	0	-14	24.1	19.8
11	0	0	21.5	-19.3
11	0	2	[illegible]	-20.3
11	0	4	19.5	-16.7
11	0	6	14.3	-12.4
11	0	8	9.5	-7.1
11	0	-2	55.2	-44.8
11	0	-4	27.7	-27.6
11	0	-8	11.8	-9.8
11	0	-10	18.1	16.5
11	0	-12	16.5	16.0
11	0	-14	9.0	9.1
12	0	0	32.0	-26.9
12	0	2	14.2	-15.9
12	0	4	21.0	-17.7
12	0	-2	27.6	-19.0
12	0	-4	17.5	-21.3
12	0	-6	9.6	5.5
12	0	-8	9.6	-8.4
12	0	-12	18.1	14.5
13	0	0	10.5	[illegible]
13	0	2	22.5	-22.8
13	0	4	9.4	-10.1
13	0	-2	23.1	-22.4
13	0	-4	6.5	-4.7
13	0	-6	20.5	-19.8
13	0	-8	15.8	-15.6
13	0	-10	10.8	8.2
13	0	-14	14.8	13.1
14	0	0	13.5	-13.6
14	0	-4	21.1	-19.6
14	0	-6	11.7	-9.2
14	0	-10	9.6	-7.1
15	0	-2	15.8	-20.1
15	0	-6	12.0	-12.4
16	0	-4	8.2	-10.6
0	1	2	113.2	-144.0
0	1	3	42.1	48.2
0	1	4	89.8	-94.4
0	1	5	6.5	11.9
0	1	6	90.1	-82.6
0	1	8	16.1	-23.7
0	1	9	23.1	27.2
0	1	10	34.5	-31.8
0	1	12	13.1	-16.0
0	1	13	10.6	-5.1
0	1	14	12.5	-12.5
0	1	16	8.3	-6.6
1	1	1	19.2	25.7
1	1	2	77.3	-87.2
1	1	3	43.7	-44.7
1	1	4	11.4	6.9
1	1	5	42.2	47.9
1	1	6	40.4	-55.2
1	1	7	9.5	12.7
1	1	8	83.8	-89.4
1	1	10	27.7	-31.8
1	1	12	8.5	-4.0
1	1	14	12.4	-11.0
1	1	-2	38.1	-27.4
1	1	-3	83.4	93.9
1	1	-4	11.4	9.5
1	1	-5	23.5	28.6
1	1	-6	28.8	27.7
1	1	-7	17.4	19.9
1	1	-9	22.5	24.2
1	1	-10	53.0	42.6
1	1	-12	38.3	30.0
1	1	-13	8.5	8.4
1	1	-14	25.3	21.4
1	1	-15	8.8	-8.8
1	1	-16	10.4	8.1
2	1	0	85.8	-102.1
2	1	1	30.2	-26.9
2	1	2	24.4	-17.9
2	1	3	46.0	51.6
2	1	4	92.9	-108.6
2	1	5	25.1	-23.8
2	1	6	10.6	-15.4
2	1	7	18.3	15.8
2	1	8	59.0	-67.2
2	1	9	12.9	-16.1
2	1	10	30.6	-29.5
2	1	11	8.3	-8.1
2	1	12	25.0	-24.2
2	1	-1	89.0	78.8
2	1	-2	132.5	-151.7
2	1	-3	103.4	117.2
2	1	-4	77.6	93.9
2	1	-5	38.7	30.0
2	1	-6	[illegible]	39.1
2	1	-7	33.3	34.3
2	1	-8	57.5	61.8
2	1	-10	24.0	31.7
2	1	-11	7.6	10.2
2	1	-12	20.8	24.4
2	1	-13	8.5	-2.9
2	1	-14	8.7	5.2
3	1	0	10.3	2.6
3	1	1	93.9	105.4
3	1	2	130.4	-138.0
3	1	3	28.6	-24.4
3	1	4	56.6	-59.8
3	1	5	27.5	28.3
3	1	6	66.4	-72.2
3	1	7	15.3	-19.0
3	1	8	9.0	-10.7
3	1	9	11.0	-10.3
3	1	10	11.7	-12.0
3	1	11	6.1	-7.0
3	1	12	13.9	-12.6
3	1	13	6.7	-6.9
3	1	-1	37.3	34.2
3	1	-2	41.2	-37.9
3	1	-3	23.6	-26.1
3	1	-4	83.9	-91.9
3	1	-5	82.8	82.9
3	1	-6	[illegible]	[illegible]
3	1	-7	34.8	32.7
3	1	-8	10.5	-11.1
3	1	-9	9.2	8.8
3	1	-10	18.2	18.9
3	1	-12	20.7	19.9
3	1	-13	11.9	10.2
3	1	-14	8.7	6.4
3	1	-15	8.8	-9.1
3	1	-16	13.7	11.6
4	1	0	125.9	-128.3
4	1	1	28.5	-25.4
4	1	2	8.3	-2.3
4	1	3	47.9	50.4
4	1	4	104.4	-113.8
4	1	5	30.1	-31.2
4	1	6	50.9	-57.5
4	1	7	9.0	-9.4
4	1	8	40.9	-43.4
4	1	10	10.5	-11.1
4	1	-1	80.2	61.2
4	1	-2	7.2	5.2
4	1	-3	39.9	30.6
4	1	-4	22.8	-26.7
4	1	-5	14.7	16.2
4	1	-6	84.9	-83.3
4	1	-7	78.6	71.7
4	1	-8	84.2	70.9
4	1	-11	9.3	11.6
4	1	-12	25.4	21.7
4	1	-13	24.3	-21.3
4	1	-15	13.9	14.7
4	1	-16	15.1	15.3
5	1	0	77.6	-73.4
5	1	1	76.2	65.4
5	1	2	103.2	-93.5
5	1	3	29.3	-26.0
5	1	6	39.1	-45.5
5	1	7	22.6	-24.5
5	1	10	22.6	-16.3
5	1	11	10.8	[illegible]
5	1	12	8.6	-6.3
5	1	-1	9.9	5.7
5	1	-2	81.7	-74.9
5	1	-3	32.7	32.2
5	1	-4	56.4	-48.0
5	1	-5	67.5	62.7
5	1	-6	27.4	-28.2
5	1	-7	52.7	-54.8
5	1	-8	55.7	-53.1
5	1	-9	36.2	35.9
5	1	-10	45.5	47.5
5	1	-12	8.1	-9.0
5	1	-13	19.0	14.6
5	1	-14	41.0	36.8
6	1	0	[illegible]	-102.9
6	1	1	33.3	-22.2
6	1	2	69.2	-68.4
6	1	3	6.9	7.5
6	1	4	34.1	-38.7
6	1	5	7.6	6.6
6	1	6	32.5	-35.2
6	1	8	12.2	-12.6
6	1	9	16.4	-18.9
6	1	11	8.6	-8.9
6	1	-1	12.7	13.2
6	1	-2	27.8	-26.6
6	1	-3	8.3	9.0
6	1	-4	57.2	-52.9
6	1	-5	19.3	[illegible]
6	1	-6	33.1	-33.0
6	1	-7	30.9	28.6
6	1	-8	17.7	21.2
6	1	-9	7.0	-2.0
6	1	-10	35.6	-30.3
6	1	-11	37.3	31.5
6	1	-12	33.7	32.0
6	1	-13	10.5	12.1
6	1	-14	8.8	-9.4
6	1	-15	12.5	11.4
6	1	-17	8.2	-7.8
7	1	0	21.6	-22.4
7	1	1	18.2	-15.3
7	1	2	42.0	-41.7
7	1	3	19.6	-19.1
7	1	4	41.4	-36.0
7	1	5	23.6	-18.8
7	1	6	13.4	10.9
7	1	8	16.0	-10.3
7	1	9	8.7	-5.6
7	1	-1	41.6	-38.5
7	1	-2	115.1	-118.2
7	1	-3	37.8	37.5
7	1	-4	19.0	-21.7
7	1	-6	21.6	-32.4
7	1	-7	12.2	14.7
7	1	-8	24.9	-39.6
7	1	-9	21.8	33.9
7	1	-11	8.2	-7.5
7	1	-12	21.8	-24.5
7	1	-13	19.4	20.9
7	1	-14	19.7	15.8
7	1	-18	10.5	12.6
8	1	0	43.4	-41.2
8	1	1	22.3	-14.3
8	1	2	32.4	-31.8
8	1	3	14.2	-14.0
8	1	4	30.7	-32.5
8	1	5	19.3	-22.1
8	1	7	22.7	-16.3
8	1	-1	34.7	25.2
8	1	-2	24.2	-27.2
8	1	-3	24.0	-20.2
8	1	-4	75.9	-75.4
8	1	-5	7.3	5.7
8	1	-6	13.9	-15.1
8	1	-7	16.9	15.0
8	1	-8	22.4	-26.2
8	1	-10	23.7	-23.9
8	1	-11	12.0	13.6
8	1	-12	15.7	12.7
8	1	-14	8.8	-6.6
8	1	-15	10.6	11.7
8	1	-16	10.2	10.8
9	1	0	23.5	-20.4
9	1	2	8.5	-8.9
9	1	5	8.8	-10.2
9	1	-1	25.4	-24.7
9	1	-2	68.0	-53.9
9	1	-3	9.7	-9.1
9	1	-4	41.3	-38.7
9	1	-5	17.7	-14.7
9	1	-6	59.1	-56.4
9	1	-7	23.3	23.4
9	1	-8	18.4	-20.3
9	1	-11	22.4	20.2
9	1	-12	12.4	-11.3
9	1	-13	8.8	6.7
9	1	-14	8.7	-7.2
9	1	-17	7.5	10.8
10	1	0	35.2	-33.6
10	1	1	25.2	-23.8
10	1	2	10.8	-13.4
10	1	3	16.5	-16.4
10	1	-1	8.5	-6.3
10	1	-2	14.7	-15.6
10	1	-3	26.6	-21.2
10	1	-4	39.5	-30.4
10	1	-5	34.3	31.6
10	1	-8	40.4	-39.1
10	1	-9	12.3	13.2
10	1	-10	8.7	-6.2
10	1	-12	10.8	-15.0
11	1	0	6.2	-0.8
11	1	-1	17.6	-15.9
11	1	-2	12.4	-13.6
11	1	-3	13.9	13.6
11	1	-5	10.7	-11.6
11	1	-6	50.4	-56.8
11	1	-8	8.8	-10.2
11	1	-9	12.5	-11.4
11	1	-10	27.7	-31.1
0	2	2	12.0	-14.0
0	2	3	10.6	14.6
0	2	4	62.1	-71.5
0	2	5	61.0	-63.9
0	2	6	52.7	-51.2
0	2	7	18.8	-18.7
0	2	8	9.5	5.5
0	2	9	12.2	[illegible]
0	2	11	[illegible]	-53.4
1	2	1	51.1	[illegible]
1	2	2	9.2	-15.3
1	2	3	107.9	-100.0
1	2	4	9.5	-18.3
1	2	5	22.4	-22.6
1	2	6	24.8	-19.6
1	2	7	30.4	-36.5
1	2	8	22.9	-23.2
1	2	9	32.1	-34.6
1	2	10	18.8	19.2
1	2	11	13.3	-13.1
1	2	13	21.4	-23.0
1	2	15	8.0	8.4
1	2	17	9.5	-11.0
1	2	-2	104.0	-111.4
1	2	-3	63.3	77.9
1	2	-4	37.8	[illegible]
1	2	-5	39.4	11.3
1	2	-6	62.5	-69.8
1	2	-7	25.2	26.4
1	2	-8	23.9	-28.0
1	2	-9	45.0	54.8
1	2	-12	22.5	-20.9
1	2	-13	31.5	33.4
2	2	0	78.0	-77.6
2	2	1	71.2	-88.8
2	2	2	32.8	-38.2
2	2	3	24.4	-22.5
2	2	4	24.7	-19.3
2	2	5	54.6	-61.8
2	2	6	14.5	8.1
2	2	7	53.0	-55.8
2	2	9	15.9	-16.2
2	2	10	10.7	-11.1
2	2	11	23.0	-25.3
2	2	12	33.7	35.2
2	2	13	8.3	9.5
2	2	14	11.5	11.7
2	2	15	13.4	-10.7
2	2	-1	21.4	-19.3
2	2	-2	112.8	-148.4
2	2	-3	55.5	-53.8
2	2	-4	69.3	-75.5
2	2	-5	59.7	59.1
2	2	-6	13.9	-13.1
2	2	-7	45.8	45.6
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2	2	-9	25.7	21.7
2	2	-10	11.7	-12.8
2	2	-11	10.2	8.6
2	2	-12	13.3	-11.4
2	2	-14	11.7	12.2
2	2	-15	32.2	30.6
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3	2	2	15.1	-24.0
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3	2	7	37.9	-38.3
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3	2	9	35.3	-37.0
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3	2	13	15.4	-14.5
3	2	-1	72.7	-72.1
3	2	-2	43.3	-44.1
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3	2	-9	18.2	14.8
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4	2	4	7.0	-4.7
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4	2	7	33.2	-37.9
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4	2	9	9.6	-7.5
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4	2	-14	23.9	-19.7
4	2	-15	10.1	9.9
5	2	0	13.5	-21.0
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5	2	3	58.1	-51.8
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5	2	-12	26.0	-29.7
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6	2	1	14.9	-16.3
6	2	2	21.9	15.3
6	2	3	66.8	-66.7
6	2	4	25.5	23.7
6	2	6	11.4	11.9
6	2	7	39.7	-45.7
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6	2	10	12.4	7.3
6	2	-1	31.5	-30.6
6	2	-2	28.4	-27.3
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6	2	-9	11.3	10.7
6	2	-10	36.3	-33.0
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6	2	-15	11.1	8.6
7	2	0	10.7	8.5
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7	2	5	23.4	-21.8
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7	2	9	13.5	-12.2
7	2	-1	96.2	-86.0
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7	2	-6	21.3	-23.0
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8	2	1	37.0	-33.6
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8	2	3	30.3	-30.1
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8	2	8	15.4	18.7
8	2	-1	44.8	-43.9
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8	2	-4	19.0	22.0
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8	2	-6	17.3	-17.1
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8	2	-8	28.8	-31.2
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8	2	-14	13.6	-13.2
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9	2	5	16.6	-15.2
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9	2	-4	11.0	-10.3
9	2	-5	61.8	-64.6
9	2	-6	24.7	-24.0
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9	2	-8	11.7	-13.2
9	2	-9	35.7	-34.5
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9	2	-12	11.1	14.4
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11	2	-12	10.8	-8.6
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12	2	-5	7.8	-9.1
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4	3	8	10.5	[illegible]
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2	4	4	19.9	-15.3
2	4	5	45.3	52.4
2	4	6	9.1	9.6
2	4	7	47.9	48.4
2	4	8	10.6	9.4
2	4	9	13.8	14.8
2	4	10	18.7	-21.2
2	4	11	32.2	36.8
2	4	12	6.7	8.5
2	4	14	6.4	-6.9
2	4	-1	49.9	35.8
2	4	-2	5.9	7.4
2	4	-3	39.3	-35.3
2	4	-4	31.0	-28.2
2	4	-5	22.7	-19.4
2	4	-6	22.8	17.9
2	4	-8	24.4	-24.0
2	4	-9	37.3	-38.8
2	4	-10	20.1	-21.6
2	4	-12	19.0	16.9
2	4	-13	11.5	-12.2
2	4	-14	21.6	-23.7
2	4	-15	19.4	-20.8
2	4	-16	16.5	19.1
3	4	0	14.0	-12.4
3	4	1	36.2	37.7
3	4	2	39.0	-43.3
3	4	3	70.1	64.5
3	4	4	16.8	12.4
3	4	5	[illegible]	50.1
3	4	7	27.5	28.7
3	4	8	9.5	-9.5
3	4	9	37.7	[illegible]
3	4	10	[illegible]	30.1
3	4	11	6.7	-8.0

H	K	L	Fo	Fc
3	4	12	10.6	-11.9
3	4	13	9.2	8.6
3	4	-1	61.7	55.5
3	4	-2	33.5	-26.5
3	4	-3	5.4	7.6
3	4	-4	1.9	-4.7
3	4	-5	40.4	33.1
3	4	-6	21.0	-25.0
3	4	-7	25.5	-23.8
3	4	-10	7.1	4.3
3	4	-11	29.9	-32.0
3	4	-13	19.5	-21.2
3	4	-14	21.6	23.5
3	4	-16	13.5	-13.8
4	4	1	37.6	40.0
4	4	2	6.9	4.5
4	4	3	42.3	51.5
4	4	5	41.7	43.5
4	4	6	16.6	-17.7
4	4	7	35.8	44.9
4	4	8	26.6	28.1
4	4	9	17.2	17.5
4	4	10	19.7	-21.5
4	4	-1	28.2	48.9
4	4	-2	4.7	-1.7
4	4	-3	80.7	82.6
4	4	-4	4.1	-2.1
4	4	-5	20.9	-16.4
4	4	-6	5.6	-3.3
4	4	-7	9.1	8.6
4	4	-8	28.2	-28.5
4	4	-9	30.1	-27.1
4	4	-10	15.4	12.6
4	4	-11	13.1	-14.5
4	4	-13	6.6	5.7
4	4	-14	9.5	-7.9
4	4	-15	13.3	-13.4
5	4	0	8.5	-10.8
5	4	1	56.4	51.5
5	4	2	11.2	-10.3
5	4	3	52.5	53.9
5	4	4	19.0	-21.5
5	4	5	42.2	45.2
5	4	6	29.6	30.9
5	4	8	19.3	-18.0
5	4	9	10.6	12.5
5	4	10	13.4	16.1
5	4	11	10.4	8.8
5	4	-1	53.1	55.9
5	4	-2	6.9	-7.9
5	4	-3	44.7	41.7
5	4	-4	17.7	-16.6
5	4	-5	42.2	39.9
5	4	-6	33.6	-27.7
5	4	-7	6.2	2.6
5	4	-8	37.2	38.9
5	4	-9	9.0	9.1
5	4	-10	17.6	-16.3
5	4	-12	9.2	9.5
5	4	-13	19.6	-18.4
5	4	-15	8.1	-7.5
5	4	-16	10.0	-10.9
5	4	-17	7.2	-9.2
6	4	0	8.0	6.8
6	4	1	63.1	62.8
6	4	2	6.7	-7.3
6	4	3	51.6	52.7
6	4	4	17.5	17.2
6	4	5	19.9	21.7
6	4	6	14.6	-14.8
6	4	7	19.4	18.7
6	4	8	8.2	6.4
6	4	9	6.7	-8.5
6	4	10	9.3	-8.6
6	4	-1	50.5	44.8
6	4	-2	14.5	-12.9
6	4	-3	36.0	37.1
6	4	-4	9.9	6.9
6	4	-5	37.2	33.9
6	4	-6	25.5	24.6
6	4	-7	37.5	34.7
6	4	-8	22.3	-25.3
6	4	-9	7.2	-3.8
6	4	-10	22.9	24.9
6	4	-11	10.1	-10.3
6	4	-12	32.1	-34.0
6	4	-13	11.6	-11.9
6	4	-14	6.7	-5.8
6	4	-16	7.7	7.4
7	4	0	10.5	-8.5
7	4	1	52.4	47.3
7	4	2	13.6	11.8
7	4	3	22.9	21.5
7	4	4	16.7	-15.9
7	4	5	6.5	9.7
7	4	6	11.5	15.3
7	4	7	12.6	12.8
7	4	9	7.9	5.6
7	4	10	7.6	6.8
7	4	-1	56.0	49.7
7	4	-2	7.7	-7.9
7	4	-3	37.5	39.0
7	4	-4	9.5	9.6
7	4	-5	27.0	30.9
7	4	-6	8.0	-8.4
7	4	-7	11.6	15.3
7	4	-8	15.7	14.9
7	4	-9	21.4	25.4
7	4	-10	38.0	-39.8
7	4	-12	17.5	18.8
8	4	1	34.1	34.7
8	4	2	6.4	6.8
8	4	4	15.1	14.3
8	4	5	9.5	8.6
8	4	6	15.3	-14.8
8	4	8	9.0	9.5
8	4	-1	47.3	47.9
8	4	-2	17.5	18.7
8	4	-3	32.3	31.1
8	4	-4	15.6	-13.6
8	4	-5	46.8	47.8
8	4	-6	6.1	6.9
8	4	-7	14.0	17.7
8	4	-8	20.2	-27.0
8	4	-9	11.1	10.6
8	4	-10	10.3	10.7
8	4	-11	15.2	14.1
8	4	-12	9.5	-10.2
9	4	0	6.5	5.5
9	4	1	10.4	14.3
9	4	2	8.2	-5.6
9	4	3	15.0	11.5
9	4	5	10.5	9.4
9	4	6	9.2	10.7
9	4	7	6.2	-6.1
9	4	-1	20.7	21.0
9	4	-2	10.1	-8.6
9	4	-3	49.9	52.0
9	4	-5	22.1	24.6
9	4	-6	11.1	-12.7
9	4	-7	11.2	13.4
9	4	-8	6.5	5.4
9	4	-9	17.4	16.6
9	4	-10	8.2	-6.8
9	4	-12	9.5	7.3
9	4	-13	17.3	17.5
10	4	3	17.4	17.5
10	4	4	7.9	8.8
10	4	5	6.3	-7.9
10	4	-1	9.5	6.9
10	4	-2	17.5	17.0
10	4	-3	23.1	23.8
10	4	-5	17.4	16.3
10	4	-7	32.6	35.9
10	4	-9	9.5	11.5
10	4	-11	17.5	21.0
10	4	-12	8.0	-12.6
11	4	2	7.8	9.1
11	4	-1	17.5	15.9
11	4	-2	9.5	-8.1
11	4	-5	24.9	27.2
11	4	-7	28.3	29.6
11	4	-9	15.1	16.8
11	4	-12	7.7	7.7
12	4	0	8.2	10.4
12	4	-1	8.9	12.8
12	4	-2	6.4	-8.0
12	4	-3	7.9	9.0
12	4	-4	6.5	6.5

H	K	L	Fo	Fc
12	4	-5	6.5	5.7
12	4	-6	7.9	8.7
12	4	-7	6.5	7.2
12	4	-9	7.7	10.5
0	5	1	38.3	44.4
0	5	2	61.4	-41.3
0	5	3	56.8	50.9
0	5	4	13.1	9.9
0	5	5	31.5	31.4
0	5	6	12.4	-9.6
0	5	7	7.2	6.9
0	5	8	31.1	36.8
0	5	9	19.5	20.2
0	5	12	9.6	12.2
0	5	13	9.7	-10.2
0	5	14	12.5	16.2
1	5	0	61.3	46.1
1	5	1	71.3	58.4
1	5	2	32.1	29.5
1	5	3	21.7	23.5
1	5	4	22.4	20.3
1	5	5	11.9	10.0
1	5	6	46.4	41.4
1	5	7	15.9	18.0
1	5	8	17.2	-18.2
1	5	10	19.4	21.5
1	5	12	10.8	10.6
1	5	-1	38.8	33.0
1	5	-2	21.3	12.1
1	5	-3	73.2	62.2
1	5	-4	41.6	-36.0
1	5	-5	63.8	62.4
1	5	-6	42.8	-48.1
1	5	-7	14.8	15.2
1	5	-9	17.4	20.8
1	5	-10	20.3	-24.2
1	5	-11	6.5	-7.8
2	5	0	37.1	34.2
2	5	1	57.5	55.4
2	5	2	37.9	36.5
2	5	3	8.0	-2.5
2	5	4	24.7	24.2
2	5	5	15.7	16.2
2	5	8	30.3	32.4
2	5	9	6.4	-6.5
2	5	11	6.8	-8.5
2	5	13	9.4	-10.2
2	5	-1	67.9	52.2
2	5	-2	85.2	-59.6
2	5	-3	93.7	83.8
2	5	-4	11.0	10.2
2	5	-5	23.0	25.6
2	5	-6	22.7	23.3
2	5	-7	27.7	33.8
2	5	-8	30.0	-29.0
2	5	-9	10.0	10.7
2	5	-10	20.0	23.4
2	5	-12	21.9	-21.5
2	5	-13	12.8	12.6
2	5	-14	8.4	-9.0
3	5	0	29.0	23.5
3	5	1	16.8	19.5
3	5	2	23.3	27.9
3	5	3	25.2	25.5
3	5	5	12.3	-12.3
3	5	6	46.0	48.3
3	5	7	7.3	6.4
3	5	9	21.6	-29.1
3	5	10	15.7	16.5
3	5	12	8.3	7.4
3	5	-1	77.4	70.6
3	5	-2	22.0	21.2
3	5	-3	15.7	18.6
3	5	-4	4.9	2.4
3	5	-5	45.5	50.1
3	5	-6	5.7	5.6
3	5	-7	47.5	47.6
3	5	-8	7.6	6.5
3	5	-9	17.2	15.0
3	5	-10	40.8	-51.4
3	5	-11	25.8	27.9
3	5	-12	11.6	8.5
3	5	-13	10.8	-13.3
3	5	-14	8.4	-10.4
4	5	0	8.0	2.8
4	5	1	27.5	27.0
4	5	2	16.7	17.1
4	5	3	5.0	3.5
4	5	4	43.8	47.5
4	5	7	16.9	-22.6
4	5	8	19.7	23.4
4	5	9	6.8	-8.5
4	5	11	12.7	-15.5
4	5	-1	14.7	16.2
4	5	-2	48.1	49.4
4	5	-3	44.7	48.9
4	5	-4	41.5	37.2
4	5	-5	53.5	55.9
4	5	-6	24.6	-26.0
4	5	-7	21.9	22.7
4	5	-8	18.1	-21.3
4	5	-9	33.0	34.2
4	5	-10	24.8	23.4
4	5	-11	15.0	-16.0
4	5	-12	23.7	-26.9
4	5	-13	8.4	8.7
4	5	-14	13.7	14.2
5	5	0	6.9	6.1
5	5	2	39.8	42.2
5	5	3	7.8	9.0
5	5	4	6.2	8.4
5	5	5	21.6	-24.9
5	5	6	35.9	42.1
5	5	7	17.7	-21.8
5	5	11	9.2	-10.7
5	5	-1	26.7	26.8
5	5	-2	19.9	21.4
5	5	-3	21.0	23.3
5	5	-4	6.8	3.8
5	5	-5	21.1	23.3
5	5	-7	30.7	32.0
5	5	-8	15.3	16.8
5	5	-10	20.6	-21.5
5	5	-11	33.0	31.4
5	5	-12	23.8	25.2
5	5	-13	10.8	9.8
5	5	-14	18.2	-19.0
6	5	0	34.9	34.6
6	5	2	8.2	-3.7
6	5	3	10.5	-9.9
6	5	4	40.2	40.6
6	5	5	9.2	-9.9
6	5	6	17.8	-21.4
6	5	7	20.4	-22.5
6	5	9	12.6	-14.1
6	5	10	15.1	13.1
6	5	11	6.1	-6.6
6	5	-1	7.6	8.3
6	5	-2	26.5	23.3
6	5	-3	9.9	11.5
6	5	-4	5.3	3.4
6	5	-5	14.5	15.5
6	5	-6	31.4	31.6
6	5	-7	24.4	21.9
6	5	-8	12.8	11.2
6	5	-9	25.0	28.9
6	5	-10	12.1	14.0
6	5	-11	13.3	11.7
6	5	-12	25.7	-26.6
6	5	-13	13.7	14.5
6	5	-14	11.7	10.5
7	5	0	22.6	21.8
7	5	1	18.3	-16.8
7	5	2	41.9	45.4
7	5	3	25.9	-25.2
7	5	4	10.5	-8.5
7	5	5	9.6	-11.6
7	5	6	15.9	15.0
7	5	8	6.7	7.1
7	5	9	12.1	-11.9
7	5	10	6.0	-6.6
7	5	11	7.8	-8.7
7	5	-1	11.8	-11.6
7	5	-2	13.0	11.2
7	5	-3	23.2	21.7
7	5	-4	9.0	8.7
7	5	-5	5.9	5.2
7	5	-6	16.0	17.1
7	5	-7	8.7	11.3

H	K	L	Fo	Fc
7	5	-9	19.3	19.0
7	5	-11	14.4	15.3
7	5	-12	12.8	12.2
7	5	-13	9.7	9.2
7	5	-14	14.2	-16.2
7	5	-15	10.2	12.8
7	5	-16	12.8	12.0
8	5	0	36.2	36.7
8	5	1	26.3	-27.2
8	5	2	17.6	-14.7
8	5	3	18.1	-17.5
8	5	4	6.8	6.4
8	5	5	20.5	-21.3
8	5	6	12.7	11.5
8	5	7	8.1	-9.3
8	5	8	7.7	-9.6
8	5	-3	6.3	-6.0
8	5	-4	35.2	35.5
8	5	-7	19.3	18.6
8	5	-8	10.4	9.4
8	5	-9	11.6	12.1
8	5	-10	10.7	11.9
8	5	-11	18.3	19.7
8	5	-13	6.7	8.1
8	5	-14	11.4	12.8
8	5	-15	6.2	5.9
9	5	0	11.7	-9.6
9	5	2	14.5	15.3
9	5	3	18.3	-18.3
9	5	4	6.8	7.8
9	5	5	10.5	-12.0
9	5	7	16.2	-15.0
9	5	8	6.9	7.5
9	5	-1	20.0	-21.9
9	5	-2	37.5	37.1
9	5	-3	21.7	-22.5
9	5	-4	6.6	7.6
9	5	-5	21.7	23.9
9	5	-6	15.5	17.0
9	5	-8	6.8	-6.3
9	5	-9	18.2	19.3
9	5	-12	8.3	11.5
9	5	-14	9.0	-9.4
10	5	0	8.4	10.2
10	5	1	6.8	-5.9
10	5	2	6.7	4.4
10	5	3	12.4	-15.0
10	5	5	9.7	-11.3
10	5	-1	24.2	-25.6
10	5	-4	27.4	31.5
10	5	-5	6.8	-7.3
10	5	-8	20.5	24.1
11	5	1	14.5	-21.7
11	5	3	8.6	-8.8
11	5	-1	8.2	-8.7
11	5	-2	11.7	14.5
11	5	-3	10.7	-11.2
11	5	-4	11.8	-12.1
11	5	-5	9.6	-9.1
0	6	1	10.1	10.9
0	6	2	49.1	38.2
0	6	3	39.5	-32.9
0	6	4	36.2	32.7
0	6	5	5.2	2.7
0	6	6	5.0	2.1
0	6	7	23.1	-19.7
0	6	8	24.9	26.5
0	6	9	7.2	-6.2
0	6	10	16.3	18.2
0	6	11	6.8	-5.9
0	6	12	8.0	-9.4
0	6	13	21.3	-24.5
1	6	0	40.8	50.0
1	6	1	47.8	-43.6
1	6	2	76.3	67.7
1	6	3	21.3	15.8
1	6	4	10.6	16.0
1	6	5	30.4	-26.6
1	6	6	6.8	-10.0
1	6	7	20.9	-22.6
1	6	8	7.9	7.7
1	6	9	7.4	7.8
1	6	10	8.7	-10.3
1	6	11	18.6	-22.2
1	6	12	7.9	6.0
1	6	13	6.7	6.9
1	6	14	7.3	-7.9
1	6	15	6.6	-5.5
1	6	-1	11.3	7.9
1	6	-2	84.0	63.5
1	6	-3	38.5	-31.6
1	6	-4	31.4	27.6
1	6	-5	53.2	50.5
1	6	-6	43.9	42.4
1	6	-7	11.7	-9.5
1	6	-8	7.4	5.5
1	6	-9	15.2	14.7
1	6	-10	9.2	-12.3
1	6	-11	28.5	27.7
1	6	-13	11.2	-14.3
1	6	-14	7.7	-9.5
1	6	-15	12.0	13.5
1	6	-16	5.6	6.1
2	6	0	52.8	48.3
2	6	1	7.7	-9.0
2	6	2	10.5	12.9
2	6	3	34.8	-38.8
2	6	4	38.3	39.2
2	6	5	7.3	-8.5
2	6	6	18.5	22.8
2	6	7	14.8	-14.6
2	6	8	15.7	-17.7
2	6	9	22.0	-23.9
2	6	10	7.9	6.7
2	6	11	6.9	7.8
2	6	12	16.8	-18.8
2	6	-1	54.2	-44.4
2	6	-2	29.7	17.9
2	6	-3	55.7	39.6
2	6	-4	32.3	32.6
2	6	-5	14.6	-15.5
2	6	-6	17.0	17.7
2	6	-7	22.3	24.9
2	6	-8	17.8	18.4
2	6	-9	20.2	22.3
2	6	-11	18.2	-22.5
2	6	-12	11.2	11.5
2	6	-13	18.7	19.7
2	6	-14	12.3	13.8
3	6	0	5.6	3.0
3	6	1	19.7	-21.5
3	6	2	7.7	8.2
3	6	3	20.4	-19.8
3	6	4	17.2	17.2
3	6	5	15.1	-17.4
3	6	6	7.7	5.7
3	6	7	26.6	-26.6
3	6	8	9.3	10.1
3	6	10	20.2	-23.2
3	6	-1	3.8	2.8
3	6	-2	59.9	51.9
3	6	-3	8.9	-8.6
3	6	-4	22.3	22.5
3	6	-5	19.6	-17.8
3	6	-6	60.6	53.7
3	6	-7	5.4	-3.5
3	6	-9	16.5	14.5
3	6	-10	27.2	24.5
3	6	-11	9.5	12.7
3	6	-12	7.9	8.7
3	6	-14	6.8	-6.9
3	6	-15	14.2	13.5
4	6	0	37.3	39.5
4	6	1	20.3	-17.5
4	6	2	8.3	-10.4
4	6	3	19.7	-19.9
4	6	4	12.5	-13.4
4	6	5	25.4	-25.0
4	6	6	8.2	8.5
4	6	7	11.1	13.0
4	6	8	19.8	-24.7
4	6	9	21.5	-22.9
4	6	10	5.6	4.0
4	6	-1	31.5	-26.3
4	6	-3	31.9	-27.5
4	6	-4	57.3	56.5
4	6	-5	9.0	-7.7
4	6	-6	11.6	14.2
4	6	-7	16.0	18.9

H	K	L	Fo	Fc
4	6	-8	27.8	27.7
4	6	-10	14.3	17.5
4	6	-11	14.8	16.0
4	6	-12	6.9	6.3
4	6	-14	7.8	7.1
4	6	-15	5.3	-4.9
4	6	16	3.9	0.0
5	6	0	17.3	14.8
5	6	1	18.9	-21.3
5	6	2	20.7	22.6
5	6	3	30.5	-35.9
5	6	4	5.0	-4.7
5	6	5	7.4	-9.2
5	6	6	23.2	-26.7
5	6	7	7.9	-6.6
5	6	9	7.9	9.6
5	6	10	8.6	-10.6
5	6	11	8.9	-7.5
5	6	-1	24.2	-22.0
5	6	-2	18.6	21.1
5	6	-3	14.9	-15.9
5	6	-4	11.5	10.4
5	6	-5	22.7	26.3
5	6	-6	26.3	24.8
5	6	-7	21.3	-17.3
5	6	-8	22.3	22.0
5	6	-9	5.2	-6.7
5	6	-10	27.8	27.1
5	6	-11	5.5	-5.5
5	6	-13	6.9	6.9
6	6	0	9.2	-7.5
6	6	1	20.8	-19.6
6	6	4	22.9	-25.2
6	6	5	21.0	-20.2
6	6	6	7.9	-9.2
6	6	7	9.7	-11.3
6	6	8	5.6	-6.6
6	6	9	5.4	-4.4
6	6	11	5.8	6.6
6	6	-2	4.6	-0.1
6	6	-3	18.6	-17.6
6	6	-4	15.4	18.7
6	6	-5	32.4	-30.3
6	6	-6	16.1	19.1
6	6	-7	6.1	4.9
6	6	-8	37.9	42.5
6	6	-9	27.6	-25.7
6	6	-10	6.7	7.5
6	6	-11	12.5	12.8
6	6	-12	10.5	12.1
6	6	-13	5.6	5.8
7	6	0	5.7	-7.1
7	6	1	6.4	-6.9
7	6	2	19.2	-18.0
7	6	3	7.7	-7.2
7	6	4	6.8	-5.8
7	6	5	11.9	15.9
7	6	6	15.2	-17.4
7	6	7	15.0	-14.3
7	6	8	7.6	-8.5
7	6	-1	32.2	-34.0
7	6	-2	29.0	27.6
7	6	-3	21.4	-24.0
7	6	-4	16.6	18.4
7	6	-5	5.1	-4.7
7	6	-6	15.6	15.8
7	6	-7	30.4	-34.2
7	6	-8	5.4	6.7
7	6	-9	28.4	33.3
7	6	-11	10.5	-13.3
7	6	-13	6.8	-6.9
7	6	-14	7.6	7.2
7	6	-15	6.2	6.1
8	6	0	14.8	-13.8
8	6	1	23.7	-21.4
8	6	2	15.1	-17.0
8	6	4	8.9	-10.4
8	6	5	12.5	-13.3
8	6	6	5.4	-6.0
8	6	7	14.1	15.2
8	6	8	7.0	-7.3
8	6	-1	21.9	-17.8
8	6	-3	5.3	6.9
8	6	-4	5.3	2.8
8	6	-5	24.1	-28.2
8	6	-6	5.4	7.0
8	6	-7	10.2	12.8
8	6	-9	20.0	-26.3
8	6	-10	8.0	9.3
8	6	-12	15.0	15.8
8	6	-14	6.4	5.8
9	6	0	6.9	-3.5
9	6	1	5.6	-4.6
9	6	2	15.2	-15.9
9	6	6	13.6	-13.5
9	6	-2	9.7	-9.5
9	6	-3	15.1	-15.6
9	6	-5	13.1	-14.3
9	6	-6	7.9	10.7
9	6	-7	15.2	-19.3
9	6	-10	6.9	6.3
9	6	-11	12.4	-14.3
9	6	-13	8.2	10.4
10	6	0	6.8	-8.4
10	6	2	5.4	-4.7
10	6	4	16.7	-18.8
10	6	-1	6.9	-7.4
10	6	-2	21.5	-23.5
10	6	-3	18.7	-21.1
10	6	-6	6.9	-6.0
10	6	-7	5.6	-5.7
10	6	-8	6.8	7.3
10	6	-9	11.4	-12.0
10	6	-11	5.3	7.7
10	6	-12	5.2	5.6
10	6	-13	6.0	-6.7
11	6	0	5.2	-4.3
11	6	2	6.9	-11.0
11	6	-1	7.6	-6.9
11	6	-2	6.6	-6.8
11	6	-3	5.4	-3.1
11	6	-4	12.8	-13.5
11	6	-5	5.5	-7.0
11	6	-7	5.4	-6.2
11	6	-10	7.3	7.8
11	6	-11	7.9	-9.1
0	7	1	20.0	-20.4
0	7	2	36.8	-28.3
0	7	3	10.0	8.5
0	7	4	27.8	-25.1
0	7	5	11.9	-11.5
0	7	6	9.5	-11.5
0	7	7	12.7	14.4
0	7	8	7.8	-10.0
0	7	9	14.3	-16.2
0	7	10	9.3	-9.0
0	7	12	15.0	-15.8
0	7	13	7.4	7.1
0	7	14	7.7	-8.0
1	7	0	5.7	-8.6
1	7	1	7.4	-5.3
1	7	2	24.2	-18.6
1	7	3	29.3	-23.2
1	7	4	31.5	-30.6
1	7	5	16.9	17.5
1	7	6	29.3	-31.2
1	7	7	10.1	-9.2
1	7	8	18.5	-21.2
1	7	9	5.3	3.8
1	7	1	15.0	-16.9
1	7	12	6.5	-4.9
1	7	-1	10.7	13.0
1	7	-2	11.2	12.3
1	7	-3	30.6	-28.5
1	7	-4	9.2	9.8
1	7	-5	16.4	14.5
1	7	-6	20.3	20.3
1	7	-7	13.9	-15.2
1	7	-8	13.3	13.9
1	7	-10	20.7	21.3
1	7	-11	7.7	11.4
1	7	-12	5.4	5.4
1	7	-14	8.0	7.7
2	7	0	8.6	-5.7
2	7	1	23.0	-18.8
2	7	2	22.0	-20.9
2	7	3	8.2	8.9

H	K	L	Fo	Fc
2	7	4	13.6	-13.2
2	7	5	23.6	-19.1
2	7	6	25.4	-22.5
2	7	7	15.4	15.0
2	7	8	20.4	-21.0
2	7	10	15.1	-14.7
2	7	12	7.4	-7.1
2	7	-1	6.3	-6.3
2	7	-2	58.4	-40.6
2	7	-3	3.1	2.7
2	7	-4	11.6	11.4
2	7	-5	20.4	-19.1
2	7	-6	12.8	11.4
2	7	-7	10.0	12.1
2	7	-8	17.5	18.8
2	7	-11	5.4	4.0
2	7	-12	5.4	4.1
2	7	-13	9.3	-10.6
2	7	-14	7.2	7.1
3	7	0	47.3	-45.2
3	7	1	19.3	17.0
3	7	2	12.9	-13.4
3	7	3	18.8	-18.6
3	7	4	31.4	-37.5
3	7	6	16.8	-20.7
3	7	7	11.0	-11.8
3	7	8	22.2	-23.1
3	7	9	16.8	19.6
3	7	12	5.0	-2.4
3	7	-1	15.1	-13.5
3	7	-2	3.3	3.1
3	7	-3	18.7	16.5
3	7	-4	16.1	-14.1
3	7	-5	12.2	13.4
3	7	-6	4.2	3.6
3	7	-7	32.3	-27.5
3	7	-8	26.0	24.1
3	7	-9	15.6	15.8
3	7	-11	23.6	-24.6
3	7	-12	8.6	10.7
3	7	-13	6.6	5.5
3	7	-14	5.2	2.8
4	7	0	23.7	-22.5
4	7	1	9.1	-8.3
4	7	2	28.4	-28.5
4	7	3	30.0	33.8
4	7	4	18.7	-18.2
4	7	5	10.0	-9.9
4	7	6	28.1	-26.7
4	7	9	6.6	-7.0
4	7	10	8.4	-8.6
4	7	-1	16.8	13.4
4	7	-2	25.2	-24.7
4	7	-3	12.0	-9.6
4	7	-4	13.6	-14.2
4	7	-5	27.8	-26.0
4	7	-6	9.9	-7.1
4	7	-7	17.1	16.4
4	7	-8	16.6	-15.5
4	7	-9	31.0	-32.3
4	7	-10	19.4	21.0
4	7	-11	12.7	15.6
4	7	-12	5.4	5.6
5	7	0	23.9	-21.9
5	7	1	16.7	15.4
5	7	2	38.3	-42.4
5	7	3	9.8	-9.9
5	7	4	22.3	-23.4
5	7	5	28.4	28.8
5	7	6	12.0	-12.3
5	7	8	8.6	-7.8
5	7	9	8.4	-9.2
5	7	10	7.1	-4.7
5	7	11	5.7	6.0
5	7	-1	28.6	-31.0
5	7	-2	16.8	-17.1
5	7	-3	4.3	-2.3
5	7	-4	26.5	-22.5
5	7	-6	8.1	-7.4
5	7	-7	7.7	-5.9
5	7	-9	16.1	19.8
5	7	-11	29.4	-24.2
5	7	-12	15.0	15.4
5	7	-13	7.6	8.4
5	7	-15	5.9	-4.9
6	7	0	26.2	-27.2
6	7	1	26.8	-25.4
6	7	2	19.9	-21.1
6	7	3	6.4	5.9
6	7	4	16.5	-17.2
6	7	5	8.6	-10.2
6	7	6	7.7	-6.5
6	7	7	8.5	8.8
6	7	8	6.4	-3.8
6	7	9	8.7	8.8
6	7	-1	28.8	30.8
6	7	-2	28.5	-27.7
6	7	-3	4.7	-2.9
6	7	-4	21.8	-22.9
6	7	-5	4.8	1.3
6	7	-6	16.7	-17.6
6	7	-8	5.2	-7.2
6	7	-9	20.8	-23.1
6	7	-11	10.9	11.9
6	7	-13	14.5	-15.4
6	7	-14	6.2	6.6
6	7	-15	7.4	9.1
7	7	0	16.1	-16.6
7	7	1	28.5	29.1
7	7	2	24.5	-24.3
7	7	3	7.6	-6.3
7	7	4	10.9	-11.2
7	7	6	7.6	-5.9
7	7	8	7.8	-7.1
7	7	-2	36.4	-39.5
7	7	-4	10.8	-12.0
7	7	-5	11.5	-11.1
7	7	-6	5.2	-6.6
7	7	-7	16.3	-18.8
7	7	-10	5.4	-4.9
7	7	-11	5.4	5.0
7	7	-12	7.6	-5.2
7	7	-13	8.2	10.5
7	7	-15	10.7	-12.1
8	7	0	32.7	-31.7
8	7	1	6.7	-4.7
8	7	3	7.7	6.2
8	7	4	10.7	-11.0
8	7	5	8.3	9.1
8	7	-2	12.0	-14.2
8	7	-3	22.1	-21.0
8	7	-4	14.7	-16.3
8	7	-5	14.8	16.2
8	7	-6	18.2	-22.6
8	7	-8	7.7	-7.6
8	7	-9	6.7	5.9
8	7	-10	11.1	-11.0
8	7	-11	5.3	7.9
8	7	-13	7.9	-8.4
8	7	-15	4.3	7.1
9	7	0	9.4	-10.9
9	7	2	9.2	-9.2
9	7	-1	12.8	-13.1
9	7	-2	12.2	-12.7
9	7	-3	25.0	28.7
9	7	-4	16.8	-21.6
9	7	-5	8.6	-8.8
9	7	-6	7.7	-8.8
9	7	-7	13.8	15.8
9	7	-8	10.1	-12.3
9	7	-11	14.4	-17.1
10	7	0	5.2	-4.5
10	7	2	6.1	-5.8
10	7	3	5.9	6.1
10	7	-1	14.7	15.0
10	7	-2	8.4	-9.3
10	7	-3	7.6	-8.2
10	7	-4	12.6	-13.6
10	7	-5	5.4	7.7
10	7	-6	14.8	-18.0
10	7	-7	6.5	-7.1
10	7	-8	6.4	-8.0
10	7	-10	7.2	-8.8
10	7	-12	5.7	-7.0
11	7	-2	6.1	-4.7
11	7	-3	11.3	11.7
11	7	-4	9.5	-10.4

H	K	L	Fo	Fc
11	7	-5	8.8	-10.4
11	7	-6	5.1	-6.1
11	7	-7	5.0	8.1
11	7	-8	9.9	-14.2
11	7	-10	5.7	-5.5
0	8	1	25.6	-34.6
0	8	2	41.8	-42.9
0	8	3	3.8	0.4
0	8	4	10.0	-6.8
0	8	5	8.8	9.0
0	8	6	9.1	-6.3
0	8	7	8.0	-8.7
0	8	11	5.1	-5.9
0	8	12	7.9	-8.8
1	8	0	32.9	-46.7
1	8	1	11.8	10.9
1	8	2	2.9	-1.2
1	8	3	9.6	-6.9
1	8	4	26.5	-23.8
1	8	5	13.2	-14.9
1	8	6	28.7	-28.4
1	8	7	6.7	8.6
1	8	9	12.0	-13.3
1	8	11	6.2	5.2
1	8	12	11.4	14.2
1	8	-1	19.8	-21.7
1	8	-2	3.6	-1.0
1	8	-3	34.7	23.9
1	8	-4	48.6	-43.3
1	8	-5	10.9	-8.9
1	8	-6	4.2	0.2
1	8	-8	11.3	-9.1
1	8	-10	19.3	-19.5
1	8	-13	6.8	7.4
2	8	0	6.7	8.6
2	8	1	3.1	0.9
2	8	2	16.2	-14.8
2	8	3	8.8	-11.6
2	8	4	8.2	10.1
2	8	5	12.6	14.8
2	8	6	7.4	-5.8
2	8	7	17.2	-20.6
2	8	8	11.9	-12.5
2	8	-1	19.7	16.0
2	8	-2	68.1	-55.5
2	8	-3	58.4	-51.9
2	8	-4	26.8	-26.4
2	8	-5	35.1	31.1
2	8	-6	26.9	-24.2
2	8	-7	5.5	-4.1
2	8	-8	20.4	-21.2
2	8	-11	9.6	10.6
2	8	-12	8.0	-8.3
2	8	-13	4.9	-3.2
3	8	0	40.2	-36.7
3	8	2	29.7	-30.5
3	8	4	4.4	2.3
3	8	5	15.0	-19.0
3	8	6	9.2	11.3
3	8	7	10.7	11.5
3	8	8	10.3	13.1
3	8	9	8.1	-11.0
3	8	10	5.0	8.3
3	8	-1	39.2	-36.5
3	8	-2	21.9	-18.8
3	8	-3	20.4	16.8
3	8	-4	28.6	-24.2
3	8	-5	5.7	-5.5
3	8	-6	24.7	-22.9
3	8	-7	18.4	17.6
3	8	-8	10.7	-9.1
4	8	0	7.0	-6.4
4	8	1	15.7	-15.1
4	8	2	6.2	-4.3
4	8	3	13.0	-12.7
4	8	4	20.4	-22.7
4	8	5	4.9	-4.4
4	8	6	14.5	16.3
4	8	7	8.1	-9.5
4	8	9	6.1	6.5
4	8	10	6.8	8.7
4	8	-1	17.7	15.1
4	8	-2	16.7	-13.0
4	8	-3	4.0	-0.9
4	8	-5	4.3	5.1
4	8	-6	25.6	-30.5
4	8	-7	16.3	-14.1
4	8	-8	18.4	-19.3
4	8	-9	7.1	6.2
4	8	-10	8.9	-10.3
4	8	-11	7.3	-6.1
4	8	-12	5.1	-3.3
4	8	-13	4.9	5.7
4	8	-14	5.6	-5.1
5	8	0	6.3	-5.9
5	8	3	4.9	2.6
5	8	4	8.7	11.4
5	8	5	8.1	-8.0
5	8	7	6.3	-7.8
5	8	8	7.9	10.7
5	8	-1	5.4	-5.2
5	8	-2	13.9	-13.6
5	8	-3	12.4	13.6
5	8	-4	31.2	-34.8
5	8	-5	26.1	-26.3
5	8	-6	5.7	-3.7
5	8	-8	14.2	-14.1
5	8	-9	5.1	4.0
5	8	-1	10.3	-9.7
5	8	-11	7.3	8.1
5	8	-12	5.0	-6.5
6	8	0	13.8	-12.4
6	8	1	6.0	-4.7
6	8	2	16.0	17.9
6	8	3	6.2	-6.8
6	8	4	5.1	4.5
6	8	-1	10.1	-8.7
6	8	-2	7.5	-8.4
6	8	-3	15.0	-13.3
6	8	-5	8.4	6.8
6	8	-6	18.5	-19.7
6	8	-8	6.2	6.0
6	8	-10	14.7	-15.2
6	8	-11	5.1	-4.9
6	8	-12	11.1	-11.0
7	8	0	10.8	9.7
7	8	1	10.2	-9.2
7	8	2	5.1	-3.7
7	8	4	16.3	18.5
7	8	5	9.4	-10.0
7	8	-4	11.7	-14.9
7	8	-6	8.8	9.7
7	8	-7	6.3	7.8
7	8	-8	23.2	-25.1
7	8	-9	9.6	-12.6
7	8	-11	5.0	-6.6
7	8	-12	6.9	-8.4
8	8	0	8.1	9.0
8	8	1	8.1	6.7
8	8	2	8.8	11.2
8	8	3	9.4	-10.0
8	8	4	6.9	7.5
8	8	5	7.5	7.6
8	8	6	12.7	14.5
8	8	-2	6.3	5.9
8	8	-3	16.4	-16.9
8	8	-4	9.6	9.9
8	8	-5	5.1	5.8
8	8	-6	18.0	-20.5
8	8	-7	10.3	-12.0
8	8	-10	14.3	-19.3
8	8	-11	4.9	4.2
9	8	0	10.7	10.7
9	8	1	11.1	-10.3
9	8	2	6.9	7.5
9	8	-5	8.9	-10.1
9	8	-8	11.2	-14.4
9	8	-10	4.8	5.4
10	8	0	8.1	8.7
10	8	2	10.3	10.5
10	8	-1	4.6	-6.7
10	8	-2	7.7	7.5
10	8	-7	6.8	-8.6
10	8	-8	4.7	4.5
10	8	-9	6.6	7.2
10	8	-10	7.1	-8.1

PART 3.

THE STRUCTURE OF ISOCALEBASSINE:

X-RAY ANALYSIS OF ISOCALEBASSINE METHYL ETHER DI-IODIDE.

3.1 INTRODUCTION.

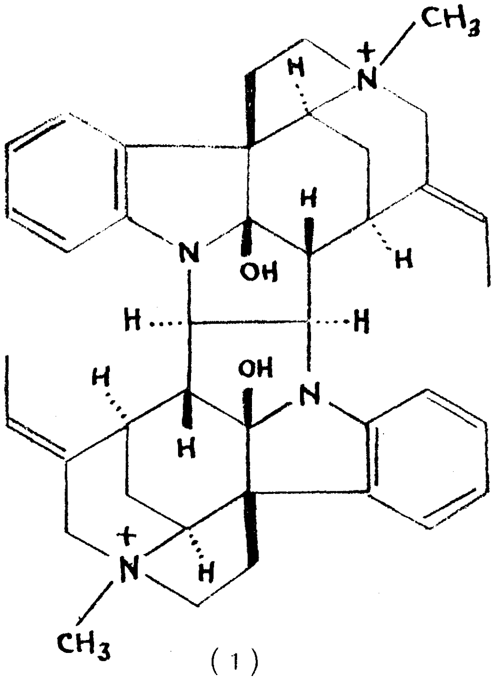
The dramatic paralysing effect of the South American Indian dart and arrow poisons known as curare has been common knowledge for very many years, and has stimulated much interest in their chemical composition. Since the name curare is a generic term which includes many types of arrow-head poison, they have been classified by Boehm (1897) into three main categories, according to the type of container used to pack the final product. These three categories are "tube-", "pot-" and "calabash-curare".

Calabash-curare originates in the Northern parts of the South American Continent, particularly in the Amazon and Orinoco basins. It is considerably more active physiologically than either tube- or pot-curare, and its chemical investigation has proved correspondingly more difficult. The barks of "Strychnos toxifera" and other "Strychnos" species are used in the preparation of calabash-curare. An exhaustive survey of work in this field has been published by Bernauer, (1959).

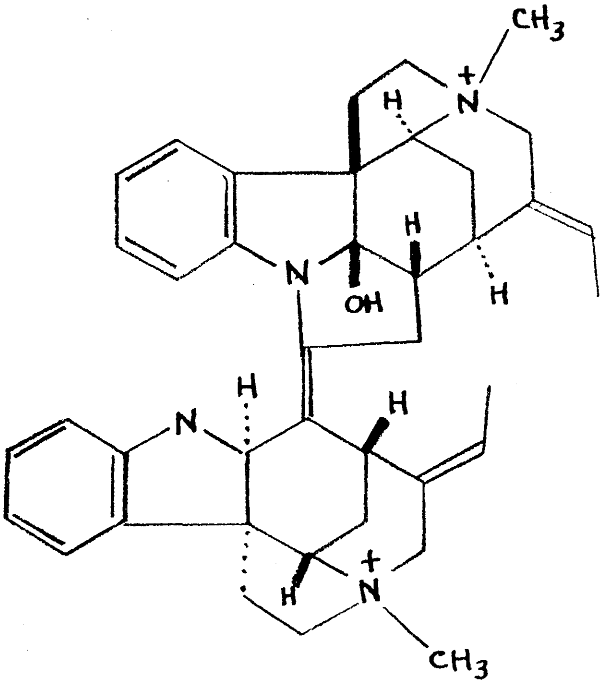
Serious chemical investigation of the calabash curares was started by Boehm in 1897, but it was not until 1937 that the first isolation of crystalline calabash-curare was achieved by Wieland and his co-workers. Curarine I Chloride (Wieland, Konz and Sonderhoff, 1937) was the first calabash-curare alkaloid to be isolated, and other alkaloids isolated in this early work were calebassine and dihydrotoxiferine I (Wieland, Bahr and Witkop, 1941). The alkaloid calebassine is of particular interest in the case of the present investigation into the structure of isocalebassine.

In the next twenty years, a considerable amount of work was carried out on calabash-curare alkaloids, and also on those of the plant material "Strychnos toxifera". Workers in this field have included King (1949), who isolated toxiferines I - XII, and Schmid and Karrer, who have carried out a number of investigations into the structures of these alkaloids.

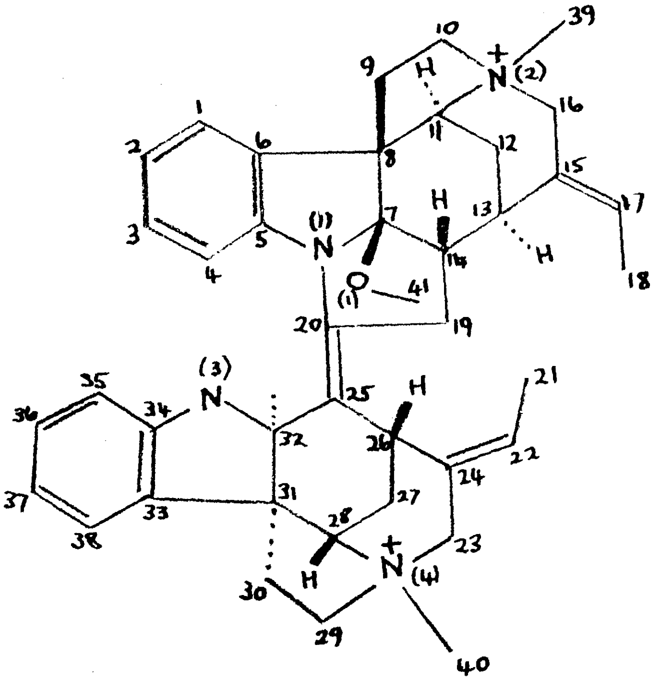
As work on these alkaloids continued, it became apparent that they fell into two main groups. One group has little or no physiological activity, while the second group contains these alkaloids with high curare activity.



(1)



(2)


10
39
+
9
H
N(2)
16
1
2
6
11
12
15
8
17
(1)
N
7
H
13
3
5
14
H
18
4
O
(1)
41
20
19
(3)
N
35
36
34
H
21
25
32
26
22
24
37
31
27
33
38
28
+
N
(4)
23
H
30
29
40

(3)

$$\begin{tikzcd}
\text{Alkaloid D} & \\
\text{Dihydrotoxiferine I} \arrow[u, "H_3O^+"] \arrow[r, "O_2/h\nu"] \arrow[d, bend left, "O_2/\text{pyridine HOAc}"] & \text{Curarine I} \arrow[d, "\text{conc HCl}"] \\
\text{Calebassine} \arrow[u, bend left, "O_2 \; h\nu"] \arrow[r, "\text{HCO.OAc}"] & \text{Fluorocurarine}
\end{tikzcd}$$

<u>REFERENCE</u>. Battersby, A.R. and Hodson, H.F. (1960), Quart.Rev. <u>14</u>, 77.

von Phillipsborn, Schmid, and Karrer (1956) have demonstrated that these highly active alkaloids have molecular formulae based upon a C_{38}-C_{40} skeleton, and that they have two quaternary nitrogens present in the molecule.

By 1960, the relationship (shown overleaf) between several alkaloids including calebassine, had been firmly established (Battersby and Hodson, 1960). At this time, the constitution of calebassine was unknown.

The structure (1) was the structure which was finally adopted as the structure of calebassine (Schmid, 1963). The alkaloid, isocalebassine, is simply prepared from calebassine, by treatment with acid. The constitution of isocalebassine was unknown, although it was clear that it must closely resemble that of calebassine. If isocalebassine is treated with methyl sulphate in alkaline solution it is converted into the O-methyl ether.

The elucidation of the structure of isocalebassine by x-ray methods has been carried out successfully using the di-iodide derivative of the O-methyl ether, crystals of which were supplied by Professor H. Schmid, and the results establish structure (2) for isocalebassine.

The numbering of the derivative used in the analysis is shown in (3).

3.2 EXPERIMENTAL.

The molecular formula of isocalebassine methyl ether di-iodide is $C_{41}H_{50}N_4O\ I_2$, and this leads to a molecular weight of 868.3.

Rotation, oscillation, and Weissenberg photographs were taken with copper K-α radiation (λ= 1.542 Å). The cell dimensions were obtained from rotation and Weissenberg photographs, and from these, the following values were obtained

a = 15.02 ± 0.05 Å
b = 33.36 ± 0.07 Å
c = 10.02 ± 0.04 Å

The volume of the unit cell was calculated from the expression

$$V = abc$$

and was found to be 5020.7 Å^3.

From examination of the zero layer Weissenberg photographs, the absent spectra were found to be h00 when h is odd, 0k0 when k is odd, and 00l when l is odd. Therefore, the space group is uniquely determined to be $P2_12_12_1$.

The number of molecules in the unit cell was taken as four, and this number of molecules leads to a calculated density of 1.15 g/ml. The linear absorption coefficient for copper K-α radiation was found to be 102.5 cm^{-1}. The total number of electrons per unit cell, F(000), is 1752. "$\sum f^2$" for the two heavy atoms is 5618, while "$\sum f^2$" for the light atoms is 1786. This gives r = $\left["\sum f_H^{2}" / "\sum f_L^{2}" \right]^{\frac{1}{2}}$ = 1.77.

The intensities were recorded using a small crystal completely bathed in a uniform x-ray beam. No adjustments were made initially to account for absorption. The data were collected on zero layer and equi-inclination upper layer Weissenberg photographs obtained by rotation of the crystal about the needle axis (c-crystal axis), the reciprocal lattice nets hk0, ..., hk6 being registered in this way. Visual methods of intensity estimation were used, all Weissenberg data having been obtained by using Robertson's multiple film technique (1943). In all, 1502 independent intensity estimations were made.

The intensity values were corrected for Lorentz, polarisation and the rotation factors appropriate to upper layers, and the values of the structure amplitudes were obtained by application of the mosaic crystal formulae. The various layers of $|Fo|$'s were all placed on an approximately absolute scale by comparison with the values of the calculated structure amplitudes obtained from the Patterson function. Throughout the refinement, the scale was adjusted to ensure that $\sum |Fo|$ always equalled $\sum |Fc|$.

3.3 LOCATION OF THE HEAVY ATOM POSITIONS.

The equivalent positions of the space group $P2_12_12_1$ are

$x, \quad y, \quad z;$

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

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

$-x, \quad \frac{1}{2}+y, \quad \frac{1}{2}-z.$

The vectors to be expected between the iodine atoms in this space group with one molecule in the asymmetric unit are

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

The two dimensional Patterson projection P(uv) was computed using 246 coefficients.

Isocalebassine methyl ether di-iodide contains two heavy atoms per asymmetric unit; thus, in the Patterson function projected down the c-axis, there should be peaks at $2x_{I(1)}, \frac{1}{2}$, and $2x_{I(2)}, \frac{1}{2}$ on the line $(u, \frac{1}{2})$, and also peaks at $\frac{1}{2}, \frac{1}{2}-2y_{I(1)}$, and at $\frac{1}{2}, \frac{1}{2}-2y_{I(2)}$ on the line $(\frac{1}{2}, v)$. There should also be two general peaks at $\frac{1}{2}-2x_{I(1)}$, $2y_{I(1)}$ and at $\frac{1}{2}-2x_{I(2)}$, $2y_{I(2)}$.

In addition to these vectors between iodine atoms related by symmetry, there should be four peaks corresponding to vectors between the two separate iodine atoms. These peaks should occur at

$x_{I(1)}-x_{I(2)}$;	$y_{I(1)}-y_{I(2)}$;
$\frac{1}{2}-x_{I(1)}-x_{I(2)}$;	$y_{I(1)}+y_{I(2)}$;
$\frac{1}{2}+x_{I(1)}-x_{I(2)}$;	$\frac{1}{2}-y_{I(1)}-y_{I(2)}$;
$x_{I(1)}+x_{I(2)}$;	$\frac{1}{2}+y_{I(1)}-y_{I(2)}$.

Thus, on the two dimensional Patterson projection, there should be ten peaks, and this was found to be the case. Fourier line sections were calculated through each of these peaks in order that the z coordinates might be determined.

The coordinates of the two heavy atoms obtained from the Patterson function were found to be

	x/a	y/b	z/c
I(1)	0.38667	0.08000	0.56500
I(2)	0.32500	0.64675	0.50000

3.4 SOLUTION OF THE STRUCTURE.

The value of $r = (\text{"}\sum f_H^{2}\text{"}/\text{"}\sum f_L^{2}\text{"})^{\frac{1}{2}} = 1.77$. This figure indicates that of the phases based on the heavy atom coordinates alone, approximately 60% will lie within ± 20° of the correct values for the phase angle (Sim, 1957).

These iodine coordinates, and isotropic temperature factors of $U = 0.05$ Å^2, were employed in the first structure factor calculation. The value of the agreement index, R, summed over all the observed terms, was 42.9%. It was decided to reject structure factors which had an $|F_o|$ value greater than twice the $|F_c|$ value. This ensures that terms which have been approximately correctly phased by the two iodine atoms are used as Fourier coefficients. After this elimination process, 1338 (or 89%) of the original 1502 terms remained.

From the first three dimensional Fourier calculation, based on the iodide ion phases, it was possible to allocate approximate coordinates to eighteen of the forty six light atoms. These were C(7), C(11), C(12), C(13), C(14), C(19), C(20), C(25), C(29), C(30), C(31), C(32), C(33), C(34), N(1), N(3), N(4), and O(1). This gave rise to the partial skeleton shown in fig. III.

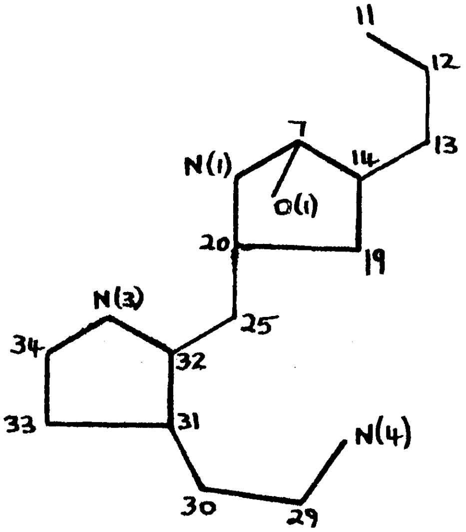
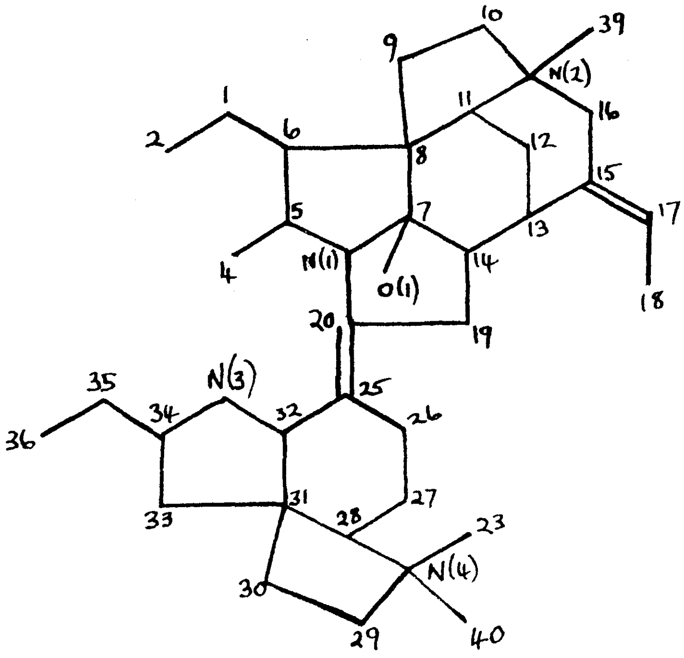


Fig. III.

At this stage, it was not possible to distinguish the individual chemical types.

The eighteen light atoms were included, all as carbon atoms, in the second structure factor calculation. Isotropic temperature factors of U = 0.05 Å were employed. This led to an overall agreement index, R, of 39.3%; that is, an overall decrease in R of 3.6% or 0.2% per extra atom included. 1418 of these were regarded as being safely sign determined, and these were included in the next Fourier synthesis. From this map, it was found to be possible to allocate approximate coordinates to a further twenty one light atoms. This left seven of the light atoms still to be located. These were C(3), C(21), C(22), C(24), C(37), C(38), and C(41). This gave rise to the partial skeleton shown in fig. IV.



On the basis of peak heights, and knowledge of the structures of other members of this series of alkaloids, it was possible to identify the hetero-atoms, and also the position of the oxygen atom. The carbon-carbon double bonds between C(15) and C(17), and also between C(20) and C(25) were tentatively assigned on the evidence of bond length and angle calculations.

The third structure factor calculation was evaluated on the basis of the coordinates of the thirty nine light atoms and two iodine atoms. The light atoms were included as their appropriate chemical type, and once again overall isotropic temperature factors of $U = 0.05$ Å^2 were employed. The value of the overall agreement index was 34.9%; that is a drop of 4.4%. 1431 of these reflections were regarded as safely sign determined, and these were included in the third Fourier synthesis, from which it was possible to distinguish the entire structure, with the exception of C(41).

The forty five light atoms were included, each as their appropriate chemical type, in the evaluation of the fourth set of structure factors. Overall temperature factors of $U = 0.05$ Å^2 were again employed.

This led to an agreement index of 33.8%. A fourth Fourier synthesis was computed from 1457 of these reflections. The position of the remaining atom, C(41), was determined from the resulting electron density map. This Fourier synthesis also indicated that the positions assigned to C(16), C(21), and C(22) were doubtful, as they either gave a very oddly shaped peak, as in the case of C(16), or were very poorly resolved, as in the case of C(21) and C(22). These three atoms were therefore excluded from the next structure factor and phasing calculations.

In the fifth structure factor calculation, forty three light and two heavy atoms were included as their appropriate chemical types. The isotropic temperature factors used in this calculation were the same as those of the previous one, namely, $U = 0.05$ Å^2. The agreement index obtained was $R = 31.2\%$. The subsequent electron density distribution was calculated employing the observed structure amplitudes, and the improved phase constants. Corrections for series termination errors were applied to the atomic coordinates by calculating "back-shift" corrections from a three dimensional $|Fc|$ Fourier synthesis computed using the same phase constants (Booth, 1946).

By comparison of the peak heights of both these Fourier syntheses, adjustments were made to the individual isotropic thermal parameters. From the |Fo| Fourier synthesis, coordinates were assigned to the three light atoms left out of the calculation; that is, C(16), C(21) and C(22). Isotropic temperature factors of U = 0.05 Å^2 were assigned to these three atoms.

This completed the structure elucidation, and the course of the analysis is indicated in Table 1.

3.5 STRUCTURE REFINEMENT.

A sixth cycle of structure factors was calculated on the basis of the coordinates and isotropic temperature factors derived from the fifth Fourier synthesis. The agreement index fell to 30.3%. An |Fo| - |Fc| synthesis was carried out in order to indicate any coordinate or temperature factor adjustments which were required. This resulted in a reduction in the overall agreement index to 30.1%; that is, only 0.2%.

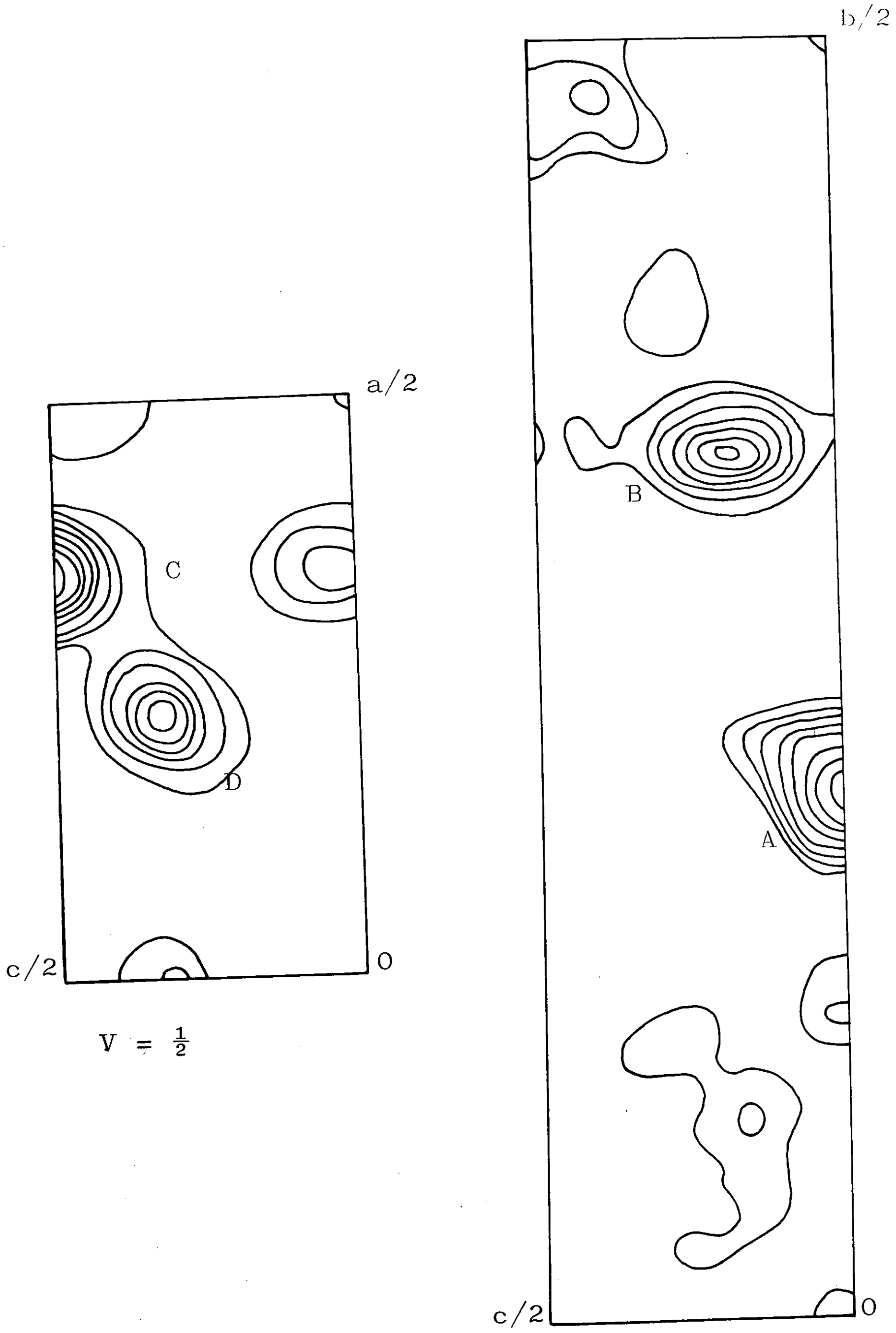
This fall in the agreement index was so disappointing that it was decided that there was very little profit in continuing the refinement in this manner, and that a re-examination of the original data was necessary.

The intensities of reflection were re-indexed, and any errors that were found were corrected. A cycle of structure factors was calculated employing the coordinates and isotropic temperature factors obtained from the difference Fourier synthesis. The overall agreement index that resulted was 28.5%. That is, a drop of 1.6%. In addition to the correction of indexing errors, it was decided to recalculate coordinates for the iodine atoms from a three dimensional Patterson synthesis. The coordinates were determined unambiguously from sections through the three dimensional Patterson function at $(\frac{1}{2},v,w)$, $(u,\frac{1}{2},w)$ and $(u,v,\frac{1}{2})$. These Harker sections are shown in figs. 1 and 2; the iodine-iodine vectors are designated A and B, C and D, and E and F respectively.

The coordinates of the iodide ions were determined to be

	x/a	y/b	z/c
I(1)	0.38350	0.07953	0.58403
I(2)	0.32322	0.64839	0.50000

These were confirmed by consulting the appropriate sections in the three dimensional Patterson function. Although the differences between these coordinates and the coordinates obtained from the line sections are small, nevertheless



V = $\frac{1}{2}$

U = $\frac{1}{2}$

Fig. 1. The Harker Sections at U=$\frac{1}{2}$ and V=$\frac{1}{2}$.

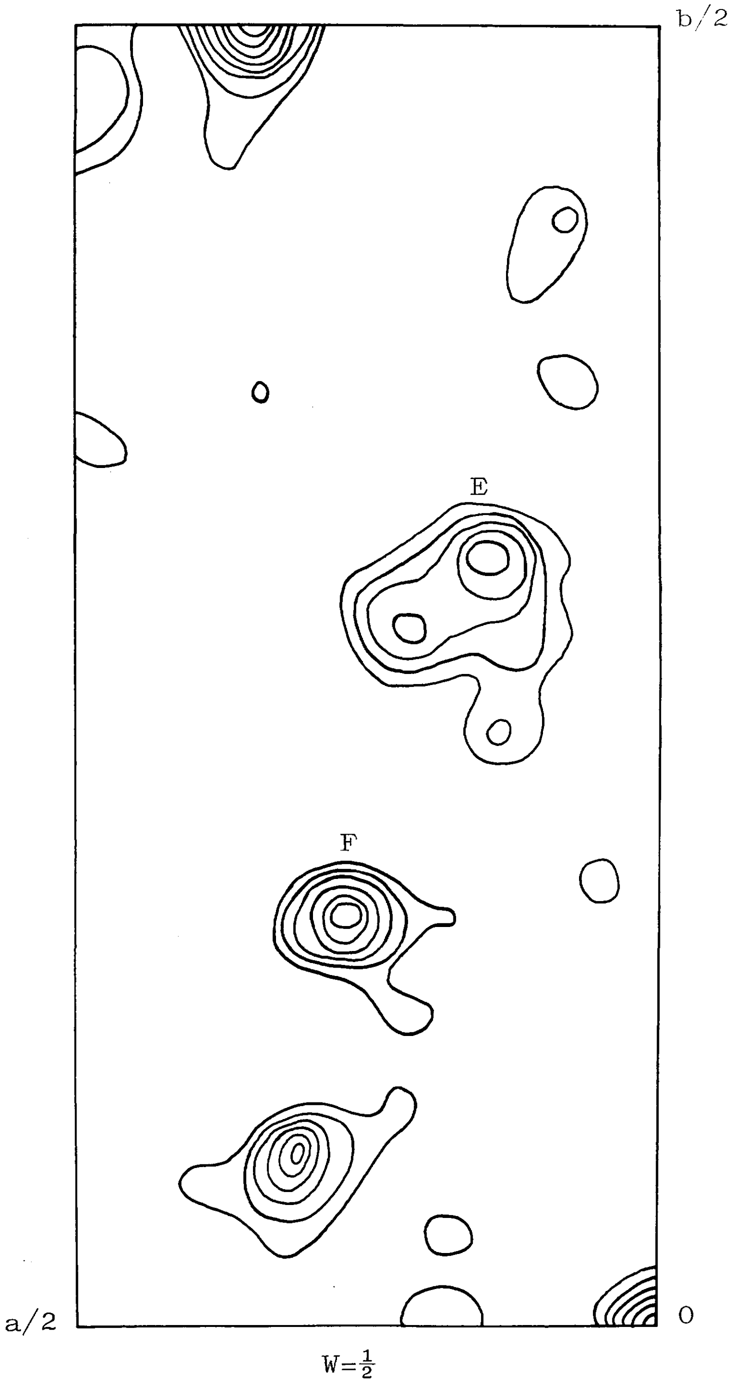


Fig. 2. The Harker Section at W=$\frac{1}{2}$.

the shifts involved are larger than those obtained from the Fourier syntheses.

Structure factors calculated using the iodide ion coordinates, and employing isotropic temperature factors of U = 0.05 Å^2, led to an agreement index, R, of 38.9%. This is 4.0% less than the agreement index obtained from the structure factors calculated using the iodine coordinates obtained from the Patterson projection and the Fourier line sections.

A cycle of structure factors was now calculated using the coordinates and temperature factors for the light atoms which were obtained from the $|Fo| - |Fc|$ synthesis, and using the new iodine coordinates obtained from the three dimensional Patterson synthesis. The temperature factors for iodine were those obtained from the $|Fo| - |Fc|$ calculation. The overall value of the agreement index which resulted was 27.1%. Thus, recalculation of the iodine coordinates, and correction of indexing errors led to a drop in the agreement index of 3.0%.

$|Fo|$ and $|Fc|$ Fouriers based on these coordinates were calculated, and "back-shift" corrections were made. A cycle of structure factors was evaluated, and this led to an agreement index of 26.2%.

The crystals of isocalebassine methyl ether di-iodide which were supplied in order to undertake the present analysis were thought to contain possibly one or more water molecules of crystallisation. Consequently, the Fourier which was calculated at this stage in the analysis was examined in order that the positions of these water molecules might be determined. There were two peaks in the electron density distribution which could have corresponded to water molecules of crystallisation, but when the cycle of structure factors mentioned above was recalculated containing all the atoms, and each of these possible water molecules in turn, it was found that the agreement index increased slightly in each case. Therefore, it was concluded that the crystals which had been supplied did not contain any water molecules of crystallisation. Examination of the Fourier synthesis which was calculated from the structure factors obtained from the final least squares cycle of refinement, confirmed this conclusion.

Refinement of the positional and thermal parameters was continued by the method of least squares. The temperature factors were still refined isotropically. Four cycles only succeeded in reducing the value of the agreement index to 22.8%; that is, a drop of 3.4%.

At this stage, it was decided that the original decision not to carry out any absorption corrections was wrong. Although small crystals were used, they were in the form of 'plates', and so a very approximate "cylindrical crystal" correction was carried out with an assumed crystal radius of 0.03 cm. This gave a value for μR of 3.1; corrections as detailed in International Tables for X-Ray Crystallography, Volume III, were made. Although this correction was very approximate, it was decided to recalculate one cycle of isotropic least squares refinement to discover what effect this correction would have on the agreement index. The value obtained for R was 20.5%, a drop of 2.3%.

One further cycle of isotropic least squares refinement reduced the value of the agreement index to 19.9%. For the next least squares cycle, anisotropic values for the temperature factors were employed for twenty eight of the forty eight atoms. These were C(1) up to C(8), C(17), C(18), C(21), C(22), C(31) up to C(41), N(1) and N(3), O(1) and I(1) and I(2). This resulted in a reduction in the overall agreement index to 17.7%.

In the next cycle of least squares, anisotropic temperature factors were used for all the atoms, and this further reduced the overall agreement index to 16.9%. Two more cycles of least squares concluded the refinement at a value of the agreement index of R = 15.8%. A diagrammatic representation of the course of the analysis is provided in Table 1.

For the structure factor calculations, theoretical scattering factors were employed; those of Berghuis et.al. (1955) for carbon, nitrogen and oxygen, and the Thomas-Fermi, (1935) values for iodine.

The weighting scheme used in the least squares refinement was that of Cruickshank et.al. (1961b); in this

$$\sqrt{w} = 1/\ (p_1 + F + p_2 . F^2)^{\frac{1}{2}}$$

The values used for the constant terms were

$p_1 = 2\ F\ \mathrm{min} = 6.5$

$p_2 = 2/F\ \mathrm{max} = 0.0053$

TABLE 1

COURSE OF THE ANALYSIS

OPERATION	ATOMS INCLUDED	R(%)
2 Dimensional Patterson synthesis, and Fourier line sections.	- - - -	----
1st 3D Fourier synthesis	2(I)	42.9
2nd " " "	2(I) + 18(C)	39.3
3rd " " "	2(I) + 34(C) + 4(N) + O	34.9
4th " " "	2(I) + 40(C) + 4(N) + O	33.8
5th " " "	2(I) + 38(C) + 4(N) + O	31.2
6th " " "	2(I) + 41(C) + 4(N) + O	30.3
7th " " "	" "	30.1
Correction of indexing errors	" "	28.5
3D Patterson synthesis	- - -	----
1st 3D Fourier synthesis (corrected)	2(I)	38.9
7th 3D Fourier synthesis (corrected)	2(I) + 41(C) + 4(N) + O	27.1
8th " " "	" "	26.2
1st least squares cycle	" "	25.9
2nd " " "	" "	24.1
3rd " " "	" "	23.2
4th " " "	" "	22.8

OPERATION	ATOMS INCLUDED	R(%)
Absorption Correction		
5th Least Squares Cycle	2(I) + 41(C) + 4(N) + O	20.5
6th " " "	" "	19.9
7th " " "	" "	17.7
8th " " "	" "	16.9
9th " " "	" "	16.2
10th " " "	" "	15.8

3.6 RESULTS OF THE ANALYSIS.

The final atomic coordinates and anisotropic temperature factor parameters given by the least squares refinement are listed in Tables 2 and 3 respectively. The standard deviations of the final atomic coordinates, which are given in Table 4, were derived from the least squares totals as detailed in section 1.9.

The interatomic bond lengths are listed in Table 5, and the interatomic bond angles are given in Table 6.

Some of the more important intramolecular non-bonded distances are listed in Table 7, and Table 8 gives the shorter intermolecular contacts, which are defined as those contacts less than or equal to four Angstroms. The deviations of the individual atoms from the best planes through the various ring systems are given in Table 9.

In Table 10, the average bond lengths for the different types of bond which occur in the molecule have been worked out. These average values are compared with the standard accepted values for the appropriate bond type. Approximate intramolecular non-bonded distances found from a molecular model are listed in Table 11, and these are compared with the actual values which are given in Table 7.

The observed and calculated structure factors are listed in Table 12, the values given being obtained from the final least squares cycle. The final agreement index, calculated over 1502 observed structure amplitudes is 15.8%. No unobserved structure amplitudes have been included in Table 12.

The final three dimensional electron density distribution over one molecule was calculated from the observed structure amplitudes and phase constants obtained from the final least squares cycle. This is shown in fig. 6 by means of superimposed contour sections drawn parallel to (001). The atomic arrangement corresponding to this is shown in fig. 7 and the packing of the molecules in the crystal as viewed along the c-axis is shown in fig. 8.

Using the formulae given in section 1.9, the standard deviations for the bond lengths and the bond angles were evaluated. The average estimated standard deviation for a carbon-carbon single bond is 0.08 Å, and for a typical tetrahedral angle it is 5°.

3.7 DISCUSSION OF RESULTS.

The constitution and stereochemistry of isocalebassine methyl ether di-iodide as established by this structure analysis are shown in fig. V.

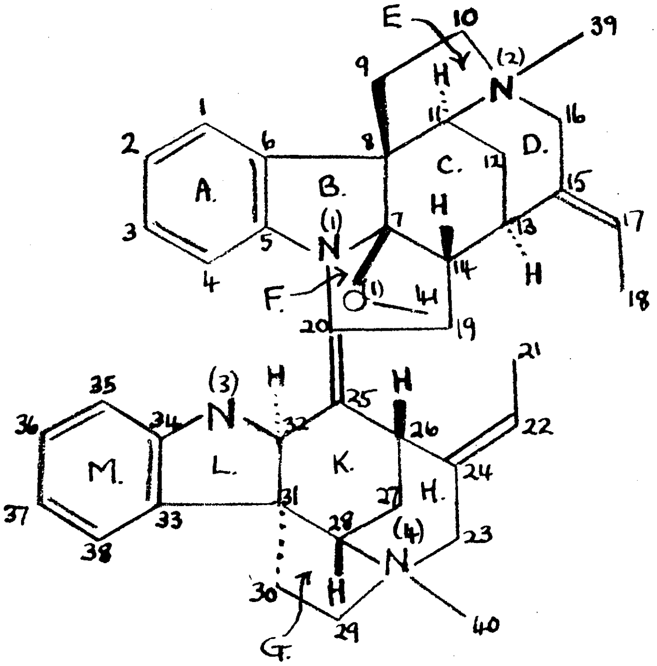


Fig. V.

The structure of isocalebassine consists of two separate ring systems joined by the carbon-carbon double bond between C(20) and C(25). The two parts are cis-fused about this double bond.

As in the structure of α-caryophyllene alcohol (part 2 of this thesis) the bond lengths and interbond angles are not determined with sufficient precision to permit a discussion of apparent differences between chemically equivalent bonds. Table 10 lists the average bond lengths in the molecule, and the accepted values, according to their type.

The average carbon-carbon bond length in the two benzene rings is 1.42 Å, which is in agreement with the expected value of 1.395 Å for a bond between aromatic carbon atoms. The average sp^3-carbon-sp^3-carbon single bond length is 1.58 Å, which is also in agreement with the standard value of 1.545 Å in diamond. The average of the carbon-carbon single bond length between sp^3- and sp^2- hybridised carbon atoms is 1.57 Å. This does not differ significantly from the accepted value of 1.53 Å. In the analyses of two similar alkaloids, caracurine II (McPhail and Sim, 1965), and macusine - A (McPhail, Robertson and Sim, 1963), the values obtained for these carbon-carbon bond lengths were 1.57 Å and 1.47 Å respectively for caracurine II, and 1.57 Å and 1.51 Å respectively in the case of macusine - A. The average value of the carbon-carbon double bond lengths, 1.37 Å, is comparable with that of 1.33 Å reported for ethylene (Bartell and Bonham, 1957).

The average values for the sp^3-hybridised carbon-quaternary nitrogen bond lengths and the sp^3-hybridised carbon-nitrogen bond lengths are 1.50 Å and 1.44 Å respectively. These are not significantly different from the accepted values of 1.48 Å and 1.47 Å, respectively, which are given in Tables of Interatomic Distances, 1958.

The mean length of the aromatic carbon-nitrogen bonds is 1.49 Å. Other values obtained for this bond are 1.47 Å in 2-chloro-4-nitro-aniline (McPhail, 1963), and 1.49 Å in the 4-bromo-3-nitro-benzoic-acid (this thesis, page 112). The average sp^3-carbon-oxygen single bond is 1.50 Å, which is in good agreement with the value of 1.48 Å found in α-caryophyllene alcohol (this thesis page 51), and 1.46 Å in hydroxy-L-proline (Donohue and Trueblood, 1952).

The average interbond angle in the benzene rings is 119.2°, and in the pyrrole rings is 107.6°. Both of these agree with the accepted values (Tables of Interatomic Distances, 1958).

In the two cyclohexane rings, the average interbond angle is 109.6°, and in the two piperidine rings, the average interbond angle is 111.9°. These also are in good agreement with the expected value for a tetrahedral angle. The average interbond angle in the remaining three five-membered rings is 104.0°. Although the difference between this angle and the tetrahedral angle is less than three times the standard deviation of the bond angles, and thus the average value is not significantly less than tetrahedral, it is tempting to presume that there is some evidence for a smaller average angle, due to non-planarity of the ring, as was observed in the case of α-caryophyllene alcohol (this thesis, page 56).

About sp^3-hybridised carbon atoms, the average bond angle is 110.5°, and about the quaternary nitrogens, the average angle is 109.1°. These results are in agreement with the expected value of 109°28' for the tetrahedral angle. The average bond angle about sp^2-hybridised carbon atoms is 122.9°, in good agreement with the expected value of 120°.

Although the average interbond angles in the ring system are in fairly good agreement with the standard values, the individual angles vary over quite a large range. In particular, the values for a tetrahedral angle of 143.2^{o} in C(7), 143.6^{o} in C(14), and 73.5^{o} in the case of C(31); also, the value obtained for a trigonal angle of 159.3^{o} in C(22). There is no particular reason why these large deviations should occur, and it is very difficult to account for them. The reason may be that these atoms have not been completely refined to their correct positions by the least squares process.

Calculations of the best planes through several sets of atoms were carried out employing the method of Schomaker et.al.(1959); the results are summarised in Table 9. Since the atomic parameters are not very accurate, the deviations of individual atoms from some of the planes which have been calculated are rather large. None of these deviations, however, are outside the limits set by the estimated standard deviations of the atomic coordinates.

The atoms N(1), C(1), C(2), C(3), C(4), C(5), C(6), C(7) and C(8) of the indoline system are coplanar within the limits of the standard deviations.

The equation of the best plane through these nine atoms is

$$0.4588\,x - 0.0827\,y + 0.8847\,z - 6.4461 = 0$$

The individual deviations of these atoms are listed in Table 9.

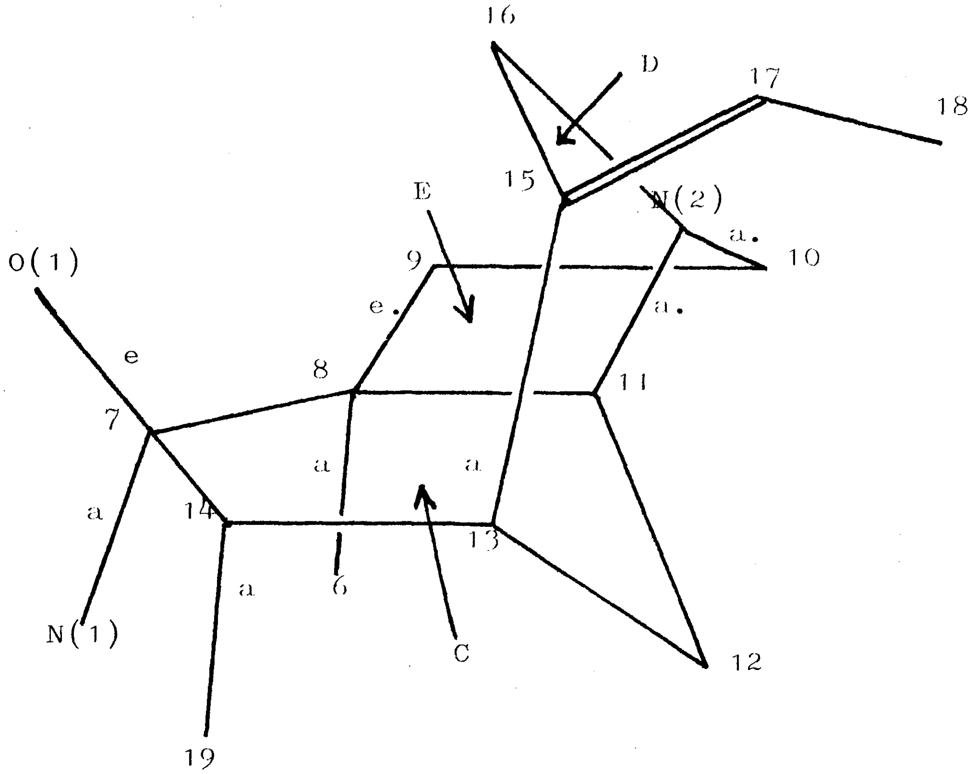
The equation of the best plane through the nine atoms of the second indoline system, C(31), C(32), C(33), C(34), C(35), C(36), C(37), C(38) and N(3) is

$$0.8968\,x - 0.0867\,y - 0.4340\,z - 4.0532 = 0$$

The individual deviations of these atoms are listed in Table 9; no deviation is significant. The best planes through the two indoline systems are mutually inclined at 88°.

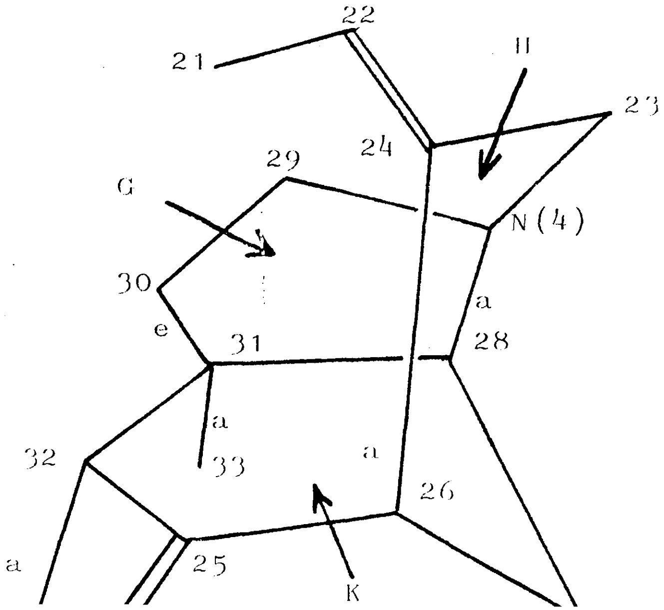
The cyclohexane ring, C, is cis-fused to ring B, and is in the "half-chair" conformation. The atoms C(7), C(8), C(11), C(13) and C(14) are coplanar, while C(12) is displaced by 0.72 Å from the plane. C(14) is displaced a short distance from this plane, but, as suggested earlier in this section, C(14) may not have been correctly refined by the method of least squares. This "half-chair" conformation for a cyclohexane ring cis-fused to an indoline system also occurs in the compound, caracurine II (McPhail and Sim, 1965), which has many structural features similar to isocalebassine.

With respect to this cyclohexane ring, C(9) and O(1) are equatorial, whereas N(1), C(6), N(2), C(15) and C(19) are axial.



The piperidine ring, D, is in the "chair" conformation, C(11), N(2), C(13), and C(15) being coplanar, while C(12) is 0.66 Å and C(16) is 0.46 Å from the best plane through these four atoms, and on opposite sides of it; C(10) is axial with respect to this ring.

In the five-membered ring, E, the atoms C(8), C(9), C(10) and C(11) are coplanar, whereas N(2) is displaced by 0.54 Å from the best plane through these four atoms. Calculation of the best plane through the five atoms, C(7), C(14), C(19), C(20) and N(1) of ring F leads to large deviations of the individual atoms from this plane. Application of the χ^2 test (Fisher and Yates, 1957) indicates that the atoms in ring F cannot be regarded as coplanar since $\sum \Delta^2 = 15.67 \times 10^{-2}$, and $\chi^2 = \sum \Delta^2/\sigma^2 = 43.5$. This leads to a probability, p, of less than 0.001. Leaving out one atom at a time, and calculating the best plane through the remaining four atoms does not lead to any significant improvement in the value of χ^2.



The cyclohexane ring, K, is once again cis-fused to the indoline system, and is in the "half-chair" conformation. The atoms C(25), C(26), C(28), C(31) and C(32) are coplanar, while C(27) is displaced by 1.05 Å from this plane. With respect to this cyclohexane ring, C(30) is equatorial, whereas C(24), N(3), C(33) and N(4) are axial. The piperidine ring, H, is in the "boat" conformation; C(24), C(26), C(28) and N(4) are coplanar, while C(23) is 0.50 Å and C(27) is 0.73 Å from the best plane through these four atoms, and on the same side of it. Although the individual deviations from this plane are rather large, they are all within the limits of the standard deviations of the atoms concerned. With respect to this ring, C(29) is axial.

The atoms C(28), C(29), C(31) and N(4) of the five-membered ring, G, are coplanar within the limits of the standard deviations, while C(30) is displaced 0.66 Å from the best plane through these four atoms.

Thus, in one half of the molecule the piperidine ring is in the "chair" conformation while in the other half of the molecule the piperidine ring is in the "boat" conformation. In the five-membered ring E, the nitrogen atom is displaced from the plane of the ring, while it is a carbon atom which is displaced from the plane of the ring

With respect to the double bond, C(15)-C(17), the atoms C(13) and C(18) are cis, and with respect to the double bond, C(22)-C(24), the atoms C(21) and C(26) are cis.

There is considerable strain involved in the central ring, F, of isocalebassine when the molecule assumes this conformation. This can be seen from the fact that the plane is markedly non-planar. A best plane calculation was carried out through the atoms around the double bond C(20)-C(25). The amount of strain involved in assuming this conformation can be seen by observing the deviation of the calculated planes from ideal behaviour. Mean planes were calculated through the two sets of atoms C(20), C(19), C(25) and N(1), and also through C(20), C(25), C(26) and C(32). The individual deviations of these atoms from the planes are listed in Table 9. These two planes were found to be mutually inclined at 13.5°, significantly different from the ideal value of 0.0°.

Some idea of the factors causing this strain can be obtained from the construction of a molecular model on the basis of standard bond lengths and angles. The conformation adopted by this model differs quite considerably from that described above.

The piperidine ring, H, assumes a distorted "boat" conformation, and in the cyclohexane ring, K, C(25), C(27), C(28), C(31) and C(32) are approximately coplanar and C(26) is displaced out of the plane through these five atoms. The approximate values for some of the intramolecular non-bonded distances in this model are given in Table 11, and are compared with the actual values obtained from the final atomic coordinates. From this table, it can be seen that the non-bonded distances C(4).........C(32), C(4)........N(3), C(19)........C(21), C(20)........C(21), and N(1)........C(21) are much longer than would be expected on the basis of the molecular model. In order to reduce any non-bonded interactions, the two parts of the molecule are rotated slightly about the C(20)-C(25) bond as axis, and this rotation is accompanied by mutual repulsion of these two parts. From examination of the molecular model, this repulsion should lead to a shortening of the N(3)........O(1) distance, and, in fact, this distance does shorten from 4.5 Å to 3.5 Å.

The molecular packing, as viewed along the c-axis is shown in fig. 8, and the intermolecular contacts less than or equal to 4.0 Å are listed in Table 8. The intermolecular contacts all correspond to normal Van der Waals' separations.

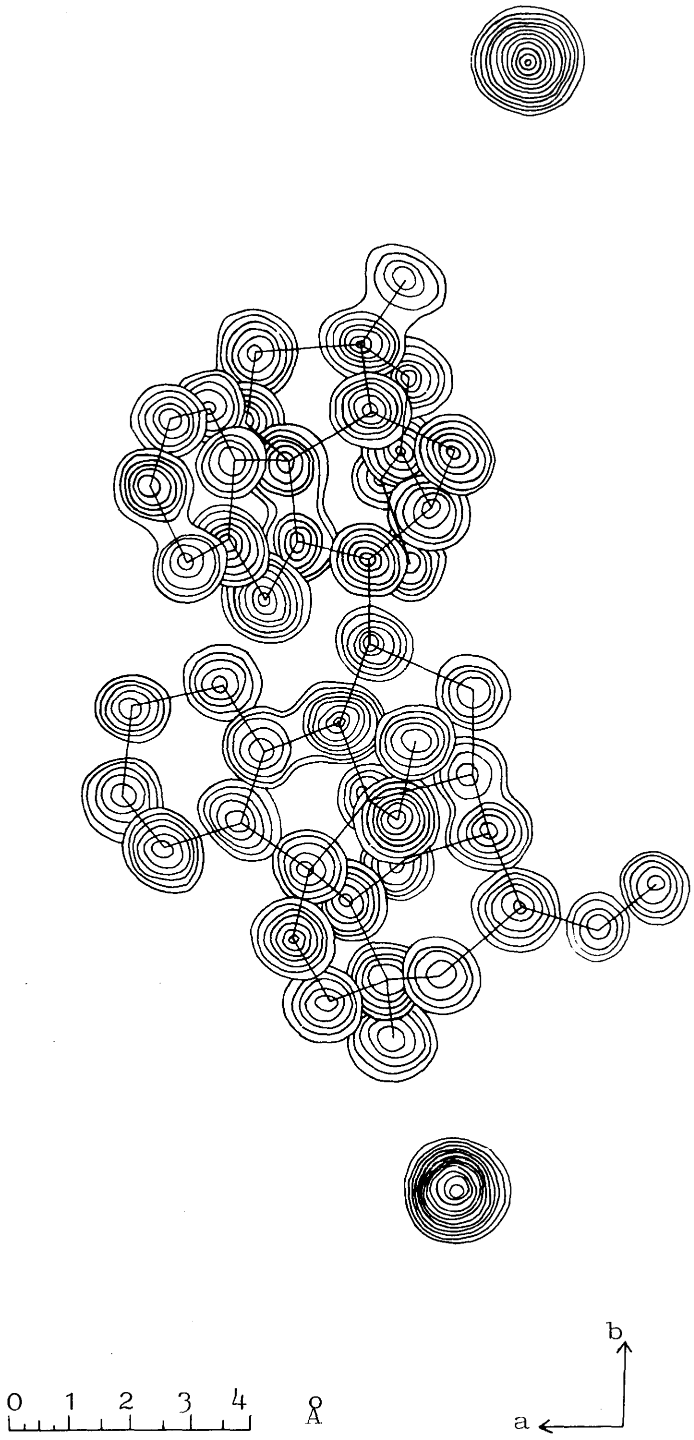


Fig. 6. The final three dimensional electron density distribution over one molecule of isocalebassine methyl ether di-iodide. The superimposed contour sections are drawn parallel to (001).

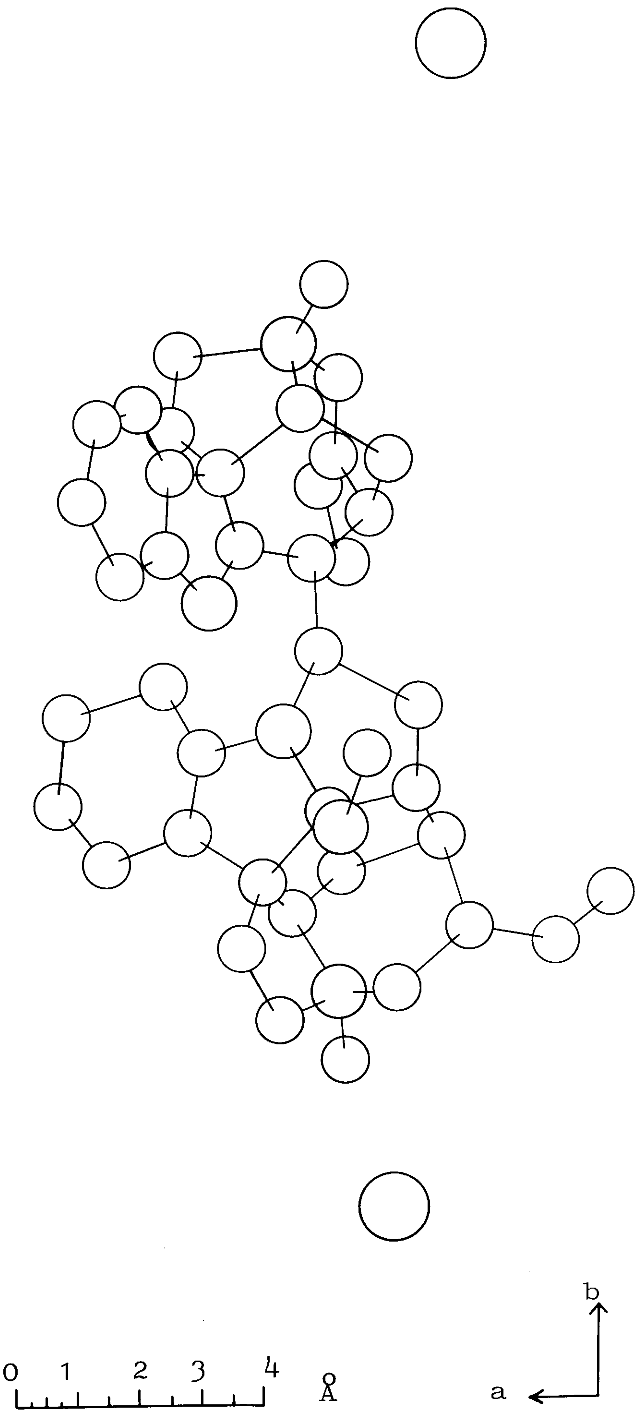


Fig. 7. The atomic arrangement corresponding to Fig. 6.

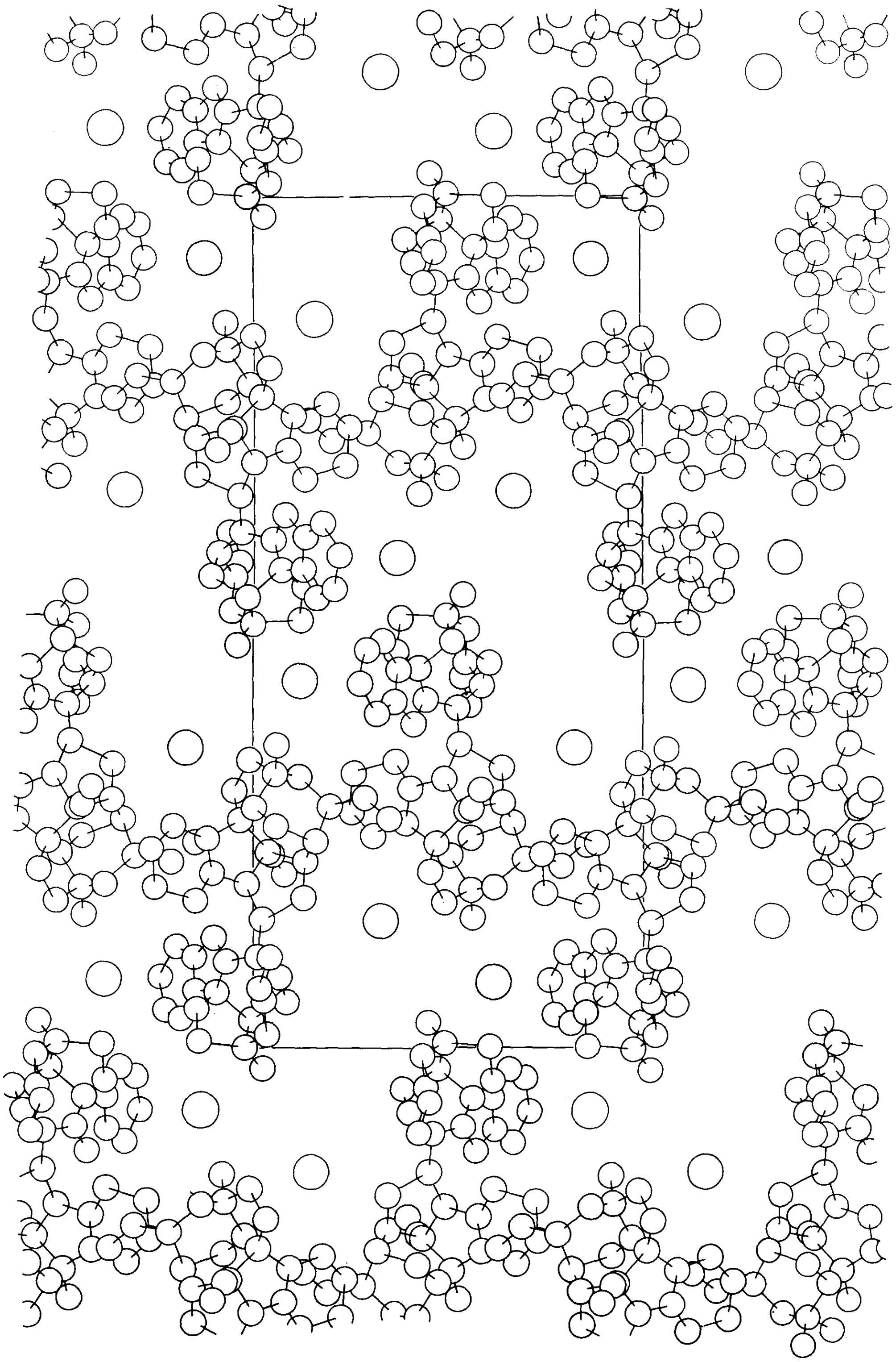


Fig. 8. The arrangement of the molecules in the crystal as viewed along the c-axis.

TABLE 2.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

FINAL ATOMIC COORDINATES.

ATOM.	x/a	y/b	z/c
C(1)	0.6852	0.2535	0.2883
C(2)	0.7480	0.2781	0.2298
C(3)	0.7359	0.3182	0.2411
C(4)	0.6611	0.3360	0.3190
C(5)	0.5953	0.3088	0.3675
C(6)	0.6137	0.2683	0.3409
C(7)	0.4602	0.2780	0.4578
C(8)	0.5219	0.2444	0.3796
C(9)	0.5353	0.2129	0.4986
C(10)	0.5093	0.1737	0.4231
C(11)	0.4886	0.2246	0.2406
C(12)	0.4327	0.2506	0.1424
C(13)	0.3409	0.2606	0.2158
C(14)	0.4003	0.2841	0.3269
C(15)	0.2939	0.2228	0.2590
C(16)	0.3627	0.1966	0.3494
C(17)	0.2096	0.2131	0.2373

TABLE 2 (Cont.).

ATOM.	x/a	y/b	z/c
C(18)	0.1434	0.2332	0.1598
C(19)	0.3765	0.3279	0.3168
C(20)	0.4612	0.3499	0.3819
C(21)	0.4450	0.3959	-0.0326
C(22)	0.4615	0.4271	0.0889
C(23)	0.4515	0.4892	0.2390
C(24)	0.4489	0.4466	0.2102
C(25)	0.4779	0.3911	0.3866
C(26)	0.4059	0.4257	0.3409
C(27)	0.3989	0.4479	0.4815
C(28)	0.4888	0.4655	0.4710
C(29)	0.5951	0.5012	0.3506
C(30)	0.6073	0.4580	0.3990
C(31)	0.5756	0.4437	0.5419
C(32)	0.5477	0.3999	0.5076
C(33)	0.6136	0.4427	0.6874
C(34)	0.6326	0.4003	0.7260
C(35)	0.6545	0.4009	0.8639
C(36)	0.7069	0.4242	0.9555
C(37)	0.6926	0.4642	0.9052
C(38)	0.6506	0.4723	0.7755

TABLE 2 (Cont.).

ATOM.	x/a	y/b	z/c
C(39)	0.4317	0.1617	0.1933
C(40)	0.4701	0.5404	0.4198
C(41)	0.4186	0.3069	0.6901
N(1)	0.5059	0.3139	0.4336
N(2)	0.4540	0.1860	0.3148
N(3)	0.5828	0.3777	0.6236
N(4)	0.4974	0.5006	0.3680
O(1)	0.4558	0.2738	0.6051
I(1)	0.3842	0.0795	0.5782
I(2)	0.3234	0.6483	0.4989

TABLE 3.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

FINAL ANISOTROPIC TEMPERATURE FACTORS (Å^2).

ATOM.	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	0.0291	0.0171	0.0357	0.0326	-0.0525	-0.0097
C(2)	0.0448	0.0381	0.0120	-0.0364	-0.0009	0.0192
C(3)	0.0367	0.0154	0.1269	0.0986	-0.0517	-0.0759
C(4)	0.0609	0.0185	0.0192	0.0129	0.0838	0.0122
C(5)	0.0129	0.0198	0.0175	0.0488	-0.0114	0.0118
C(6)	0.0136	0.0585	0.0536	0.0307	-0.0165	-0.0561
C(7)	0.0536	0.0109	0.0335	0.0355	-0.0236	0.0189
C(8)	0.0387	0.0166	0.0226	0.0066	-0.0078	0.0398
C(9)	0.0622	0.0331	0.0361	0.0521	-0.0184	-0.0025
C(10)	0.0355	0.0265	0.0472	-0.0536	-0.0645	0.0203
C(11)	0.0264	0.0383	0.0160	0.0370	-0.0368	-0.0150
C(12)	0.0657	0.0834	0.1548	0.0350	-0.0970	0.0142
C(13)	0.0293	0.0268	0.0178	0.0447	0.0449	-0.0328
C(14)	0.0377	0.0390	0.0638	-0.0124	0.0408	0.0156
C(15)	0.0138	0.0128	0.0342	-0.0409	-0.0278	-0.0029
C(16)	0.0329	0.0263	0.0600	0.0111	-0.0815	-0.0380
C(17)	0.0510	0.0509	0.0468	-0.0388	0.1133	-0.0375
C(18)	0.0559	0.1274	0.0139	0.1648	-0.0405	0.0185

TABLE 3 (Cont.).

ATOM.	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(19)	0.0321	0.0391	0.0290	-0.0232	0.0077	0.0045
C(20)	0.0149	0.0132	0.0184	0.0279	-0.0015	0.0037
C(21)	0.0167	0.0825	0.0248	0.0408	-0.0306	-0.0063
C(22)	0.0181	0.0615	0.1001	-0.0337	0.0348	-0.0096
C(23)	0.0133	0.0183	0.0147	-0.0173	-0.0134	-0.0069
C(24)	0.0110	0.0149	0.0210	0.0247	-0.0027	0.0153
C(25)	0.0182	0.0128	0.0110	0.0075	-0.0017	0.0059
C(26)	0.0704	0.0140	0.0373	0.0211	-0.0252	0.0632
C(27)	0.0125	0.0311	0.0446	0.0507	0.0093	0.0265
C(28)	0.0145	0.0118	0.0281	0.0275	-0.0104	0.0043
C(29)	0.0503	0.0353	0.0217	0.0595	-0.0349	-0.0082
C(30)	0.0268	0.0104	0.0110	0.0385	0.0315	0.0145
C(31)	0.0270	0.0215	0.0483	0.0171	0.0736	0.0373
C(32)	0.0418	0.0307	0.0228	-0.0307	0.0751	0.0391
C(33)	0.0106	0.0142	0.0269	0.0057	-0.0887	-0.0561
C(34)	0.0527	0.0445	0.0169	-0.0181	0.0126	-0.0098
C(35)	0.0221	0.0325	0.0204	-0.0360	-0.0496	0.0126
C(36)	0.0576	0.0535	0.0644	0.1321	0.0579	0.0059
C(37)	0.0278	0.0211	0.0535	0.0166	0.0763	-0.0343
C(38)	0.0538	0.0331	0.0544	0.0359	0.0440	0.0457

TABLE 3 (Cont.).

ATOM.	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(39)	0.0232	0.0214	0.0782	-0.0567	-0.0214	-0.0474
C(40)	0.0490	0.0322	0.0711	-0.0796	-0.1268	0.0178
C(41)	0.0447	0.0197	0.0195	-0.1138	0.0430	-0.0277
N(1)	0.0366	0.0247	0.0337	0.0215	-0.0075	-0.0037
N(2)	0.0560	0.0522	0.0881	0.0335	-0.0522	0.0058
N(3)	0.0481	0.0190	0.0229	-0.0427	-0.0177	-0.0142
N(4)	0.0400	0.0274	0.0228	0.0320	0.0254	-0.0042
O(1)	0.0448	0.0244	0.0202	-0.0352	-0.0973	-0.0164
I(1)	0.0620	0.0426	0.0445	0.0260	0.0236	-0.0084
I(2)	0.0695	0.0625	0.0647	0.0125	0.0408	0.0103

TABLE 4.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

STANDARD DEVIATIONS OF THE FINAL ATOMIC COORDINATES (Å).

ATOM.	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0.054	0.044	0.053
C(2)	0.067	0.061	0.060
C(3)	0.066	0.054	0.078
C(4)	0.061	0.047	0.056
C(5)	0.053	0.053	0.053
C(6)	0.056	0.062	0.057
C(7)	0.056	0.043	0.054
C(8)	0.060	0.054	0.062
C(9)	0.068	0.062	0.070
C(10)	0.060	0.058	0.070
C(11)	0.062	0.060	0.065
C(12)	0.082	0.085	0.088
C(13)	0.059	0.056	0.058
C(14)	0.065	0.066	0.067
C(15)	0.051	0.048	0.058
C(16)	0.060	0.055	0.057
C(17)	0.068	0.067	0.072

TABLE 4 (Cont.).

ATOM.	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(18)	0.074	0.089	0.066
C(19)	0.061	0.062	0.063
C(20)	0.046	0.045	0.050
C(21)	0.054	0.067	0.058
C(22)	0.050	0.066	0.077
C(23)	0.051	0.046	0.055
C(24)	0.048	0.046	0.056
C(25)	0.049	0.046	0.054
C(26)	0.067	0.061	0.064
C(27)	0.053	0.052	0.062
C(28)	0.046	0.045	0.055
C(29)	0.062	0.061	0.061
C(30)	0.054	0.044	0.051
C(31)	0.055	0.055	0.068
C(32)	0.057	0.057	0.061
C(33)	0.049	0.046	0.050
C(34)	0.068	0.062	0.060
C(35)	0.059	0.056	0.055
C(36)	0.069	0.070	0.076
C(37)	0.056	0.049	0.063
C(38)	0.066	0.063	0.069

TABLE 4 (Cont.).

ATOM.	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(39)	0.053	0.050	0.064
C(40)	0.066	0.057	0.074
C(41)	0.059	0.052	0.059
N(1)	0.044	0.037	0.046
N(2)	0.061	0.059	0.063
N(3)	0.050	0.043	0.049
N(4)	0.047	0.047	0.052
O(1)	0.038	0.034	0.039
I(1)	0.005	0.004	0.005
I(2)	0.005	0.005	0.005

TABLE 5.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

BOND LENGTHS. (Å).

C(1)	-	C(2)	1.38	C(13)	-	C(15)	1.51
C(1)	-	C(6)	1.30	C(14)	-	C(19)	1.51
C(2)	-	C(3)	1.36	C(15)	-	C(16)	1.63
C(3)	-	C(4)	1.49	C(15)	-	C(17)	1.32
C(4)	-	C(5)	1.43	C(16)	-	N(2)	1.46
C(5)	-	C(6)	1.41	C(17)	-	C(18)	1.43
C(5)	-	N(1)	1.51	C(19)	-	C(20)	1.61
C(6)	-	C(8)	1.64	C(20)	-	N(1)	1.47
C(7)	-	C(8)	1.65	C(20)	-	C(25)	1.40
C(7)	-	C(14)	1.60	C(21)	-	C(22)	1.62
C(7)	-	N(1)	1.40	C(22)	-	C(24)	1.39
C(7)	-	O(1)	1.49	C(23)	-	C(24)	1.45
C(8)	-	C(9)	1.60	C(23)	-	N(4)	1.51
C(8)	-	C(11)	1.62	C(24)	-	C(26)	1.62
C(9)	-	C(10)	1.56	C(25)	-	C(26)	1.65
C(10)	-	N(2)	1.43	C(25)	-	C(32)	1.63
C(11)	-	C(12)	1.56	C(26)	-	C(27)	1.60
C(11)	-	N(2)	1.58	C(27)	-	C(28)	1.47
C(12)	-	C(13)	1.60	C(28)	-	C(31)	1.65
C(13)	-	C(14)	1.63	C(28)	-	N(4)	1.57

TABLE 5 (Cont.).

C(29) -	N(4)	1.48	C(34) -	N(3)	1.48
C(29) -	C(30)	1.53	C(34) -	C(35)	1.42
C(30) -	C(31)	1.58	C(35) -	C(36)	1.44
C(31) -	C(32)	1.56	C(36) -	C(37)	1.45
C(31) -	C(33)	1.57	C(37) -	C(38)	1.47
C(32) -	N(3)	1.48	C(39) -	N(2)	1.50
C(33) -	C(34)	1.50	C(40) -	N(4)	1.49
C(33) -	C(38)	1.44	C(41) -	O(1)	1.51

TABLE 6.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

BOND ANGLES ($^{\circ}$).

C(2) -C(1) -C(6)	121	C(7) -C(8) -C(9)	99
C(1) -C(2) -C(3)	117	C(7) -C(8) -C(11)	121
C(2) -C(3) -C(4)	123	C(9) -C(8) -C(11)	114
C(3) -C(4) -C(5)	117	C(8) -C(9) -C(10)	99
C(4) -C(5) -C(6)	114	C(9) -C(10)-N(2)	106
C(4) -C(5) -N(1)	134	C(8) -C(11)-C(12)	119
C(6) -C(5) -N(1)	111	C(8) -C(11)-N(2)	92
C(1) -C(6) -C(5)	128	C(12)-C(11)-N(2)	125
C(1) -C(6) -C(8)	127	C(11)-C(12)-C(13)	107
C(5) -C(6) -C(8)	105	C(12)-C(13)-C(15)	111
C(8) -C(7) -C(14)	91	C(12)-C(13)-C(14)	87
C(8) -C(7) -N(1)	103	C(14)-C(13)-C(15)	118
C(8) -C(7) -O(1)	116	C(7) -C(14)-C(13)	144
C(14)-C(7) -N(1)	91	C(7) -C(14)-C(19)	108
C(14)-C(7) -O(1)	143	C(13)-C(14)-C(19)	107
N(1) -C(7) -O(1)	106	C(13)-C(15)-C(16)	108
C(6) -C(8) -C(7)	105	C(13)-C(15)-C(17)	127
C(6) -C(8) -C(9)	113	C(16)-C(15)-C(17)	124
C(6) -C(8) -C(11)	105	C(15)-C(16)-N(2)	126

TABLE 6 (Cont.).

C(15)-C(17)-C(18)	130	C(29)-C(30)-C(31)	122
C(14)-C(19)-C(20)	103	C(28)-C(31)-C(30)	74
C(19)-C(20)-C(25)	127	C(28)-C(31)-C(32)	96
C(19)-C(20)-N(1)	98	C(28)-C(31)-C(33)	134
C(25)-C(20)-N(1)	135	C(30)-C(31)-C(32)	99
C(21)-C(22)-C(24)	159	C(30)-C(31)-C(33)	138
C(24)-C(23)-N(4)	115	C(32)-C(31)-C(33)	106
C(22)-C(24)-C(23)	129	C(25)-C(32)-C(31)	120
C(22)-C(24)-C(26)	124	C(25)-C(32)-N(3)	136
C(23)-C(24)-C(26)	106	C(31)-C(32)-N(3)	102
C(20)-C(25)-C(26)	124	C(31)-C(33)-C(34)	109
C(20)-C(25)-C(32)	109	C(31)-C(33)-C(38)	134
C(26)-C(25)-C(32)	120	C(34)-C(33)-C(38)	115
C(24)-C(26)-C(25)	105	C(33)-C(34)-C(35)	106
C(24)-C(26)-C(27)	123	C(33)-C(34)-N(3)	102
C(25)-C(26)-C(27)	97	C(35)-C(34)-N(3)	143
C(26)-C(27)-C(28)	94	C(34)-C(35)-C(36)	139
C(27)-C(28)-C(31)	121	C(35)-C(36)-C(37)	101
C(27)-C(28)-N(4)	115	C(36)-C(37)-C(38)	123
C(31)-C(28)-N(4)	123	C(33)-C(38)-C(37)	126
C(30)-C(29)-N(4)	94	C(5) -N(1) -C(7)	115

TABLE 6 (Cont.).

C(5) -N(1) -C(20)	110	C(32)-N(3) C(34)	118
C(7) -N(1) -C(20)	122	C(23)-N(4) -C(28)	110
C(10)-N(2) -C(11)	114	C(23)-N(4) -C(29)	111
C(10)-N(2) -C(16)	116	C(23)-N(4) -C(40)	114
C(10)-N(2) -C(39)	126	C(28)-N(4) -C(29)	100
C(11)-N(2) -C(16)	103	C(28)-N(4) -C(40)	115
C(11)-N(2) -C(39)	98	C(29)-N(4) -C(40)	108
C(16)-N(2) -C(39)	96	C(7) -O(1) -C(41)	121

TABLE 7.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

SOME INTRAMOLECULAR NON-BONDED DISTANCES (Å).

C(1)......C(7)	3.87	C(7)......C(9)	2.48
C(1)......C(8)	2.64	C(7)......C(10)	3.58
C(1)......N(1)	3.67	C(7)......C(15)	3.69
C(2)......C(8)	3.88	C(7)......C(16)	3.27
C(3)......N(1)	3.96	C(7)......C(20)	2.52
C(4)......C(8)	3.75	C(7)......C(25)	3.85
C(4)......C(20)	3.10	C(7)......C(41)	2.60
C(4)......C(25)	3.38	C(7)......N(2)	3.39
C(4)......C(32)	3.32	C(8)......C(16)	2.89
C(4)......C(34)	4.60	C(8)......C(19)	3.60
C(4)......N(3)	3.55	C(8)......C(20)	3.64
C(5)......C(12)	3.85	C(8)......N(2)	2.29
C(5)......C(20)	2.44	C(8)......O(1)	2.66
C(5)......C(25)	3.27	C(8)......C(15)	3.70
C(5)......C(32)	3.43	C(9)......C(11)	2.71
C(5)......N(3)	3.45	C(9)......C(16)	3.04
C(5)......O(1)	3.38	C(9)......N(1)	3.46
C(6)......C(12)	3.42	C(9)......O(1)	2.59
C(6)......O(1)	3.56	C(10)......C(11)	2.52

TABLE 7 (Cont.).

C(10).....C(12)	3.98	C(16).....O(1)	3.90
C(10).....O(1)	3.89	C(19).....C(21)	4.30
C(11).....C(15)	2.93	C(19).....C(22)	4.20
C(11).....C(16)	2.38	C(19).....C(24)	4.20
C(11).....C(19)	3.91	C(19).....C(26)	3.30
C(11).....N(1)	3.56	C(19).....C(32)	4.00
C(12).....C(17)	3.70	C(19).....C(25)	2.69
C(12).....N(1)	3.77	C(20).....C(21)	4.40
C(13).....C(17)	2.54	C(20).....C(22)	3.91
C(13).....C(18)	3.16	C(20).....C(26)	2.70
C(13).....C(19)	2.52	C(20).....C(27)	3.55
C(13).....C(20)	3.86	C(20).....C(28)	3.98
C(13).....N(1)	3.75	C(20).....C(31)	3.92
C(14).....C(16)	2.99	C(20).....C(32)	2.46
C(14).....C(21)	5.20	C(20).....N(3)	3.17
C(14).....C(25)	3.81	C(21).....C(24)	2.96
C(15).....C(18)	2.49	C(21).....C(26)	3.92
C(15).....C(19)	3.77	C(21).....N(1)	5.50
C(15).....C(39)	2.98	C(22).....C(26)	2.66
C(15).....N(2)	2.76	C(22).....C(23)	2.57
C(16).....C(17)	2.62	C(22).....C(25)	3.23
C(16).....C(18)	3.99	C(22).....C(30)	3.94
C(16).....C(39)	2.21	C(22).....N(4)	3.76

TABLE 7 (Cont.).

C(23).....C(25)	3.62	C(27).....N(3)	3.89
C(23).....C(29)	2.46	C(28).....C(33)	2.97
C(23).....C(30)	3.02	C(28).....C(34)	3.99
C(23).....C(31)	3.87	C(28).....C(38)	3.91
C(23).....C(40)	2.51	C(28).....N(3)	3.60
C(24).....C(29)	3.18	C(29).....C(32)	3.80
C(24).....C(30)	3.06	C(30).....C(32)	2.40
C(24).....C(31)	3.83	C(30).....N(3)	3.52
C(24).....C(32)	3.67	C(31).....C(35)	3.72
C(24).....C(40)	3.79	C(31).....C(38)	2.77
C(24).....C(25)	2.60	C(31).....N(4)	2.83
C(25).....C(27)	2.43	C(32).....C(35)	3.91
C(25).....C(28)	2.63	C(32).....C(38)	3.93
C(25).....C(30)	2.96	C(32).....N(1)	3.03
C(25).....N(1)	2.65	C(38).....N(3)	3.65
C(25).....N(3)	2.88	C(41).....N(1)	2.89
C(25).....N(4)	3.67	C(41).....N(3)	3.48
C(26).....C(29)	3.80	N(1)......N(3)	3.08
C(26).....C(30)	3.26	N(1)......O(1)	2.31
C(26).....N(1)	4.01	N(3)......O(1)	3.96
C(26).....N(4)	2.87		

TABLE 8.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

INTERMOLECULAR CONTACTS LESS THAN 4 Å.

C(21).....C(35)$_{II}$	3.32	C(2)......C(41)$_{I}$	3.91
C(29).....C(37)$_{III}$	3.44	C(22).....C(36)$_{II}$	3.92
O(1)......C(18)$_{I}$	3.68	C(41).....C(18)$_{I}$	3.93
C(21).....C(34)$_{II}$	3.72	C(2)......O(1)$_{I}$	3.93
C(22).....C(35)$_{II}$	3.78	C(30).....C(37)$_{III}$	3.97
N(3)......C(17)$_{I}$	3.84	C(34).....C(17)$_{I}$	3.98
C(38).....I(1)$_{IV}$	3.90	C(29).....C(38)$_{III}$	3.99

The subscripts refer to the following equivalent positions.

I	$\frac{1}{2} + x$;	$\frac{1}{2} - y$;	$1 - z$.
II	x;	y;	$-1 + z$.
III	$3/2 - x$;	$1 - y$;	$-\frac{1}{2} + z$.
IV	$1 - x$;	$\frac{1}{2} + y$;	$3/2 - z$.

TABLE 9.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

DEVIATIONS FROM THE BEST PLANES THROUGH SETS OF ATOMS. (Å)

(a). PLANE DEFINED BY C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8) and N(1).

ATOM.	DEVIATION.	ATOM.	DEVIATION.
C(1)	-0.13	C(6)	-0.06
C(2)	0.02	C(7)	-0.02
C(3)	0.12	C(8)	0.16
C(4)	-0.01	N(1)	-0.02
C(5)	-0.06		

(b). PLANE (C) DEFINED BY C(7),C(8),C(11),C(13) and C(14).

ATOM	DEVIATION	ATOM	DEVIATION
C(7)	-0.14	C(13)	-0.14
C(8)	-0.00	C(14)	0.24
C(11)	0.04	C(12)	0.73

(c). PLANE (D) DEFINED BY C(11),C(13),C(15) and N(2).

ATOM	DEVIATION	ATOM	DEVIATION
C(11)	0.07	N(2)	-0.07
C(13)	-0.07	C(12)	0.67
C(15)	0.07	C(16)	-0.46

TABLE 9 (Cont.).

(d). PLANE (E) DEFINED BY C(8),C(9),C(10) and C(11).

ATOM	DEVIATION	ATOM	DEVIATION
C(8)	0.00	C(11)	-0.00
C(9)	-0.00	N(2)	-0.54
C(10)	0.00		

(e) PLANE (F) DEFINED BY C(7),C(14),C(19),C(20) and N(1).

ATOM	DEVIATION	ATOM	DEVIATION
C(7)	-0.23	C(20)	-0.05
C(14)	0.23	N(1)	0.15
C(19)	-0.16		

(f) PLANE DEFINED BY C(31),C(32),C(33),C(34),C(35),C(36), C(37),C(38) and N(3).

ATOM	DEVIATION	ATOM	DEVIATION
C(31)	0.06	C(36)	0.08
C(32)	-0.04	C(37)	-0.00
C(33)	-0.06	C(38)	-0.03
C(34)	0.15	N(3)	-0.01
C(35)	-0.15		

(g) PLANE (G) DEFINED BY C(28),C(29),C(31) and N(4).

ATOM	DEVIATION	ATOM	DEVIATION
C(28)	0.04	N(4)	-0.04
C(29)	0.02	C(30)	0.66
C(31)	-0.02		

TABLE 9 (Cont.).

(h). PLANE (H) DEFINED BY C(24),C(26),C(28) and N(4).

ATOM	DEVIATION	ATOM	DEVIATION
C(24)	0.16	N(4)	-0.17
C(26)	-0.18	C(23)	-0.50
C(28)	0.19	C(27)	-0.73

(i) PLANE (K) DEFINED BY C(25),C(26),C(28),C(31) and C(32).

ATOM	DEVIATION	ATOM	DEVIATION.
C(25)	0.10	C(31)	0.10
C(26)	-0.02	C(32)	-0.14
C(28)	-0.04	C(27)	-1.05

(j) PLANE DEFINED BY C(19),C(20),C(25) and N(1).

ATOM	DEVIATION	ATOM	DEVIATION
C(19)	-0.00	C(25)	-0.01
C(20)	0.01	N(1)	-0.00

(k) PLANE DEFINED BY C(20),C(25),C(26) and C(32).

ATOM	DEVIATION	ATOM	DEVIATION
C(20)	-0.06	C(26)	-0.06
C(25)	-0.17	C(32)	-0.05

TABLE 10.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

AVERAGE BOND LENGTHS IN THE MOLECULE. (Å).

BOND.	NUMBER OF BONDS.	MEAN VALUE	STANDARD VALUE
CARBON-CARBON (Aromatic)	12	1.42	1.395
CARBON(sp^3)-CARBON(sp^3)	15	1.58	1.545
CARBON(sp^3)-CARBON(sp^2)	9	1.56	1.53
CARBON(sp^2)-CARBON(sp^2)	3	1.37	1.337
CARBON(sp^3)-CARBON (Aromatic)	2	1.60	1.525
CARBON(sp^3)-NITROGEN (Quaternary)	8	1.50	1.479
CARBON(sp^3)-NITROGEN (Trigonal)	2	1.44	1.472
CARBON(Aromatic)-NITROGEN (Trigonal).	2	1.49	1.47
CARBON(sp^3)-OXYGEN.	2	1.50	1.43

TABLE 11.

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

COMPARISON OF SOME INTRAMOLECULAR NON-BONDED CONTACTS. (Å)

	MOLECULAR MODEL	CALCULATED VALUE FROM TRUE CONFORMATION
C(4)......C(32)	2.3	3.3
C(4)......C(34)	3.7	4.6
C(4)......N(3)	2.9	3.6
C(14).....C(21)	4.4	5.2
C(19).....C(21)	3.4	4.3
C(19).....C(22)	3.9	4.2
C(19).....C(24)	3.9	4.2
C(19).....C(26)	2.9	3.3
C(19).....C(32)	3.9	4.0
C(20).....C(21)	3.4	4.4
C(20).....C(22)	3.7	3.9
C(20).....N(3)	2.8	3.2
C(21).....N(1)	4.1	5.5
C(32).....N(1)	2.8	3.0
N(1)......N(3)	2.6	3.1
N(3)......C(41)	4.5	3.5
N(3)......O(1)	4.5	4.0

TABLE 12 (Overleaf).

ISOCALEBASSINE METHYL ETHER DI-IODIDE.

THE OBSERVED AND CALCULATED STRUCTURE AMPLITUDES.

H	K	L	Fo	Fc
0	4	0	40.9	33.3
0	6	0	116.9	123.0
0	8	0	110.2	93.8
0	10	0	144.3	113.7
0	12	0	222.2	177.2
0	14	0	215.1	172.7
0	16	0	134.1	101.6
0	18	0	92.1	73.5
0	26	0	168.1	145.2
0	28	0	63.2	59.1
0	30	0	112.9	113.6
1	2	0	46.9	38.2
1	3	0	123.7	129.3
1	4	0	41.4	51.3
1	5	0	31.2	35.6
1	6	0	126.1	112.1
1	7	0	319.0	323.7
1	9	0	84.7	82.0
1	10	0	189.8	172.6
1	11	0	208.5	165.1
1	12	0	131.8	96.4
1	13	0	36.3	45.3
1	14	0	132.2	96.6
1	15	0	26.9	18.8
1	16	0	205.8	186.9
1	17	0	68.8	62.8
1	19	0	160.9	122.1
1	20	0	77.2	68.1
1	21	0	103.3	92.6
1	22	0	87.1	79.1
1	23	0	110.3	88.0
1	24	0	63.2	51.2
1	25	0	81.3	69.2
1	28	0	60.3	60.6
1	30	0	76.1	64.3
1	32	0	38.0	28.7
2	0	0	179.3	198.6
2	1	0	5.5	9.7
2	2	0	79.3	84.4
2	3	0	42.3	54.4
2	4	0	122.4	117.2
2	5	0	167.7	214.4
2	6	0	86.8	69.5
2	7	0	66.8	71.1
2	8	0	84.5	52.6
2	9	0	298.8	327.0
2	10	0	107.7	114.0
2	11	0	54.1	57.2
2	12	0	3.0	7.6
2	13	0	59.3	59.8
2	14	0	55.0	65.9
2	15	0	83.4	79.0
2	16	0	93.6	88.1
2	17	0	126.7	129.6
2	18	0	77.9	61.0
2	19	0	87.2	80.2
2	20	0	19.2	26.0
2	21	0	131.5	124.6
2	23	0	99.6	85.8
2	25	0	22.4	34.2
2	27	0	81.2	84.2
2	29	0	53.2	35.7
2	35	0	64.8	78.0
3	1	0	147.4	116.4
3	2	0	201.3	197.4
3	3	0	14.0	3.5
3	4	0	39.1	20.4
3	5	0	192.5	163.8
3	6	0	194.6	167.4
3	8	0	43.0	59.8
3	9	0	61.9	72.1
3	10	0	70.4	80.8
3	11	0	79.8	111.8
3	12	0	90.0	122.4
3	13	0	79.7	78.8
3	14	0	61.2	61.4
3	15	0	47.9	66.1
3	16	0	217.0	204.0
3	17	0	60.1	58.3
3	18	0	43.0	51.4
3	19	0	99.7	88.0
3	20	0	38.2	37.8
3	21	0	36.7	8.3
3	22	0	41.8	60.5
3	24	0	38.4	33.4
3	25	0	81.8	82.2
3	26	0	66.0	65.4
3	28	0	125.1	112.5
3	32	0	37.5	35.0
4	0	0	195.9	200.2
4	1	0	262.4	273.8
4	2	0	108.3	108.8
4	3	0	142.4	129.4
4	4	0	150.9	138.7
4	5	0	89.9	94.2
4	6	0	163.1	147.2
4	7	0	28.9	48.7
4	8	0	124.5	106.7
4	9	0	117.6	106.5
4	11	0	141.2	145.5
4	12	0	142.8	133.4
4	14	0	94.3	99.8
4	15	0	145.5	157.0
4	18	0	108.2	121.2
4	19	0	58.0	72.8
4	21	0	43.8	53.6
4	24	0	87.2	74.2
4	25	0	68.7	86.6
4	26	0	68.3	71.8
4	29	0	61.3	74.7
4	30	0	29.4	29.4
4	32	0	44.0	55.2
5	1	0	142.2	105.6
5	2	0	14.8	20.7
5	3	0	156.7	154.8
5	4	0	168.9	172.2
5	5	0	42.8	51.8
5	6	0	35.3	37.3
5	7	0	159.0	175.9
5	8	0	151.1	156.6
5	9	0	65.8	58.0
5	10	0	146.4	134.2
5	11	0	50.8	53.8
5	12	0	138.7	111.7
5	14	0	70.8	60.4
5	15	0	22.0	23.0
5	16	0	75.4	73.8
5	18	0	76.6	88.5
5	19	0	38.0	49.6
5	20	0	25.5	26.7
5	21	0	42.9	47.7
5	22	0	85.2	123.4
5	23	0	38.9	34.7
5	24	0	72.6	63.5
5	25	0	46.7	45.7
5	29	0	16.5	8.6
6	0	0	81.7	95.4
6	1	0	67.3	65.3
6	2	0	122.4	81.2
6	3	0	138.1	136.3
6	4	0	32.9	42.4
6	6	0	147.0	142.5
6	8	0	164.2	134.4
6	9	0	137.5	121.4
6	10	0	122.0	120.6
6	11	0	89.3	108.2
6	12	0	13.3	10.4
6	15	0	86.2	103.9
6	16	0	79.2	97.6
6	17	0	93.9	100.6
6	19	0	61.5	68.2
6	20	0	55.1	71.2
6	21	0	49.5	57.7
6	23	0	78.1	105.6
6	24	0	46.9	57.8
6	28	0	49.6	57.4
6	33	0	34.7	34.1
7	1	0	212.6	236.5
7	2	0	61.7	64.5
7	3	0	98.9	102.4
7	4	0	47.2	62.3
7	5	0	32.7	42.0
7	8	0	54.3	53.7
7	10	0	56.5	57.9
7	11	0	53.2	50.3
7	12	0	18.6	25.0
7	13	0	181.4	186.8
7	15	0	51.0	52.2
7	16	0	45.8	48.8
7	17	0	53.5	81.1
7	19	0	21.9	33.2
7	25	0	22.6	28.9
7	26	0	33.0	32.8
7	27	0	66.6	84.4
7	29	0	50.2	40.3
7	31	0	50.7	61.5
8	0	0	14.7	10.8
8	2	0	99.5	68.8
8	3	0	55.5	65.3
8	4	0	71.8	60.9
8	5	0	30.9	35.1
8	6	0	94.7	120.4
8	8	0	122.4	120.8
8	10	0	134.4	121.0
8	11	0	89.3	73.6
8	12	0	77.1	67.1
8	13	0	24.8	23.0
8	15	0	61.6	69.6
8	19	0	39.4	51.9
8	20	0	78.4	118.0
8	23	0	54.8	42.7
9	1	0	6.7	4.2
9	3	0	42.6	36.1
9	4	0	162.9	130.1
9	5	0	49.3	37.5
9	7	0	19.7	15.0
9	8	0	131.8	156.0
9	9	0	28.6	35.8
9	10	0	42.3	46.4
9	11	0	25.5	26.5
9	13	0	30.4	30.5
9	14	0	55.2	59.7
9	15	0	22.2	24.9
9	17	0	48.5	57.6
9	18	0	61.1	78.3
9	19	0	28.7	38.8
9	21	0	33.3	38.8
9	22	0	61.1	73.5
10	0	0	40.8	46.1
10	1	0	83.1	94.3
10	2	0	64.8	47.1
10	3	0	96.5	111.6
10	5	0	53.0	51.3
10	6	0	21.0	24.8
10	11	0	53.9	64.5
10	12	0	22.3	28.0
10	13	0	27.7	23.8
10	14	0	28.0	31.8
10	15	0	89.6	115.8
10	16	0	28.6	23.0
10	18	0	36.3	40.8
11	1	0	48.9	57.7
11	2	0	63.9	58.8
11	5	0	38.4	42.5
11	7	0	69.1	74.4
11	8	0	39.1	47.4
11	10	0	28.1	24.7
11	12	0	68.0	84.9
11	13	0	64.8	81.8
11	14	0	51.3	62.1
11	17	0	29.4	36.4
11	18	0	29.5	34.1
11	19	0	44.0	51.7
12	0	0	36.5	32.7
12	1	0	40.0	42.8
12	2	0	32.7	36.0
12	3	0	49.5	49.8
12	5	0	36.8	47.8
12	6	0	90.5	103.9
12	8	0	45.9	49.8
12	9	0	58.4	70.8
12	10	0	23.7	30.4
13	1	0	33.7	34.4
13	2	0	29.3	36.5
14	0	0	68.9	77.2
14	1	0	38.0	39.0
0	3	1	42.2	38.6
0	4	1	88.1	82.9
0	5	1	240.9	291.5
0	7	1	38.0	43.2
0	8	1	12.9	10.3
0	9	1	366.9	328.6
0	10	1	184.2	140.7
0	11	1	54.4	50.1
0	12	1	54.1	50.8
0	13	1	89.0	76.6
0	14	1	100.8	74.8
0	16	1	63.5	58.3
0	17	1	86.0	87.1
0	19	1	129.0	105.0
0	20	1	36.1	19.8
0	21	1	176.4	152.9
0	22	1	47.0	41.0
0	23	1	91.8	82.3
0	25	1	76.1	52.4
0	26	1	68.3	50.2
0	27	1	58.3	48.2
0	28	1	44.7	38.5
0	30	1	45.5	49.6
0	35	1	75.8	84.7
1	0	1	150.8	166.4
1	1	1	75.5	88.1
1	2	1	250.6	276.4
1	3	1	101.9	87.9
1	4	1	118.4	120.4
1	5	1	159.5	148.1
1	6	1	145.0	173.2
1	7	1	220.3	198.6
1	8	1	91.6	90.0
1	9	1	63.3	56.8
1	10	1	110.2	104.0
1	11	1	167.5	171.4
1	12	1	129.6	137.4
1	13	1	46.7	47.0
1	14	1	73.9	81.4
1	15	1	63.7	46.1
1	16	1	163.6	146.0
1	17	1	58.2	54.1
1	18	1	96.6	72.7
1	19	1	98.7	114.5
1	20	1	120.2	85.7
1	21	1	112.1	98.2
1	23	1	49.0	51.2
1	24	1	54.5	48.7
1	25	1	67.2	60.0
1	27	1	31.2	36.2
1	28	1	80.7	66.6
1	31	1	55.6	47.6
1	33	1	44.3	38.2
2	0	1	310.8	311.1
2	1	1	314.0	299.6
2	2	1	40.6	25.5
2	3	1	100.0	80.9
2	4	1	215.6	202.7
2	5	1	209.8	191.9
2	6	1	53.6	42.0
2	7	1	113.8	99.6
2	8	1	89.6	81.8
2	9	1	46.9	46.7
2	10	1	63.0	70.0
2	12	1	109.2	125.4
2	13	1	80.2	77.7
2	14	1	198.1	201.5
2	15	1	87.2	82.6
2	16	1	133.5	125.4
2	17	1	46.5	37.3
2	18	1	156.1	145.7
2	19	1	46.9	53.5
2	20	1	55.1	43.7
2	21	1	50.2	49.5
2	23	1	49.5	36.8
2	25	1	74.8	71.8
2	26	1	119.3	108.9
2	28	1	31.7	45.1
2	30	1	93.7	78.9
2	31	1	68.0	60.8
2	32	1	59.4	56.3
3	0	1	128.6	135.7
3	1	1	62.2	58.2
3	2	1	189.8	181.9
3	3	1	169.8	191.9
3	4	1	175.5	219.8
3	5	1	68.9	69.7
3	6	1	42.7	53.0
3	7	1	227.5	223.7
3	8	1	124.2	112.5
3	9	1	136.9	132.9
3	10	1	156.2	143.1
3	11	1	141.0	146.7
3	12	1	34.1	42.7
3	13	1	52.3	65.7
3	15	1	56.6	57.9
3	16	1	51.5	54.0
3	17	1	33.8	50.3
3	18	1	63.2	65.3
3	19	1	99.3	109.1
3	20	1	37.4	43.2
3	21	1	86.5	92.1
3	22	1	59.8	63.5
3	23	1	73.9	76.5
3	24	1	43.3	36.3
3	25	1	57.0	54.5
3	26	1	38.2	39.5
3	27	1	31.5	31.6
3	28	1	37.4	35.2
3	30	1	39.3	31.1
3	33	1	43.8	43.1
3	37	1	46.3	41.1
4	0	1	244.9	219.3
4	1	1	34.1	31.2
4	2	1	72.5	51.5
4	3	1	223.7	197.7
4	4	1	138.0	146.4
4	5	1	212.1	183.2
4	6	1	113.1	106.5
4	7	1	21.9	21.9
4	8	1	113.0	98.4
4	9	1	197.3	177.5
4	10	1	101.7	126.6
4	11	1	63.5	79.5
4	12	1	76.5	72.5
4	13	1	47.2	40.8
4	14	1	104.8	107.2
4	15	1	49.1	52.8
4	16	1	53.5	54.6
4	17	1	78.3	85.4
4	20	1	110.7	118.8
4	21	1	87.9	81.4
4	22	1	64.5	78.7
4	23	1	75.4	73.2
4	24	1	32.6	64.3
4	25	1	43.7	30.6
4	26	1	49.7	43.9
4	27	1	92.7	75.0
4	29	1	32.2	32.2
4	31	1	38.9	37.2
4	35	1	46.3	42.6
5	0	1	115.5	99.0
5	1	1	129.3	117.4
5	2	1	130.2	134.2
5	3	1	131.7	116.9
5	4	1	103.4	68.9
5	5	1	70.8	80.4
5	6	1	108.3	80.9
5	7	1	40.6	44.2
5	9	1	45.2	36.2
5	10	1	29.4	23.9
5	11	1	62.6	64.8
5	12	1	132.4	136.4
5	13	1	132.1	157.2
5	14	1	95.6	106.3
5	15	1	38.4	46.4
5	16	1	91.9	108.6
5	17	1	135.3	133.2
5	18	1	46.1	42.5
5	19	1	47.3	57.7
5	20	1	39.8	47.3
5	24	1	37.7	45.3
5	25	1	31.3	33.2
5	27	1	71.6	90.1
5	28	1	68.2	67.9
5	29	1	45.4	32.1
5	30	1	39.0	30.2
5	31	1	31.4	47.6
6	0	1	49.3	60.6
6	1	1	101.6	107.3
6	2	1	43.6	55.8
6	3	1	122.7	129.7
6	4	1	73.1	56.5
6	5	1	63.8	80.3
6	6	1	153.0	164.8
6	7	1	98.2	84.4
6	8	1	131.8	107.3
6	9	1	46.4	52.3
6	10	1	105.2	85.9
6	11	1	120.6	100.2
6	12	1	95.8	111.1
6	13	1	95.4	108.5
6	14	1	39.3	42.2
6	15	1	74.6	97.0
6	16	1	37.2	43.2
6	17	1	27.0	21.7
6	18	1	33.9	49.4
6	19	1	63.5	81.9
6	20	1	46.0	60.2
6	22	1	30.4	37.7
6	23	1	37.9	32.7
6	24	1	58.7	71.5
6	25	1	44.9	44.8
7	1	1	67.7	60.8
7	2	1	43.0	43.5
7	3	1	63.1	46.3
7	4	1	84.6	114.3
7	5	1	75.0	60.5
7	6	1	86.8	103.2
7	7	1	39.5	44.5
7	8	1	166.7	181.4
7	9	1	47.3	46.2
7	10	1	51.1	44.7
7	11	1	24.6	20.0
7	12	1	56.3	68.0
7	13	1	36.4	36.1
7	14	1	32.2	29.9
7	15	1	42.7	51.0
7	18	1	88.9	93.4
7	22	1	107.0	122.4
7	24	1	39.0	29.0
8	0	1	37.1	34.7
8	1	1	135.9	143.2
8	2	1	110.4	87.6
8	3	1	147.9	138.7
8	4	1	29.4	13.0
8	5	1	53.8	58.0
8	6	1	94.3	101.6
8	8	1	32.0	38.8
8	9	1	31.2	25.7
8	10	1	40.9	54.8
8	11	1	93.1	100.3
8	12	1	42.4	48.4
8	13	1	33.5	22.3
8	15	1	30.9	104.3
8	16	1	41.0	47.7
8	17	1	46.7	48.3
8	19	1	45.4	62.7
8	23	1	32.0	37.1
8	29	1	51.7	59.7
9	0	1	25.5	24.6
9	1	1	74.4	79.2
9	2	1	40.5	48.7
9	3	1	77.1	87.5
9	4	1	81.8	90.8
9	5	1	76.1	77.2
9	6	1	67.1	59.8
9	8	1	38.0	49.7
9	9	1	51.0	56.9
9	10	1	58.6	62.3
9	12	1	49.3	64.0
9	13	1	141.4	149.5
9	17	1	74.0	94.3
9	18	1	37.6	40.4
10	1	1	33.7	44.9
10	2	1	39.0	54.7
10	3	1	51.8	53.6
10	4	1	44.0	37.8
10	5	1	39.6	44.6
10	6	1	100.7	109.4
10	8	1	53.7	58.7
10	10	1	72.8	82.4
10	11	1	41.9	43.0
10	12	1	47.4	44.4
10	13	1	30.4	38.7
10	15	1	31.0	21.6
10	17	1	38.7	43.2
10	20	1	67.1	78.5
11	1	1	65.8	66.1
11	3	1	46.7	52.4
11	4	1	51.3	57.3
11	7	1	30.1	42.2
11	8	1	43.0	59.5
11	10	1	37.7	56.8
11	11	1	38.0	37.5
11	13	1	38.5	44.2
11	15	1	31.9	43.3
12	0	1	74.3	92.4
12	1	1	57.9	65.1
12	2	1	43.8	48.6
12	4	1	62.3	69.4
12	5	1	38.2	38.0
12	10	1	39.0	34.7
12	11	1	39.1	50.0
12	15	1	74.1	32.1
13	1	1	50.5	53.1
13	3	1	32.0	34.2
13	4	1	45.2	48.3
13	5	1	32.0	28.2
13	6	1	32.1	30.9
13	7	1	55.6	53.9
13	8	1	45.5	48.7
13	11	1	39.3	49.7
13	12	1	56.2	62.1
14	2	1	32.1	31.4
14	5	1	52.2	51.1
15	1	1	31.2	26.7
15	2	1	52.3	56.6
15	3	1	38.2	25.2
0	2	2	89.4	139.1
0	4	2	246.0	287.5
0	5	2	77.6	82.0
0	6	2	8.0	8.0
0	7	2	71.5	82.2
0	8	2	61.8	47.7
0	10	2	158.0	134.2
0	11	2	105.8	100.2
0	12	2	44.9	43.5
0	13	2	177.5	164.4
0	14	2	175.0	163.0
0	16	2	116.6	95.9
0	17	2	113.2	97.6
0	18	2	126.3	108.1
0	19	2	37.4	42.9
0	20	2	28.3	27.6
0	23	2	64.8	54.7
0	25	2	128.5	107.2
0	26	2	87.1	70.2
0	27	2	114.6	89.4
0	28	2	82.0	62.3
0	30	2	53.0	53.4
0	31	2	56.4	49.3
1	0	2	133.2	163.2
1	1	2	82.1	89.6
1	2	2	101.3	123.3
1	3	2	223.7	261.7
1	4	2	40.6	23.8
1	5	2	172.4	158.1
1	6	2	125.0	112.6
1	7	2	155.4	172.1
1	8	2	49.1	57.6
1	9	2	41.4	52.0
1	10	2	75.1	62.7
1	11	2	156.0	173.5
1	12	2	127.2	133.7
1	13	2	72.2	65.3
1	14	2	87.9	76.3
1	15	2	117.5	95.9
1	16	2	113.7	103.3
1	17	2	99.7	84.6
1	18	2	63.0	63.2
1	19	2	119.7	93.3
1	20	2	49.3	41.6
1	21	2	85.8	83.4
1	23	2	67.6	68.2
1	24	2	66.4	63.4
1	25	2	87.4	80.0
1	26	2	72.5	74.1
1	27	2	62.3	62.7
1	28	2	28.1	28.6
1	30	2	75.0	59.5
1	33	2	47.2	47.7
2	0	2	103.3	61.3
2	1	2	74.0	84.4
2	2	2	109.4	132.0
2	3	2	74.0	73.3
2	4	2	180.6	208.1
2	5	2	214.3	214.4
2	6	2	156.8	148.6
2	7	2	90.1	88.2
2	8	2	75.3	99.5
2	9	2	113.3	159.9
2	10	2	137.2	170.0
2	11	2	60.3	51.9
2	12	2	54.4	72.0
2	13	2	58.9	65.9
2	14	2	134.6	129.4
2	15	2	39.1	45.0
2	16	2	137.2	122.3
2	17	2	55.9	48.5
2	18	2	69.4	55.2
2	19	2	78.7	74.4
2	20	2	86.4	76.4
2	21	2	100.2	81.8
2	22	2	120.1	94.9
2	23	2	81.5	74.2
2	24	2	41.8	33.1
2	25	2	42.7	42.6
2	26	2	56.2	54.7
2	27	2	55.9	40.9
2	28	2	45.4	46.8
2	31	2	20.3	24.5
2	32	2	61.9	50.3
2	35	2	47.3	49.6
3	0	2	143.8	128.9
3	1	2	80.5	69.9
3	2	2	259.0	279.8
3	3	2	94.1	97.6
3	4	2	98.1	81.1
3	5	2	64.2	49.5
3	6	2	88.2	115.6
3	7	2	77.7	58.7
3	8	2	60.9	80.1
3	9	2	93.2	91.5
3	11	2	76.3	68.8
3	12	2	128.9	170.0
3	13	2	77.1	91.0
3	14	2	114.2	142.8
3	15	2	40.3	51.2
3	16	2	55.4	73.9
3	17	2	79.8	88.4
3	18	2	82.6	87.9
3	19	2	40.2	46.0
3	20	2	53.7	59.7
3	21	2	23.9	28.9
3	22	2	40.2	58.1
3	24	2	59.7	63.6
3	26	2	73.4	83.0
3	27	2	24.5	21.8
3	28	2	40.0	34.5
3	30	2	28.3	21.9
3	31	2	44.2	33.4
3	32	2	38.9	46.6
4	0	2	29.4	27.7
4	1	2	150.0	128.7
4	2	2	123.5	97.0
4	3	2	58.9	66.8
4	4	2	70.1	86.3
4	5	2	113.3	136.0
4	6	2	104.3	86.1
4	7	2	149.7	154.7
4	8	2	48.0	35.2
4	9	2	108.0	104.1
4	11	2	131.4	119.1
4	12	2	32.8	45.5
4	13	2	115.3	159.1
4	14	2	108.5	131.1
4	15	2	109.9	130.5
4	16	2	21.7	18.3
4	17	2	35.5	45.5
4	18	2	28.4	32.8
4	19	2	92.6	108.7
4	20	2	24.6	30.2
4	21	2	45.3	51.5
4	22	2	31.8	31.9
4	23	2	56.4	55.8
4	24	2	38.3	44.7
4	25	2	101.4	105.1
4	26	2	59.3	46.0
4	29	2	34.7	36.6
4	30	2	52.6	62.8
4	31	2	43.8	45.1
4	32	2	38.4	34.2
5	0	2	75.6	70.7
5	1	2	119.4	95.0
5	2	2	50.4	59.5
5	3	2	145.2	135.4
5	4	2	160.8	141.0
5	5	2	57.7	45.9
5	6	2	122.3	112.5
5	7	2	153.3	166.5
5	8	2	136.5	156.6
5	9	2	108.3	94.7
5	10	2	42.4	59.0
5	11	2	71.8	73.9
5	12	2	61.6	63.4
5	13	2	36.9	53.2
5	16	2	45.4	30.6
5	17	2	40.5	68.9
5	18	2	76.0	90.5
5	19	2	55.3	63.3
5	21	2	55.1	68.5
5	22	2	77.4	92.6
5	23	2	79.0	92.0
5	24	2	27.5	32.0
5	25	2	25.4	18.7
5	26	2	44.5	41.9
5	29	2	39.8	39.9
6	0	2	126.5	110.7
6	1	2	111.7	90.7
6	2	2	109.8	114.7
6	3	2	135.2	125.7
6	4	2	136.8	143.0
6	5	2	48.6	54.4
6	6	2	164.1	163.2
6	7	2	55.5	36.8
6	8	2	61.5	78.2
6	9	2	63.0	47.3
6	10	2	79.0	116.9
6	11	2	72.4	72.7
6	12	2	40.1	44.2
6	13	2	85.2	73.1
6	14	2	59.7	83.0
6	15	2	51.8	76.8
6	16	2	69.4	90.0
6	17	2	54.6	46.4
6	18	2	35.4	50.1
6	19	2	50.2	43.4
6	20	2	41.4	61.5
6	22	2	73.2	77.4
6	24	2	53.9	60.3
6	25	2	44.6	34.2
6	26	2	34.7	39.6
6	27	2	40.1	32.9
6	28	2	40.2	39.2
7	0	2	56.7	56.5
7	1	2	147.2	124.1
7	2	2	132.1	88.1
7	3	2	172.9	140.4
7	4	2	77.0	64.6
7	5	2	82.9	58.0
7	6	2	40.8	48.6
7	7	2	46.3	45.7
7	8	2	44.7	45.9
7	9	2	61.2	73.4
7	10	2	55.8	59.6
7	11	2	35.4	42.[illegible]
7	12	2	61.7	66.3
7	13	2	124.6	127.3
7	14	2	69.6	76.2
7	15	2	45.6	43.1
7	17	2	101.2	119.0
7	18	2	52.2	60.5
7	20	2	27.0	30.0
7	21	2	38.7	33.6
7	23	2	28.0	28.8
7	26	2	56.6	65.2
7	27	2	62.9	70.1
8	0	2	45.2	46.1
8	1	2	113.9	94.3

H	K	L	Fo	Fc
8	2	2	62.4	58.9
8	4	2	105.2	101.7
8	6	2	76.6	77.6
8	7	2	92.4	86.4
8	8	2	66.2	65.9
8	9	2	23.2	23.9
8	10	2	69.2	78.5
8	11	2	75.4	66.4
8	12	2	34.3	43.9
8	13	2	57.2	60.2
8	16	2	58.3	57.3
8	18	2	46.0	40.7
8	19	2	47.1	59.1
8	20	2	60.5	69.8
8	22	2	34.1	37.1
8	23	2	60.1	52.8
8	24	2	49.1	65.3
9	3	2	111.8	99.9
9	4	2	68.3	74.9
9	5	2	47.2	32.7
9	6	2	37.7	44.3
9	7	2	53.8	65.1
9	8	2	100.4	110.5
9	9	2	58.9	61.8
9	10	2	79.0	77.7
9	11	2	25.3	38.3
9	12	2	53.1	51.6
9	13	2	57.6	53.9
9	15	2	62.8	63.3
9	17	2	43.5	48.6
9	18	2	48.5	48.6
9	21	2	38.3	32.6
10	0	2	43.4	41.7
10	1	2	146.7	106.1
10	2	2	58.4	65.9
10	3	2	95.8	75.2
10	5	2	34.2	31.8
10	6	2	44.4	24.7
10	7	2	43.8	52.9
10	8	2	63.9	51.3
10	10	2	58.3	54.1
10	11	2	65.8	81.8
10	12	2	29.7	23.8
10	13	2	60.1	43.4
10	15	2	64.9	80.4
10	16	2	30.8	37.6
11	2	2	65.4	49.9
11	3	2	35.9	27.5
11	4	2	46.5	44.4
11	5	2	46.7	50.3
11	6	2	84.0	87.1
11	8	2	47.5	48.3
11	9	2	37.0	36.7
11	10	2	43.0	25.4
11	12	2	65.3	62.2
11	13	2	30.9	37.9
12	1	2	48.3	30.1
12	4	2	48.5	37.6
12	5	2	68.8	76.8
12	6	2	65.4	71.6
12	8	2	53.7	37.9
12	10	2	60.3	55.3
12	13	2	38.9	27.1
12	16	2	43.5	20.0
13	1	2	62.6	48.4
13	2	2	44.2	36.9
13	3	2	49.4	43.8
13	9	2	71.7	60.2
14	0	2	51.3	53.2
14	7	2	43.4	39.7
0	2	3	106.1	135.1
0	3	3	42.4	42.5
0	4	3	70.6	112.4
0	5	3	152.1	214.7
0	6	3	41.3	52.2
0	8	3	194.0	160.5
0	7	3	44.9	60.6
0	9	3	73.6	76.7
0	10	3	181.5	147.0
0	11	3	144.7	106.2
0	12	3	38.3	31.6
0	13	3	38.7	29.0
0	14	3	75.9	55.8
0	15	3	92.1	74.9
0	16	3	186.3	152.9
0	19	3	108.1	96.9
0	20	3	59.6	43.6
0	22	3	101.6	81.8
0	25	3	67.4	62.0
0	28	3	99.9	73.1
0	29	3	42.0	27.3
1	0	3	62.2	68.5
1	1	3	44.8	48.3
1	2	3	171.5	160.1
1	3	3	115.7	98.4
1	4	3	87.9	88.7
1	5	3	84.3	80.4
1	6	3	187.9	195.5
1	7	3	45.7	58.7
1	8	3	72.5	90.6
1	9	3	[illegible]	95.1
1	11	3	72.4	79.2
1	12	3	118.5	131.4
1	14	3	142.6	124.7
1	15	3	129.4	94.1
1	16	3	98.2	84.7
1	17	3	77.5	65.8
1	18	3	86.9	87.4
1	20	3	126.3	99.8
1	21	3	94.5	67.8
1	22	3	40.1	50.5
1	24	3	66.4	56.9
1	25	3	52.4	50.3
1	26	3	81.1	71.3
1	27	3	57.8	33.6
1	28	3	43.9	51.2
1	29	3	43.8	27.4
1	30	3	53.4	40.7
1	31	3	31.2	23.0
1	32	3	47.0	52.9
1	33	3	35.4	35.1
2	0	3	170.3	145.1
2	1	3	104.8	152.1
2	2	3	52.9	56.7
2	3	3	37.2	38.5
2	4	3	54.4	63.2
2	5	3	167.3	164.3
2	6	3	94.1	82.1
2	7	3	149.0	153.1
2	8	3	45.6	64.4
2	9	3	68.5	94.5
2	10	3	189.8	191.4
2	11	3	83.8	103.2
2	12	3	38.1	39.7
2	13	3	102.9	123.5
2	14	3	73.5	90.1
2	15	3	95.8	104.5
2	17	3	65.1	64.5
2	18	3	36.0	24.8
2	19	3	98.3	103.8
2	20	3	78.9	77.8
2	21	3	89.3	74.1
2	23	3	50.7	49.0
2	24	3	42.2	30.6
2	25	3	56.8	72.8
2	26	3	67.2	49.3
2	27	3	69.2	54.7
2	28	3	38.4	28.5
2	29	3	33.2	27.1
2	31	3	64.1	58.7
3	0	3	147.4	153.4
3	1	3	83.3	92.3
3	3	3	187.0	185.0
3	4	3	66.2	57.2
3	5	3	120.4	123.4
3	6	3	101.7	84.6
3	7	3	159.6	156.0
3	8	3	44.1	59.4
3	9	3	95.5	111.3
3	10	3	52.2	46.1
3	11	3	93.4	115.1
3	12	3	115.3	123.3
3	13	3	82.3	112.9
3	14	3	36.0	49.0
3	15	3	56.9	69.2
3	17	3	79.7	112.3
3	18	3	36.7	61.4
3	19	3	70.8	64.4
3	20	3	38.0	36.3
3	21	3	111.4	112.0
3	23	3	86.2	69.9
3	24	3	79.2	62.3
3	26	3	48.8	50.9
3	27	3	69.4	71.8
3	29	3	56.0	59.1
4	0	3	171.8	144.5
4	1	3	92.6	95.8
4	2	3	155.3	137.6
4	3	3	39.0	21.9
4	4	3	226.6	215.9
4	5	3	64.1	62.5
4	6	3	69.6	90.9
4	7	3	78.8	69.0
4	9	3	24.8	19.9
4	10	3	120.6	145.8
4	12	3	65.0	58.3
4	14	3	99.3	115.0
4	15	3	38.7	33.2
4	16	3	79.8	106.6
4	17	3	36.7	28.9
4	18	3	55.9	62.0
4	19	3	43.4	30.4
4	20	3	74.5	89.7
4	22	3	80.2	79.0
4	25	3	43.5	25.5
4	26	3	38.0	38.2
4	28	3	65.7	54.4
4	30	3	52.4	50.8
5	0	3	135.7	114.7
5	1	3	92.0	104.8
5	2	3	71.4	91.1
5	3	3	132.9	133.5
5	4	3	150.1	114.8
5	5	3	42.5	27.0
5	7	3	81.4	75.0
5	8	3	79.3	83.0
5	9	3	48.5	59.6
5	10	3	35.2	40.7
5	11	3	45.8	65.9
5	12	3	114.1	120.0
5	14	3	78.6	71.6
5	16	3	52.5	62.2
5	17	3	54.2	74.4
5	18	3	49.8	71.0
5	20	3	40.9	46.7
5	21	3	36.0	45.2
5	23	3	52.6	55.2
5	24	3	43.5	51.6
5	26	3	43.9	47.2
5	27	3	53.7	50.8
5	30	3	47.1	44.4
6	1	3	69.6	81.4
6	2	3	29.7	43.3
6	3	3	66.9	41.3
6	4	3	47.8	41.2
6	5	3	129.1	132.2
6	6	3	69.6	62.6
6	7	3	133.4	103.1
6	8	3	32.3	32.9
6	9	3	112.9	106.9
6	10	3	69.4	78.1
6	11	3	132.3	146.6
6	12	3	24.9	25.8
6	13	3	89.3	105.6
6	15	3	82.6	92.6
6	16	3	38.6	36.4
6	17	3	50.2	50.2
6	19	3	61.4	73.3
6	21	3	67.3	88.1
6	23	3	43.5	45.7
6	24	3	37.9	35.5
6	25	3	38.1	49.1
6	26	3	43.8	32.0
7	2	3	136.8	127.5
7	3	3	125.3	137.6
7	4	3	30.7	34.2
7	5	3	33.2	41.1
7	6	3	75.3	82.2
7	7	3	70.4	45.8
7	8	3	74.6	82.6
7	9	3	72.7	97.2
7	11	3	81.8	74.5
7	12	3	69.7	78.2
7	14	3	61.3	61.8
7	15	3	55.9	68.9
7	16	3	42.3	26.5
7	17	3	53.8	58.2
7	18	3	62.5	81.6
7	19	3	36.6	40.6
7	22	3	69.1	91.4
7	23	3	69.4	87.0
7	25	3	20.3	27.1
8	1	3	92.7	59.6
8	2	3	97.9	106.3
8	4	3	122.0	120.9
8	5	3	80.2	82.7
8	6	3	40.5	39.2
8	7	3	36.6	37.7
8	8	3	62.5	61.6
8	9	3	53.2	49.2
8	10	3	61.7	71.0
8	11	3	47.4	47.3
8	13	3	44.7	46.3
8	14	3	49.7	48.2
8	15	3	58.3	64.5
8	16	3	51.2	62.9
8	19	3	43.2	58.7
8	20	3	37.8	33.5
8	24	3	48.3	27.5
9	1	3	34.4	77.4
9	2	3	59.8	50.6
9	3	3	57.0	53.5
9	4	3	38.1	46.6
9	5	3	85.9	52.2
9	6	3	89.7	82.2
9	7	3	33.9	36.4
9	8	3	59.2	66.6
9	9	3	39.8	25.6
9	13	3	62.6	66.7
9	14	3	60.3	64.9
9	18	3	65.0	75.9
9	20	3	49.1	65.1
10	0	3	53.1	52.9
10	1	3	56.8	55.9
10	2	3	63.7	70.0
10	4	3	49.7	63.4
10	5	3	45.6	40.3
10	6	3	114.1	93.1
10	7	3	50.5	61.0
10	8	3	92.9	83.4
10	10	3	58.2	59.1
10	13	3	75.4	68.7
10	16	3	53.6	38.7
10	18	3	38.1	32.8
10	19	3	38.0	41.9
11	1	3	94.4	75.1
11	2	3	42.3	34.4
11	3	3	59.9	60.2
11	9	3	53.6	67.9
11	11	3	60.7	64.2
11	12	3	43.8	38.9
11	13	3	38.1	40.8
11	15	3	43.8	50.1
11	17	3	43.4	54.9
12	0	3	65.3	61.8
12	1	3	53.4	58.0
12	2	3	43.6	47.2
12	4	3	43.7	31.6
12	5	3	48.9	54.8
12	6	3	11.2	16.6
12	8	3	49.1	48.4
12	10	3	43.9	42.6
12	11	3	22.0	17.4
12	13	3	39.7	35.0
13	3	3	36.1	25.5
13	4	3	36.1	20.9
13	6	3	43.3	44.0
14	2	3	43.3	35.5
14	4	3	43.3	35.5
0	3	4	20.5	17.7
0	4	4	40.9	51.3
0	5	4	76.2	90.8
0	6	4	93.3	100.0
0	7	4	190.4	173.4
0	8	4	45.8	39.5
0	10	4	128.6	135.0
0	11	4	68.7	81.0
0	12	4	73.3	52.1
0	14	4	78.4	70.0
0	15	4	91.3	80.5
0	16	4	114.8	92.3
0	17	4	59.4	74.8
0	19	4	94.0	102.7
0	20	4	77.2	72.4
0	23	4	28.9	28.5
0	24	4	134.8	103.4
0	26	4	79.2	63.7
0	27	4	89.0	72.7
1	0	4	51.2	64.5
1	1	4	118.3	130.6
1	2	4	77.9	86.1
1	3	4	134.0	130.4
1	4	4	178.0	152.6
1	5	4	101.6	87.3
1	6	4	83.3	95.7
1	7	4	119.8	120.9
1	8	4	99.4	114.1
1	9	4	53.3	103.7
1	10	4	98.3	89.2
1	11	4	92.1	76.4
1	12	4	122.8	104.4
1	14	4	92.1	71.2
1	15	4	92.1	88.9
1	17	4	117.7	96.9
1	18	4	67.6	70.3
1	20	4	98.3	74.3
1	21	4	141.3	94.3
1	23	4	122.8	84.3
1	25	4	69.6	48.2
1	26	4	78.8	70.1
1	28	4	63.5	40.0
1	29	4	44.0	37.4
1	31	4	43.0	46.2
2	0	4	166.8	149.7
2	1	4	93.4	111.6
2	2	4	156.0	154.5
2	3	4	66.7	85.8
2	4	4	84.3	84.1
2	5	4	89.6	95.8
2	6	4	60.2	68.1
2	8	4	105.0	124.1
2	10	4	88.8	113.1
2	11	4	83.7	105.1
2	12	4	81.0	63.7
2	13	4	34.4	33.6
2	14	4	80.1	87.1
2	15	4	155.0	151.7
2	16	4	54.9	65.7
2	17	4	39.9	19.6
2	18	4	78.8	63.2
2	19	4	60.0	71.2
2	24	4	61.6	53.5
2	26	4	61.6	59.5
2	28	4	56.8	59.6
2	30	4	56.8	46.3
2	31	4	47.5	32.6
3	0	4	55.2	57.8
3	1	4	97.1	126.0
3	2	4	94.8	114.9
3	3	4	47.7	31.3
3	4	4	82.0	90.9
3	5	4	49.8	33.6
3	6	4	112.1	103.5
3	7	4	69.1	78.0
3	8	4	142.9	168.8
3	9	4	53.1	64.1
3	10	4	36.8	42.7
3	11	4	52.6	66.4
3	12	4	138.6	137.0
3	13	4	35.7	49.2
3	14	4	52.4	66.4
3	15	4	44.3	47.9
3	18	4	95.3	108.4
3	19	4	50.0	30.7
3	20	4	72.2	67.5
3	21	4	35.8	32.9
3	22	4	59.4	61.9
3	23	4	46.7	52.8
3	25	4	47.6	40.4
3	29	4	53.6	42.7
4	0	4	77.8	75.2
4	1	4	95.3	97.4
4	2	4	38.6	46.6
4	3	4	78.8	47.9
4	4	4	36.6	45.4
4	5	4	153.9	161.2
4	6	4	87.3	68.6
4	7	4	139.6	126.6
4	8	4	68.7	69.6
4	9	4	77.3	99.9
4	10	4	73.3	79.6
4	11	4	63.6	81.5
4	12	4	36.2	21.3
4	13	4	81.7	90.0
4	14	4	49.8	31.0
4	15	4	39.7	71.1
4	17	4	48.6	45.5
4	19	4	77.4	91.4
4	20	4	64.3	83.4
4	21	4	53.0	61.6
4	29	4	37.9	23.8
5	0	4	48.5	65.9
5	1	4	98.2	85.4
5	2	4	135.4	138.5
5	3	4	129.4	141.9
5	4	4	68.1	56.1
5	5	4	55.6	56.6
5	6	4	64.5	75.3
5	9	4	96.7	115.5
5	10	4	36.2	31.7
5	11	4	71.3	77.4
5	12	4	55.6	80.9
5	13	4	71.2	92.4
5	14	4	57.0	72.0
5	15	4	53.4	61.3
5	16	4	54.6	61.4
5	17	4	50.0	73.4
5	18	4	55.5	65.3
5	21	4	85.1	100.5
5	23	4	54.9	66.9
6	0	4	91.7	103.3
6	1	4	49.6	46.6
6	2	4	73.6	86.5
6	4	4	107.9	109.9
6	8	4	71.0	63.3
6	9	4	81.8	70.6
6	10	4	94.8	108.1
6	12	4	58.7	62.0
6	13	4	47.7	54.7
6	14	4	30.8	38.2
6	16	4	94.9	104.9
6	18	4	52.6	78.2
6	20	4	46.8	58.1
6	21	4	47.3	46.5
6	22	4	68.1	63.4
6	24	4	67.4	55.1
7	0	4	105.8	110.8
7	2	4	43.0	48.3
7	3	4	93.3	76.3
7	5	4	35.4	45.9
7	6	4	94.8	89.3
7	7	4	94.1	111.9
7	9	4	57.2	42.6
7	11	4	54.1	63.8
7	12	4	62.0	66.8
7	14	4	44.1	47.5
7	15	4	36.6	33.4
7	16	4	37.0	25.6
8	0	4	132.4	115.2
8	1	4	51.9	67.5
8	2	4	34.2	17.2
8	4	4	52.6	53.8
8	5	4	134.3	104.1
8	6	4	35.6	35.4
8	7	4	73.9	82.7
8	8	4	43.9	37.6
8	9	4	42.9	46.9
8	11	4	56.9	54.8
8	12	4	36.4	35.3
8	13	4	52.1	55.6
8	14	4	52.8	69.6
8	15	4	46.2	41.2
8	16	4	38.1	28.3
8	17	4	54.4	50.1
9	0	4	44.6	67.2
9	1	4	65.8	82.7
9	2	4	70.4	79.3
9	3	4	87.2	85.0
9	6	4	50.3	39.0
9	8	4	44.7	40.7
9	9	4	36.8	40.9
9	10	4	45.5	24.9
9	11	4	45.9	41.4
9	12	4	59.8	58.1
9	14	4	38.4	40.1
9	15	4	54.6	73.5
10	2	4	52.5	51.6
10	3	4	37.1	16.1
10	7	4	60.7	43.6
10	9	4	100.6	94.7
10	10	4	66.2	58.2
10	11	4	74.7	61.0
11	0	4	63.5	73.0
11	2	4	66.6	72.6
11	3	4	54.4	43.4
11	4	4	47.2	35.9
11	6	4	61.1	74.0
11	8	4	47.6	56.0
12	1	4	72.4	63.4
12	3	4	47.7	36.8
12	5	4	58.9	52.6
12	7	4	33.9	41.3
12	8	4	38.8	29.8
12	10	4	54.6	64.2
13	1	4	60.7	53.1
13	3	4	54.2	37.6
13	4	4	47.0	24.2
0	3	5	93.3	91.6
0	5	5	61.6	73.9
0	6	5	29.5	22.0
0	7	5	45.4	61.7
0	8	5	50.2	53.3
0	9	5	21.4	22.1
0	10	5	70.5	79.3
0	11	5	105.1	120.4
0	12	5	38.5	22.2
0	13	5	36.8	33.9
0	14	5	10.0	14.7
0	15	5	143.7	147.6
0	17	5	52.2	50.8
0	18	5	36.0	30.5
0	25	5	75.9	67.9
0	27	5	59.9	47.9
0	29	5	70.0	92.9
1	0	5	82.9	88.1
1	2	5	76.8	76.6
1	4	5	63.9	105.9
1	5	5	70.5	83.9
1	6	5	76.3	77.5
1	8	5	134.1	133.3
1	9	5	83.7	93.4
1	11	5	53.7	50.6
1	12	5	83.3	100.0
1	13	5	87.1	97.2
1	14	5	61.0	53.2
1	15	5	40.1	25.5
1	17	5	90.7	96.2
1	18	5	88.0	83.0
1	19	5	55.1	43.2
1	22	5	106.3	101.9
1	24	5	34.1	44.0
1	25	5	34.1	32.2
1	26	5	67.1	63.0
2	0	5	34.7	25.2
2	1	5	112.3	117.9
2	2	5	71.9	83.0
2	3	5	49.4	36.3
2	6	5	168.2	193.6
2	7	5	38.6	39.3
2	8	5	59.2	67.9
2	10	5	70.4	88.9
2	12	5	51.6	75.2
2	13	5	66.4	67.2
2	15	5	53.3	63.1
2	19	5	35.2	69.1
2	20	5	63.2	69.2
3	0	5	73.6	90.2
3	1	5	150.6	145.0
3	2	5	58.0	75.3
3	3	5	143.2	134.2
3	7	5	60.0	64.2
3	8	5	83.0	94.0
3	9	5	83.7	88.6
3	10	5	43.2	63.1
3	11	5	36.6	43.1
3	14	5	39.1	35.9
3	16	5	30.5	35.8
3	17	5	77.2	85.1
3	20	5	74.1	77.5
3	21	5	58.1	53.5
3	22	5	63.1	67.3
3	23	5	90.2	80.7
3	24	5	68.3	56.2
4	0	5	101.2	113.0
4	2	5	56.5	53.4
4	3	5	33.1	92.6
4	4	5	111.7	115.1
4	5	5	40.4	39.4
4	8	5	48.7	47.6
4	10	5	63.3	90.1
4	12	5	56.2	50.5
4	14	5	112.4	124.9
4	15	5	69.4	90.3
4	16	5	94.2	97.3
4	17	5	55.3	61.8
4	18	5	35.4	24.2
4	19	5	46.3	43.5
4	23	5	49.9	57.0
4	24	5	74.9	74.6
5	0	5	131.4	137.0
5	1	5	58.5	41.8
5	3	5	66.0	70.6
5	4	5	74.1	75.7
5	5	5	83.3	76.3
5	6	5	62.2	61.7
5	7	5	153.5	148.7
5	8	5	77.8	84.4
5	9	5	55.7	59.2
5	11	5	86.3	92.2
5	12	5	70.6	62.2
5	15	5	43.7	44.2
6	1	5	102.4	71.9
6	5	5	86.6	94.2
6	7	5	48.9	66.7
6	8	5	57.4	40.1
6	9	5	68.6	63.5
6	11	5	61.1	63.7
6	12	5	61.9	72.1
6	13	5	44.5	38.5
7	1	5	57.5	36.4
7	2	5	189.3	171.0
7	3	5	41.1	37.8
7	5	5	51.0	47.7
7	6	5	48.7	42.9
7	11	5	44.9	45.4
7	12	5	69.5	73.8
7	13	5	43.9	31.6
7	14	5	65.6	84.1
7	15	5	60.8	67.2
8	0	5	32.2	16.7
8	1	5	43.6	34.8
8	5	5	39.5	37.9
8	7	5	55.1	37.2
8	9	5	101.6	103.0
8	10	5	73.3	74.0
8	12	5	57.6	53.6
9	0	5	61.7	57.0
9	2	5	46.1	43.9
9	3	5	65.3	56.2
9	6	5	73.9	57.3
9	7	5	104.4	103.9
9	8	5	53.1	43.2
9	9	5	47.4	50.9
9	10	5	26.6	23.8
10	0	5	100.9	90.2
10	4	5	32.7	34.9
10	5	5	75.6	52.5
10	9	5	63.6	51.9
10	10	5	59.0	33.9
11	3	5	59.2	53.1
11	4	5	60.8	53.6
11	10	5	63.7	42.6
12	5	5	74.9	50.0
12	6	5	74.9	50.2
0	7	6	27.9	24.2
0	10	6	106.6	106.2
0	18	6	53.9	40.1
0	19	6	63.2	70.2
0	20	6	159.9	149.7
1	0	6	11.4	12.0
1	2	6	33.7	33.8
1	3	6	32.0	34.6
1	4	6	36.3	119.4
1	5	6	65.8	67.6
1	6	6	59.9	52.9
1	7	6	23.6	14.1
1	8	6	32.2	39.1
1	9	6	39.6	49.4
1	10	6	79.8	32.5
1	12	6	52.6	34.5
1	13	6	81.9	99.5
1	15	6	41.9	23.2
1	17	6	91.8	112.4
1	18	6	76.3	53.2
1	19	6	44.7	44.3
1	22	6	64.6	30.5
2	1	6	121.2	122.6
2	4	6	65.3	71.6
2	5	6	14.7	19.9
2	7	6	48.2	65.3
2	8	6	32.1	29.4
2	9	6	67.4	41.7
2	11	6	114.9	124.9
2	15	6	113.1	139.7
3	3	6	24.5	26.1
3	4	6	72.3	74.5
3	5	6	131.6	104.0
3	6	6	77.9	58.4
3	7	6	64.2	72.3
3	8	6	104.9	126.5
3	9	6	54.2	40.9
3	11	6	71.6	79.9
4	2	6	112.9	109.2
4	4	6	52.5	52.1
4	5	6	100.9	111.9
4	7	6	46.9	27.0
4	8	6	53.0	44.6
4	9	6	58.6	31.4
4	10	6	58.2	56.7
4	11	6	61.9	65.0
4	12	6	65.7	63.8
5	1	6	71.2	34.5
5	2	6	143.3	135.7
5	3	6	36.7	27.5
5	4	6	42.8	53.5
5	5	6	48.7	64.0
5	7	6	55.4	45.0
5	9	6	56.3	61.7
5	10	6	68.2	75.9
6	1	6	21.7	10.4
6	4	6	74.0	85.9
6	6	6	74.1	36.1
6	7	6	[illegible]	37.7
6	8	6	48.7	33.5
6	10	6	66.4	55.3
7	1	6	42.3	45.4
7	3	6	34.6	41.8
7	4	6	34.9	17.5
7	5	6	99.6	82.9
7	7	6	101.3	127.3
8	0	6	107.3	110.5
8	4	6	81.8	94.6
8	6	6	36.9	33.7
10	5	6	73.3	82.6

PART 4.

X-RAY ANALYSIS OF 4-BROMO-3-NITRO BENZOIC ACID.

4.1 INTRODUCTION.

In the crystals of many simple derivatives of benzene, repulsion between non-bonded atoms of the aromatic system may lead to deformation of the regular pattern. Molecules in which such deformations occur are said to be "overcrowded". A number of these "overcrowded" molecules have been examined by x-ray crystallographic methods in recent years.

Halogen derivatives of benzene and simple aromatic compounds closely related to benzene, would be expected to be subject to steric effects because of the close proximity of the halogen atom to neighbouring groups. In the case of the polyhalogeno-benzene derivatives, the positions of the heavy atoms may be determined with some precision, but the lighter atoms in the presence of the halogen atoms may not be located with sufficient accuracy to permit a detailed description of the structure. This is clearly shown in the case of 1:2:4:5 tetrabromobenzene (Gafner and Herbstein, 1960), in which the standard deviations of the positional parameters of the bromine atoms are 0.003 Å, while the standard deviations of the carbon atoms are 0.026 Å.

When an x-ray analysis of a polysubstituted benzene derivative containing only one halogen atom is carried out, then the lighter atoms can be located with more accuracy, and thus a more detailed description of the molecular geometry may be undertaken. The kind of results that may be obtained from the accurate x-ray analyses of this type of molecule are shown by the work on the structures of some "overcrowded" benzoic acids by Ferguson and Sim. They have studied o-chloro benzoic acid (1961), o-bromo benzoic acid (1962a), and 2-chloro-5-nitro benzoic acid (1962b). Other workers in this field are McPhail (1963), who has studied the structure of 2-chloro-4-nitro aniline, and Islam (1966), who has studied the structure of o-chloro benzoyl acetylene.

The results of all these analyses show that, in the solid state, both in the plane of the benzene ring, and out of the plane of the benzene ring, there are measureable displacements of adjacent substituents, leading to "splaying-out" of bond angles, and to rotation of substituent groups about the bond joining them to the benzene ring.

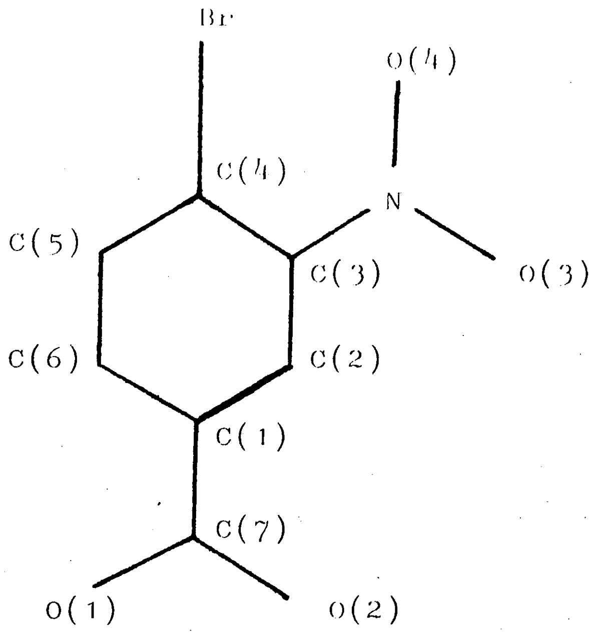


Figure 1.

Crystals of 4-bromo-3-nitro benzoic acid (fig. 1), suitable for x-ray investigation were obtained by recrystallising the crude, commercially available material from an alcohol-ether mixture. In the calculations involved in the analysis, the atoms were numbered as shown.

Preliminary work on this compound was undertaken by Dr. G. Ferguson, (1961), as part of his investigations into the structures of a series of "overcrowded" benzoic acid derivatives, as mentioned earlier in this section.

4.2 EXPERIMENTAL.

4-bromo-3-nitro benzoic acid has molecular formula $C_7H_4N\ O_4Br$. The molecular weight is therefore 246.0.

Rotation, oscillation, and Weissenberg photographs were taken with copper K-α radiation (λ= 1.542 Å). The cell dimensions were calculated from rotation and Weissenberg photographs, and from these the following values were obtained.

$a = 7.48 \pm 0.02$ Å
$b = 5.82 \pm 0.02$ Å
$c = 19.27 \pm 0.04$ Å
$\beta = 103^\circ 3'$

The volume of the unit cell was calculated from the cell dimensions, and was found to be 817 $Å^3$.

From an examination of the Weissenberg photographs, it could be seen that the h0l reflections were absent when l was odd, and also that the 0k0 reflections were absent when k was odd. Thus, the space group was uniquely determined to be $P2_1/c$.

The density of the crystal is 1.99 gm per ml.. and therefore the number of molecules per unit cell is found to be four. This number leads to a calculated density of 2.00 gm. per ml.

The value of the linear absorption coefficient for copper K-α radiation was found to be 74.5 cm.$^{-1}$. The total number of electrons in the unit cell, F(000), was found to be 480. "$\sum f^2$" for the heavy bromine atom is 1225, while "$\sum f^2$" for the light atoms is 561. From this, it is possible to calculate r, where

$$\underline{r}^2 = "\sum f^2_H"/"\sum f^2_L"$$

The value found for r is 1.48, and thus between 80% and 90% of the phases calculated from the heavy atom alone will be correct (Sim, 1957).

Intensity data were obtained from equatorial and equi-inclination multiple film Weissenberg photographs, obtained by rotating the crystal about the needle axis (b-crystal axis). The reciprocal lattice nets h01,... ...,h31 were recorded in this way. The intensities were estimated visually, and 960 independent intensity estimations were made.

The intensity values were corrected for Lorentz, polarisation and the rotation factors appropriate to the upper layers (Tunell, 1939), and the structure amplitudes were derived by the usual mosaic crystal formulae.

Small crystals were used, and therefore no absorption corrections were carried out. The four sets of structure amplitudes were placed on the same scale by comparison with the calculated structure amplitudes obtained from the Patterson function, and the scaling factors were adjusted throughout the three dimensional refinements to ensure that the observed structure amplitudes were always correctly scaled.

4.3 STRUCTURE DETERMINATION AND REFINEMENT.

4.3.1 STRUCTURE DETERMINATION.

In 1961, as part of his investigations into "overcrowding" in benzoic acids, Dr. G. Ferguson began the structure determination of 4-bromo-3-nitro benzoic acid. Therefore, before the present analysis of this compound is described, it is necessary to give a brief summary of the work done by Dr. Ferguson.

In this preliminary work, structure amplitudes were obtained for the h0l and h3l layers only. The Patterson projection on (010) was calculated, and this is shown in fig. 2. The large peak on this projection at a general position was chosen as representing the bromine-bromine vector. Structure factors were then calculated using the bromine coordinates obtained, and this led to an agreement index, R, of 40%. From the first two dimensional Fourier synthesis, the position of all the remaining atoms, with the exception of hydrogens, could be clearly distinguished. Therefore, $\underline{x}$ and $\underline{z}$ coordinates for the carbon, nitrogen and oxygen atoms were obtained, and those of the bromine atom were improved.

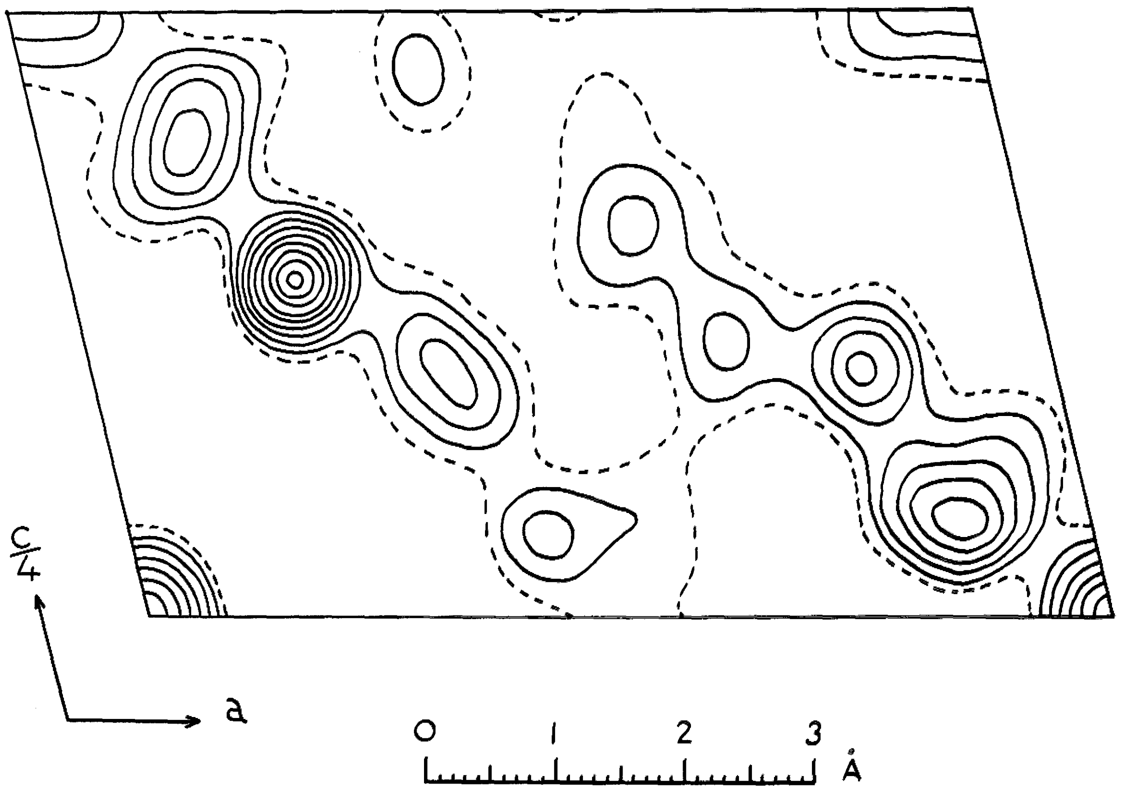


Fig. 2. The Patterson Projection on (010).

These thirteen atoms were included as their appropriate chemical types in the evaluation of two further sets of structure factors. The isotropic temperature factors employed were $U = 0.05$ Å^2. Two Fourier syntheses were calculated, one based upon $|Fo|$ and the other based upon $|Fc|$. "Back-shift" corrections to allow for the effect of termination of series errors in Fourier summations were carried out. The value of the agreement index fell to 21%.

Using the h31 data, three dimensional Patterson line sections were calculated in order to find the y coordinate of the bromine atom. It was assumed that the seven carbon atoms and the bromine atom were coplanar, and from considerations of known bond lengths, approximate y coordinates for the carbon atoms were calculated.

Using the x and z coordinates obtained from the (010) projection, and the calculated y coordinates, structure factors for the h31 layer were calculated on the basis of the bromine and carbon contributions only. This led to an agreement index of 42%. Using only the h31 data, Fourier line syntheses parallel to the y direction were calculated through the known x and z positions of the atoms.

In this way, y coordinates for all the thirteen atoms were obtained. A cycle of structure factors based on these coordinates was evaluated, using isotropic temperature factors of $U = 0.05$ Å^2. This led to an agreement index of 28%. Refinement of the coordinates was continued by $|Fo|$ and $|Fc|$ Fourier calculations for two more cycles, and this resulted in values of the agreement index of 18.5% for the h0l data, and 21.6% for the h3l data.

The structure analysis of 4-bromo-3-nitro benzoic acid had reached this stage when the present investigations were begun. Dr. Ferguson only collected part of the available data, and, in addition, the intensity data which were collected were not very accurate. Therefore, it was decided to restart the analysis of 4-bromo-3-nitro benzoic acid by estimating a completely new set of intensity data. In this way, 960 independent observed structure amplitudes were obtained.

4.3.2 STRUCTURE REFINEMENT.

Using the new values obtained for the observed structure amplitudes, and the fractional coordinates for all the atoms (except hydrogens), which had been determined by Dr. Ferguson, a cycle of structure factors was evaluated. Once again, overall isotropic temperature factors of U = 0.05 Å^2 were used. This led to a value of the agreement index, over all observed structure amplitudes, of 20.1%.

Anisotropic temperature factors were calculated for all the atoms. Refinement of the positional and thermal parameters was continued by the method of least squares. After five cycles of block diagonal refinement, the parameter shifts became very small, and the value of the agreement index for each zone in turn was reduced to 9.08% for the h0l layer, 9.19% for the h1l layer, 10.84% for the h2l layer and 10.71% for the h3l layer, the overall value being 9.90%. At this stage, it was decided to include in the analysis the four hydrogen atoms present in the molecule, which were as yet undetected. Structure factors obtained from the last least squares cycle were employed in the calculation of a three dimensional Fourier synthesis, with coefficients $|Fo| - |Fc|$. Small peaks of about 0.6 - 0.9 electrons per cubic Angstrom appeared in the positions expected for the four hydrogen atoms, and coordinates for these four atoms were then calculated by the method due to Booth (1948b).

A final structure factor calculation, employing an overall isotropic temperature factor of $U = 0.05\ Å^2$ for the hydrogen atoms, and individual anisotropic temperature factors for the other thirteen atoms, was then calculated. This led to a final value for the agreement index of 9.4%. The course of the analysis is shown in diagrammatic form in Table 1.

Theoretical atomic scattering factors were employed for the structure factor calculations; those of Berghuis et.al. (1955) for carbon, oxygen and nitrogen, that of McWeeny (1951) for hydrogen, and the Thomas-Fermi (1935) values for bromine.

For the least squares refinement, the weighting scheme used was that of Cruickshank et.al. (1961b), where

$$\sqrt{w} = 1/\left(p_1 + F + p_2.F^2\right)^{\frac{1}{2}}$$

In this, the constant terms are

$$p_1 = 2.F\ \text{min} = 2.0$$

$$p_2 = 2/F\ \text{max} = 0.013$$

TABLE 1

COURSE OF THE ANALYSIS.

OPERATION.	ATOMS INCLUDED	R(%)
a. Using h01 data only.		
Two dimensional Patterson synthesis	- - -	- - -
1st 2D Fourier synthesis	(Br)	40.0
2nd " "	(Br) + 4(O) + N + 7(C)	29.0
3rd " "	" "	21.0
b. Using h31 data only.		
Fourier line sections	(Br) + 7(C)	42.0
Fourier line sections	(Br) + 7(C) + 4(O) + N	28.0
c. Using all the data.		
3D Fourier Synthesis	" "	20.1
1st Least Squares Cycle	" "	18.3
2nd " "	" "	16.0
3rd " "	" "	12.9
4th " "	" "	11.2
5th " "	" "	9.9
Final SF Calculation	(Br) + 7(C) + 4(O) + N + 4(H)	9.5

4.4 RESULTS OF THE ANALYSIS

The final atomic coordinates are listed in Table 2. The anisotropic temperature factors given by the least squares refinement are listed in Table 3. The standard deviations of the final atomic coordinates, with the exception of the hydrogen atoms are given in Table 4. The standard deviations were obtained from the least squares totals in the manner detailed in section 1.9.

The interatomic bond lengths are listed in Table 5, and the interatomic bond angles are given in Table 6.

Table 7 lists some of the intramolecular non-bonded distances, and the shorter intermolecular distances, which are those contacts less than or equal to 3.90 Å, are given in Table 8. The deviations of individual atoms from the best planes through different sets of atoms are given in Table 9.

The observed and calculated structure factors are given in Table 10, the values being those obtained from the final least squares cycle. The final value for the agreement index, calculated over 960 observed structure amplitudes, is 9.47%.

The atomic arrangement of the molecule as viewed along the b-axis is shown in fig. 3, and the packing of the molecules in the crystal as viewed along the b-axis is shown in fig. 4.

Using the formulae given in section 1.9, the standard deviations for the bond lengths and the bond angles can be calculated. The average estimated standard deviation for a carbon-carbon single bond is 0.02 Å, and for a typical trigonal angle it is 1°.

4.5 DISCUSSION OF RESULTS.

The atomic coordinates which are listed in Table 2 were used for the calculation of a series of best planes through various groups of atoms in the molecule. These planes were calculated by the method of Schomaker et.al. (1959).

The best plane through the six carbon atoms of the benzene ring was found to have the equation

$$0.0704\ x + 0.6202\ y - 0.7812\ z + 0.1094 = 0$$

The displacements of the individual atoms from this plane are shown in Table 9. None of these displacements is significant. Also in Table 9 are shown the distances of the remaining carbon atom, the nitrogen atom, the four oxygen atoms and the bromine atom from this plane. A feature of particular interest is the large deviation of 0.20 Å of the halogen atom from this plane. This deviation is considerably greater than the displacement of 0.06 Å of the bromine atom in o-bromo benzoic acid (Ferguson and Sim, 1961).

The equation of the best plane through the four atoms C(1), C(7), O(1) and O(2) of the carboxyl group is

$$0.0728\ x - 0.5617\ y + 0.8241\ z + 0.0219 = 0$$

The deviations of the individual atoms from this plane are also shown in Table 9; no deviation is significant.

The atoms of the nitro group N(1), O(3) and O(4) and also the carbon atom C(3) of the benzene ring are coplanar to within the limits of the standard deviations, the equation of the best plane through these atoms being

$$0.6339\ x - 0.6754\ y + 0.3767\ z + 3.2513 = 0$$

Once again, the deviations of these four atoms from the best plane are given in Table 9.

The nitro group is tilted at an angle of 48.0^{o} to the plane of the benzene ring. The rotation of the nitro group out of the plane is a little larger than that found in 4-chloro-3-nitro benzoic acid (Ferguson, 1966) where the value is 46^{o}. The angle of inclination of the carboxyl group to the plane of the benzene ring is only 9.2^{o}, while in o-bromo benzoic acid (Ferguson and Sim, 1961) the inclination of the carboxyl group is 18.3^{o}. This difference is caused by the different relative positions of the other substituents to the carboxyl group. In o-bromo benzoic acid, the bromine atom is adjacent to the carboxyl group, and thus has a more direct influence on the rotation of the carboxyl group than in 4-bromo-3-nitro benzoic acid, where the nearest substituent to the carboxyl group is <u>meta</u>.

In the case of o-bromo benzoyl acetylene (Ferguson and Islam, 1966) a compound in which the two substituents are <u>ortho</u> to each other, the angle of rotation out of the plane of the benzene ring is 13.1°.

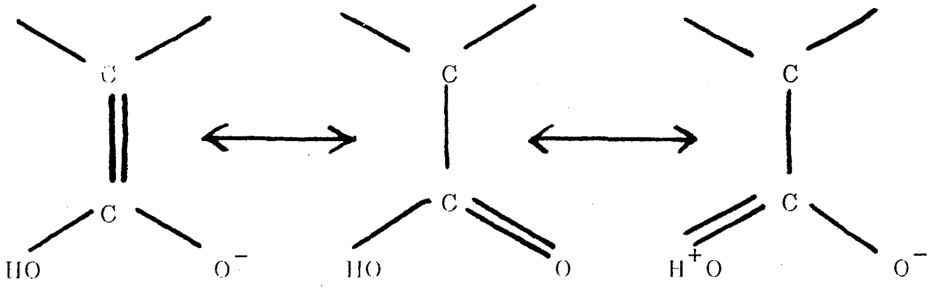
In addition to the "out-of-plane" bending of the carboxyl and nitro groups, significant "in-the-plane" splaying out of the exocyclic valency bonds was noted. The angle between exocyclic carbon-nitrogen and carbon-bromine bonds, which in a regular planar model is 60°, is increased beyond this value to 65.8°. This can be compared with o-chloro benzoyl acetylene (Islam, 1966), where the angle between the carbon-chlorine bond and the exocyclic carbon-carbon bond is 67.2°. This splaying out is also apparent in the intramolecular non-bonded bromine-nitrogen distance, which is increased from its expected value of 3.10 Å to 3.21 Å.

The carbon-carbon bond lengths in the benzene ring vary from 1.36 Å to 1.43 Å, the average value being 1.39 Å. This value is in good agreement with the figure of 1.393 Å reported for the carbon-carbon bond distance in p-nitro-aniline (Trueblood et.al., 1961), and that of 1.394 Å found in o-bromo benzoic acid (Ferguson and Sim, 1961). The standard value, given in International Tables for X-Ray Crystallography, Volume III, is 1.396 Å.

The length of the exocyclic carbon-carbon bond is 1.45 Å. The standard single bond distance between sp^2-hybridised carbon atoms has been estimated as 1.479 Å (Dewar and Schmeising, 1959). Thus, the value obtained agrees well with this estimate, and also with the values of 1.477 Å found in p-benzoquinone (Trotter, 1960), and 1.483 Å found in butadiene (Tables of Interatomic Distances, 1958).

The lengths of the carbon-oxygen bonds in the carboxyl group are 1.26 Å and 1.31 Å. The difference between these two distances is therefore 0.05 Å, while in the case of o-bromo benzoic acid and o-chloro benzoic acid the differences are 0.15 Å and 0.09 Å respectively. In 4-bromo-3-nitro benzoic acid the C-C-O angles have values of 121.1° and 119.6°, which can be compared with the values of 126.0° and 113.7° in o-bromo benzoic acid, and 122.2° and 113.3° in o-chloro benzoic acid. Therefore, these last two compounds conform to the customary pattern of carboxyl groups, in which there is a significant difference between the two angles, whereas 4-bromo-3-nitro benzoic acid does not.

This bond length and angle pattern round the carbon atom of a carboxyl group also occurs in the analysis of benzoic acid (Sim, 1955). Sim, Robertson and Goodwin (1955) have pointed out that shortening of the exocyclic carbon-carbon bond can be correlated with an increase in the sum of the lengths of the two carbon-oxygen bonds. The results of Sim (1955), suggest that in the benzene carboxylic acids, the following three resonance forms make significant contributions to the structure of the carboxyl group.



Therefore, the interbond angles round C(7) should all be nearly equal, and the carbon-carbon bond, C(1)-C(7) will be slightly shortened.

The carbon-nitrogen bond, C(3)-N(1) has length 1.49 Å, which does not differ significantly from the value of 1.486 Å found in nitrobenzene (Trotter, 1959), and 1.470 Å in m-dinitrobenzene (Trotter, 1961). The nitrogen-oxygen bond lengths are 1.24 Å and 1.25 Å, and these are in excellent agreement with the value of 1.243 Å obtained for the s-trinitrobenzene complex of azulene (Hanson,1965) and the value of 1.245 Å found in 2-nitrobenzaldehyde (Coppens,1964). The nitrogen-oxygen bond length found in the case of p-nitro aniline (Trueblood, et.al.,1961) was 1.246 ± 0.007 Å. The angles about the nitrogen atom of this group conform to the expected pattern, in that the angle O-N-O exceeds 120°, whereas both the C-N-O angles are less than 120°. These angular variations can be explained qualitatively in terms of inter-electron repulsions decreasing in the order non-bond...non-bond pairs, non-bond...bond pairs, and bond... ...bond pairs.

The carbon-bromine distance is 1.91 Å, and this is longer than the value of 1.85 Å quoted for the aromatic carbon-bromine distance in Tables of Interatomic Distances (1958). However, this value agrees well with the value of 1.89 Å found in o-bromo benzoic acid (Ferguson, 1961) and also the value of 1.90 Å obtained in the case of β-1:2-4:5-tetrabromobenzene (Gafner and Herbstein, 1960).

The closest intermolecular approach occurs between oxygen atoms of adjacent carboxyl groups, which are related by a centre of symmetry. The O-H.......O distance was found to be 2.67 Å. This distance is normal for this type of hydrogen bonding. All other intermolecular contacts, which are listed in Table 8, are greater than 3.0 Å, and correspond to normal Van der Waal's interactions.

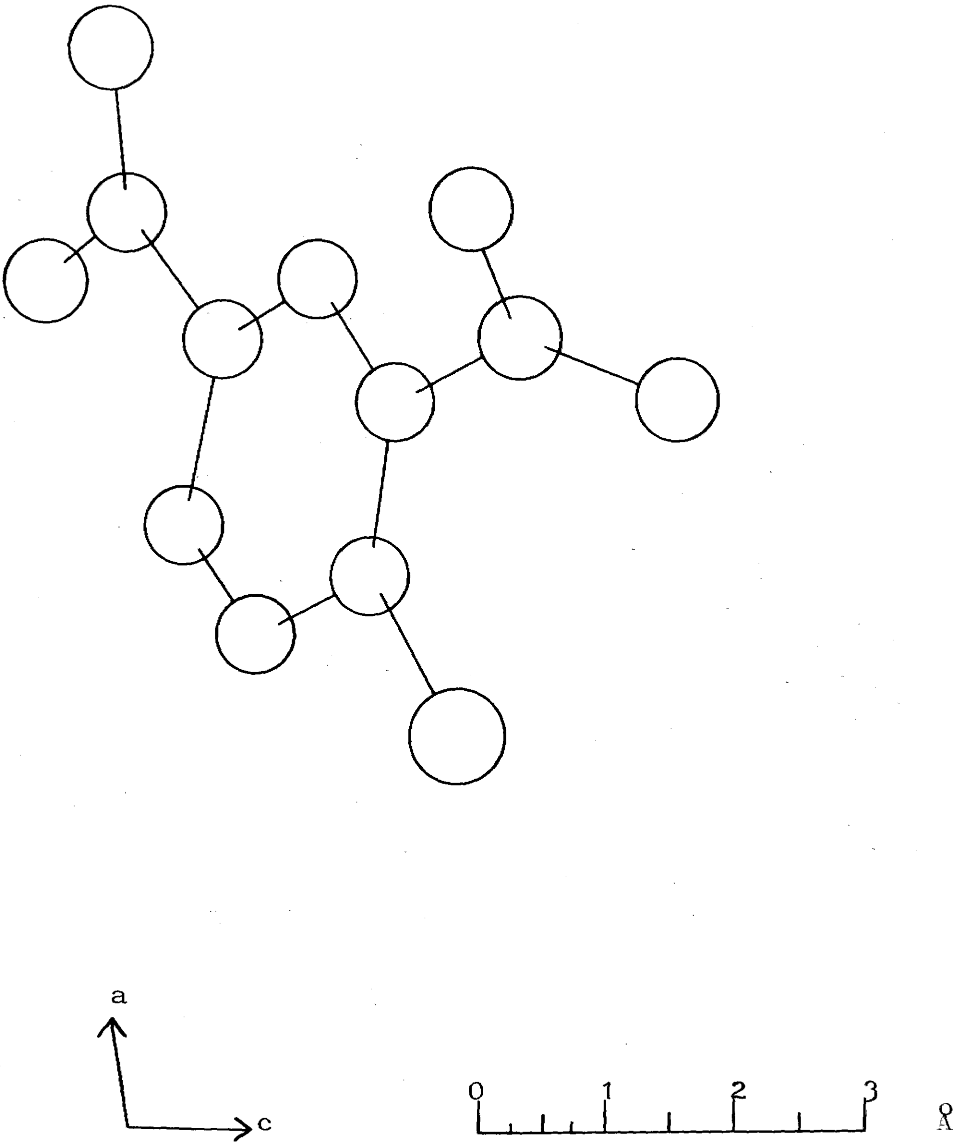


Fig. 3. The atomic arrangement of the molecule as viewed along the b-axis.

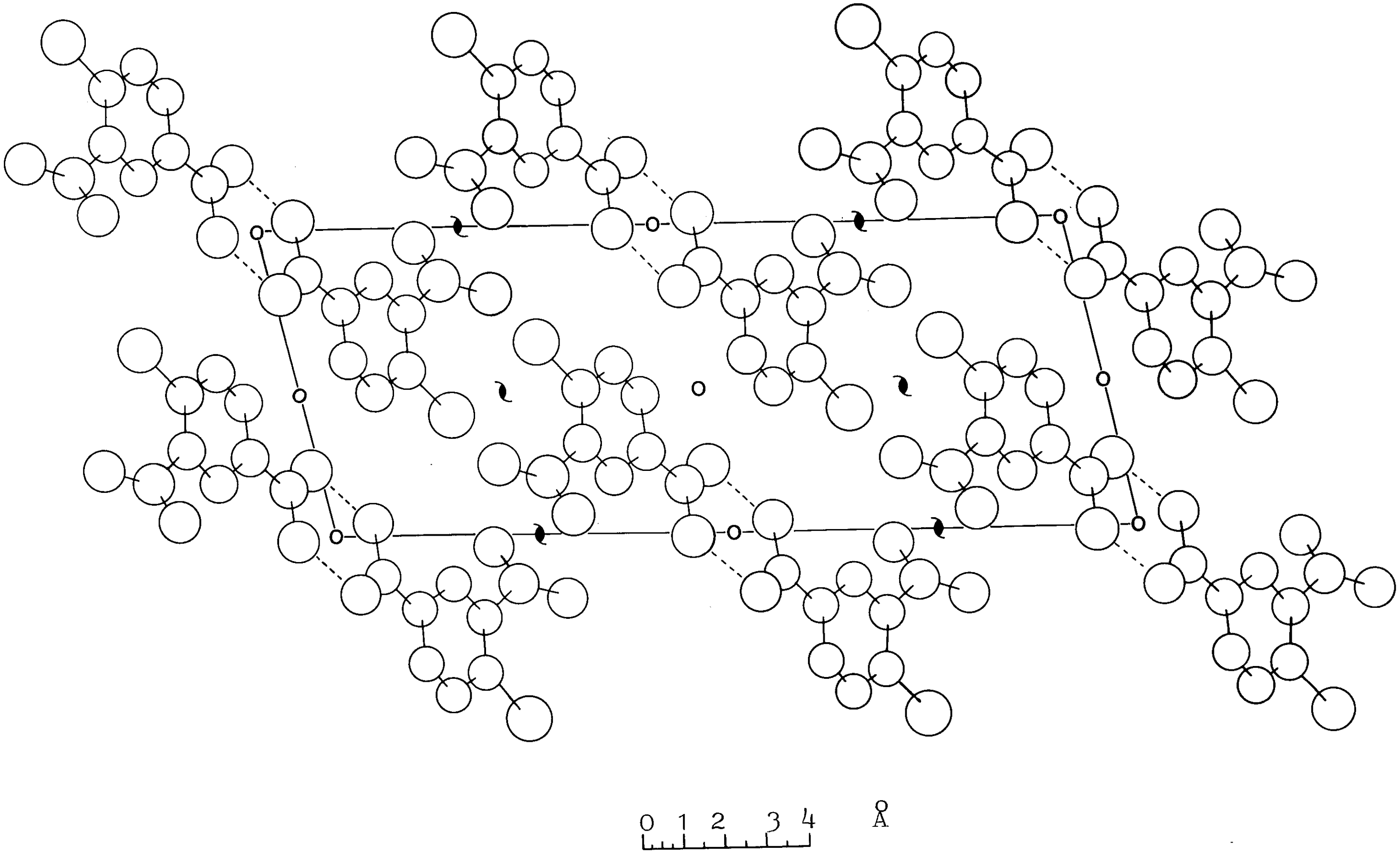


Fig. 4. The arrangement of the molecules in the crystal as viewed along the b-axis.

TABLE 2.

4-BROMO-3-NITRO BENZOIC ACID.

FINAL ATOMIC COORDINATES.

ATOM.	x/a	y/b	z/c
C(1)	-0.2501	0.3558	0.0839
C(2)	-0.1684	0.5330	0.1288
C(3)	-0.2748	0.6712	0.1599
C(4)	-0.4641	0.6541	0.1459
C(5)	-0.5472	0.4836	0.1015
C(6)	-0.4443	0.3272	0.0730
C(7)	-0.1421	0.2062	0.0493
N(1)	-0.1765	0.8461	0.2114
O(1)	-0.2200	0.0300	0.0126
O(2)	0.0241	0.2494	0.0511
O(3)	-0.0593	0.9665	0.1923
O(4)	-0.2214	0.8565	0.2702
Br(1)	-0.6164	0.8682	0.1814
H(1)	-0.6822	0.4703	0.0915
H(2)	-0.5059	0.2022	0.0426
H(3)	-0.0330	0.5550	0.1384
H(4)	0.1463	0.1000	0.0169

TABLE 3.

4-BROMO-3-NITRO BENZOIC ACID.

FINAL ANISOTROPIC TEMPERATURE FACTORS.(Å^2)

ATOM.	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	0.0505	0.0309	0.0437	0.0111	0.0313	-0.0205
C(2)	0.0371	0.0113	0.0340	0.0151	0.0308	0.0017
C(3)	0.0373	0.0436	0.0293	0.0038	0.0204	-0.0094
C(4)	0.0343	0.0323	0.0356	0.0089	0.0326	0.0266
C(5)	0.0384	0.0479	0.0326	0.0151	0.0304	0.0137
C(6)	0.0434	0.0518	0.0437	0.0049	0.0294	-0.0208
C(7)	0.0445	0.0367	0.0408	0.0039	0.0321	0.0021
N(1)	0.0427	0.0509	0.0364	-0.0020	0.0252	0.0055
O(1)	0.0516	0.0421	0.0666	-0.0235	0.0349	-0.0312
O(2)	0.0467	0.0389	0.0648	-0.0447	0.0401	-0.0185
O(3)	0.0620	0.0323	0.0673	0.0033	0.0216	-0.0217
O(4)	0.0490	0.0815	0.0436	-0.0297	0.0394	-0.0221
Br(1)	0.0463	0.0492	0.0530	-0.0080	0.0407	0.0130

TABLE 4.

4-BROMO-3-NITRO BENZOIC ACID.

STANDARD DEVIATIONS OF FINAL ATOMIC COORDINATES.

ATOM.	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0.012	0.015	0.011
C(2)	0.009	0.014	0.010
C(3)	0.010	0.014	0.010
C(4)	0.010	0.013	0.010
C(5)	0.010	0.015	0.010
C(6)	0.011	0.015	0.012
C(7)	0.011	0.015	0.011
N(1)	0.009	0.012	0.009
O(1)	0.008	0.011	0.009
O(2)	0.007	0.012	0.009
O(3)	0.009	0.012	0.009
O(4)	0.008	0.011	0.008
Br(1)	0.001	0.002	0.001

TABLE 5.

4-BROMO-3-NITRO BENZOIC ACID.

BOND LENGTHS. (Å).

C(1)	-	C(2)	1.39	C(7)	-	O(1)	1.31
C(1)	-	C(6)	1.43	C(7)	-	O(2)	1.26
C(1)	-	C(7)	1.45	N(1)	-	O(3)	1.24
C(2)	-	C(3)	1.36	N(1)	-	O(4)	1.25
C(3)	-	C(4)	1.38	C(2)	-	H(3)	1.00
C(3)	-	N(1)	1.49	C(5)	-	H(1)	0.99
C(4)	-	C(5)	1.37	C(6)	-	H(2)	0.98
C(4)	-	Br(1)	1.91	O(1)	-	H(4)	1.16
C(5)	-	C(6)	1.38				

TABLE 6.

4-BROMO-3-NITRO BENZOIC ACID.

BOND ANGLES.(°).

C(2) - C(1) - C(6)	117.7	C(3) - C(4) - Br(1)	123.2
C(2) - C(1) - C(7)	121.2	C(4) - C(5) - C(6)	119.8
C(6) - C(1) - C(7)	121.1	C(5) - C(6) - C(1)	120.2
C(1) - C(2) - C(3)	119.5	C(1) - C(7) - O(1)	119.6
C(2) - C(3) - C(4)	120.2	C(1) - C(7) - O(2)	121.1
C(2) - C(3) - N(1)	116.5	O(1) - C(7) - O(2)	119.2
C(4) - C(3) - N(1)	123.4	C(3) - N(1) - O(3)	117.6
C(3) - C(4) - C(5)	118.4	C(3) - N(1) - O(4)	116.1
C(5) - C(4) - Br(1)	118.3	O(3) - N(1) - O(4)	126.3

TABLE 7.

4-BROMO-3-NITRO BENZOIC ACID.

SOME INTRAMOLECULAR NON-BONDED CONTACTS.(Å).

C(1)......C(3)	2.38	C(3)......O(3)	2.34
C(1)......C(4)	2.76	C(3)......O(4)	2.34
C(1)......C(5)	2.44	C(3)......Br(1)	2.91
C(1)......N(1)	3.72	C(4)......C(6)	2.39
C(1)......O(1)	2.38	C(4)......N(1)	2.50
C(1)......O(2)	2.36	C(4)......O(3)	3.47
C(2)......C(4)	2.39	C(4)......O(4)	2.91
C(2)......C(5)	2.78	C(5)......C(7)	3.77
C(2)......C(6)	2.42	C(5)......N(1)	3.74
C(2)......C(7)	2.48	C(5)......Br(1)	2.83
C(2)......N(1)	2.43	C(6)......C(7)	2.51
C(2)......O(1)	3.65	C(6)......O(1)	2.84
C(2)......O(2)	2.83	C(6)......O(2)	3.65
C(2)......O(4)	3.41	N(1)......Br(1)	3.21
C(3)......C(5)	2.36	O(1)......O(2)	2.21
C(3)......C(6)	2.73	O(3)......O(4)	2.23
C(3)......C(7)	3.72	O(4)......Br(1)	3.06

TABLE 8.

4-BROMO-3-NITRO BENZOIC ACID.

INTERMOLECULAR CONTACTS LESS THAN 3.90 Å.

O(1)......O(2)$_{VII}$	2.67	O(2)......O(4)$_{II}$	3.48
C(7)......O(3)$_{I}$	3.03	C(7)......O(1)$_{VII}$	3.49
O(4)......O(3)$_{II}$	3.07	O(2)......O(2)$_{VIII}$	3.49
N(1)......O(3)$_{II}$	3.16	C(2)......O(3)$_{II}$	3.51
C(1)......O(3)$_{I}$	3.19	C(7)......O(2)$_{VII}$	3.51
C(2)......O(4)$_{II}$	3.28	C(5)......C(6)$_{V}$	3.53
O(4)......Br(1)$_{III}$	3.31	C(3)......O(3)$_{II}$	3.54
O(2)......O(3)$_{I}$	3.36	C(2)......O(3)$_{I}$	3.55
C(6)......O(1)$_{VI}$	3.39	C(4)......O(4)$_{III}$	3.55
C(5)......O(4)$_{III}$	3.40	C(4)......Br(1)$_{III}$	3.62
C(6)......C(6)$_{V}$	3.41	O(1)......C(3)$_{I}$	3.62
Br(1).....O(3)$_{IV}$	3.42	O(1)......C(2)$_{I}$	3.63
Br(1).....O(4)$_{III}$	3.42	O(3)......O(3)$_{II}$	3.65
O(1)......O(3)$_{I}$	3.42	C(1)......C(5)$_{V}$	3.67
C(5)......O(2)$_{IV}$	3.42	C(2)......N(1)$_{II}$	3.71
O(1)......O(1)$_{VII}$	3.45	O(1)......Br(1)$_{V}$	3.71
O(2)......O(2)$_{VII}$	3.48	C(5)......C(7)$_{V}$	3.75

TABLE 8 (Cont.).

C(5)......O(1)$_{\mathrm{V}}$	3.76	C(7)......N(1)$_{\mathrm{I}}$	3.82
C(3)......Br(1)$_{\mathrm{III}}$	3.78	C(1)......C(6)$_{\mathrm{V}}$	3.83
C(6)......Br(1)$_{\mathrm{I}}$	3.79	C(6)......O(3)$_{\mathrm{I}}$	3.87
C(1)......N(1)$_{\mathrm{I}}$	3.81	C(5)......O(1)$_{\mathrm{VI}}$	3.88

The subscripts refer to the following equivalent positions:

I	x;	$-1 + y$;	z.
II	$-x$;	$-\frac{1}{2} + y$;	$\frac{1}{2} - z$.
III	$-1 - x$;	$-\frac{1}{2} + y$;	$\frac{1}{2} - z$.
IV	$-1 + x$;	y;	z.
V	$-1 - x$;	$1 - y$;	$-z$.
VI	$-1 - x$;	$-y$;	$-z$.
VII	$-x$;	$-y$;	$-z$.
VIII	$-x$;	$1 - y$;	$-z$.

TABLE 9.

4-BROMO-3-NITRO BENZOIC ACID.

DEVIATIONS FROM THE BEST PLANES THROUGH SETS OF ATOMS.(Å).

(a). PLANE DEFINED BY C(1),C(2),C(3),C(4),C(5) and C(6).

ATOM	DEVIATION.	ATOM	DEVIATION
C(1)	0.005	C(7)	0.042
C(2)	0.016	N(1)	-0.094
C(3)	-0.007	O(1)	-0.086
C(4)	-0.025	O(2)	0.258
C(5)	0.047	O(3)	0.688
C(6)	-0.036	O(4)	-0.961
		Br(1)	0.204

(b). PLANE DEFINED BY C(3),N(1),O(3) and O(4).

ATOM	DEVIATION	ATOM	DEVIATION
C(3)	0.000	O(3)	0.000
N(1)	-0.000	O(4)	0.000

(c). PLANE DEFINED BY C(1),C(7),O(1) and O(2).

ATOM	DEVIATION	ATOM	DEVIATION
C(1)	0.005	O(1)	0.006
C(7)	-0.017	O(2)	0.006

TABLE 10 (Overleaf).

4-BROMO-3-NITRO BENZOIC ACID.
THE OBSERVED AND CALCULATED
STRUCTURE AMPLITUDES.

H	K	L	Fo	Fc
0	0	4	21.6	-18.5
0	0	6	80.7	78.7
0	0	8	96.3	-103.4
0	0	10	21.7	26.2
0	0	12	20.2	20.7
0	0	14	26.5	-31.3
0	0	16	22.1	26.4
0	0	20	12.6	-10.6
0	0	22	16.5	17.7
0	0	24	5.5	-6.3
1	0	0	63.0	-60.3
1	0	2	79.2	67.5
1	0	4	150.8	142.8
1	0	6	76.9	-72.6
1	0	8	39.6	35.3
1	0	10	17.3	14.3
1	0	12	66.9	-67.1
1	0	14	28.3	30.0
1	0	16	15.8	16.8
1	0	18	15.5	-15.7
1	0	20	21.7	22.0
1	0	22	11.5	-9.4
1	0	-2	38.4	40.3
1	0	-4	12.3	-14.6
1	0	-6	21.4	-28.2
1	0	-8	28.0	32.3
1	0	-10	64.7	-63.9
1	0	-12	17.5	-17.9
1	0	-14	24.0	27.3
1	0	-16	50.5	-48.2
1	0	-18	29.3	30.0
1	0	-20	5.8	-4.6
1	0	-22	4.9	-5.3
1	0	-24	18.7	16.3
2	0	0	6.9	-7.6
2	0	2	130.1	116.5
2	0	4	146.1	-140.2
2	0	6	63.5	57.0
2	0	8	27.7	-20.5
2	0	10	50.0	-44.2
2	0	12	52.2	46.9
2	0	14	31.7	-31.2
2	0	16	7.6	-5.8
2	0	18	12.8	14.1
2	0	20	5.9	-4.8
2	0	-2	91.0	-101.3
2	0	-4	90.4	79.9
2	0	-6	74.4	-67.6
2	0	-8	65.6	-65.8
2	0	-12	61.9	-87.4
2	0	-14	13.6	12.4
2	0	-16	34.6	37.1
2	0	-18	32.4	-35.9
2	0	-20	28.3	26.0
2	0	-22	5.0	3.0
2	0	-24	26.2	-24.5
3	0	0	5.1	2.8
3	0	2	93.1	-85.1
3	0	4	34.2	33.0
3	0	6	23.7	25.1
3	0	8	82.5	-70.8
3	0	10	47.5	42.5
3	0	12	21.4	-20.5
3	0	14	28.9	-28.4
3	0	16	21.5	22.3
3	0	18	10.3	-9.1
3	0	-2	33.2	36.3
3	0	-4	51.8	-55.3
3	0	-6	78.4	74.5
3	0	-8	41.9	-41.8
3	0	-10	52.0	-50.9
3	0	-12	31.5	39.0
3	0	-14	34.7	-42.9
3	0	-16	6.1	4.8
3	0	-18	19.0	18.1
3	0	-20	16.6	-17.2
3	0	-22	5.9	5.4
3	0	-24	7.8	6.8
4	0	0	26.8	-30.4
4	0	2	51.6	49.5
4	0	4	21.3	-20.4
4	0	6	49.0	-42.6
4	0	8	43.9	37.1
4	0	10	29.7	-28.5
4	0	12	17.1	14.5
4	0	14	31.1	28.0
4	0	16	25.6	-28.7
4	0	-2	57.8	56.0
4	0	-4	50.1	58.9
4	0	-6	53.3	-68.3
4	0	-8	68.4	83.0
4	0	-10	7.5	-5.9
4	0	-12	34.1	-33.5
4	0	-14	44.2	43.5
4	0	-16	21.5	-21.3
4	0	-20	25.2	25.3
4	0	-22	25.5	-24.8
5	0	0	72.0	72.4
5	0	2	5.6	-3.9
5	0	4	26.4	-21.2
5	0	6	31.4	30.6
5	0	8	15.3	-12.8
5	0	10	13.5	-13.0
5	0	12	15.3	13.6
5	0	14	6.3	-6.3
5	0	16	14.3	15.3
5	0	-2	57.4	-57.6
5	0	-4	45.0	54.4
5	0	-6	22.4	29.1
5	0	-8	51.6	-64.0
5	0	-10	62.6	73.0
5	0	-12	13.0	-15.0
5	0	-14	39.9	-39.6
5	0	-16	19.5	20.7
5	0	-18	17.9	-17.8
5	0	-20	11.8	-11.5
5	0	-22	22.7	21.3
6	0	0	13.5	-16.0
6	0	2	28.5	-28.8
6	0	4	30.9	30.4
6	0	6	28.2	-24.2
6	0	8	6.0	-4.6
6	0	10	15.5	13.4
6	0	12	12.9	-12.4
6	0	14	5.9	5.8
6	0	-2	56.8	55.0
6	0	-4	33.9	-40.8
6	0	-6	15.8	19.0
6	0	-8	40.1	41.6
6	0	-10	51.5	-57.4
6	0	-12	19.6	-13.7
6	0	-16	33.3	-28.0
6	0	-18	30.0	27.5
6	0	-20	10.7	-10.0
7	0	0	11.2	-9.2
7	0	2	34.7	36.4
7	0	4	39.8	-41.8
7	0	8	8.3	7.7
7	0	10	13.2	-14.3
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6	2	-1	23.4	26.6
6	2	-2	16.2	-19.5
6	2	-3	25.8	-24.6
6	2	-4	9.6	-11.6
6	2	-5	23.1	29.5
6	2	-6	12.6	-15.1
6	2	-7	6.4	-4.1
6	2	-8	5.4	4.7
6	2	-9	26.7	-28.9
6	2	-11	30.2	32.2
6	2	-13	8.2	-7.7
6	2	-14	8.0	8.3
6	2	-15	17.4	-17.3
6	2	-17	36.0	36.3
6	2	-19	26.0	-24.6
7	2	1	25.1	-22.9
7	2	3	28.2	25.6
7	2	5	12.5	-16.9
7	2	-1	5.3	5.2
7	2	-2	9.5	-9.7
7	2	-3	14.1	20.3
7	2	-4	7.2	-9.3
7	2	-5	42.2	-42.4
7	2	-7	20.6	24.9
7	2	-8	1.4	-4.1
7	2	-9	12.1	14.0
7	2	-10	5.1	5.4
7	2	-11	24.7	-31.5
7	2	-15	9.0	-6.4
7	2	-17	25.1	-21.7
8	2	0	6.7	-7.2
8	2	1	14.6	16.1
8	2	3	6.9	-8.1
8	2	4	6.4	5.3
8	2	5	5.1	-5.4
8	2	6	4.4	-4.4
8	2	-1	9.3	-12.3
8	2	-5	15.9	19.3
8	2	-7	15.7	-19.1
8	2	-8	6.9	6.7
8	2	-10	4.2	-4.2
8	2	-11	14.8	14.8
8	2	-12	2.2	3.9
8	2	-13	24.4	-27.7
8	2	-14	12.1	11.4
8	2	-15	14.4	15.8
0	3	7	13.3	10.8
0	3	8	21.9	24.7
0	3	9	15.8	13.5
0	3	10	25.0	-29.7
0	3	11	22.7	-25.4
0	3	12	13.9	14.0
0	3	13	34.7	39.8
0	3	14	21.9	-19.8
0	3	15	2.3	1.3
0	3	16	12.0	-11.0
0	3	17	20.2	-19.4
0	3	18	5.6	10.3
0	3	19	5.0	7.4
0	3	20	7.1	-6.3
0	3	21	5.1	-4.7
1	3	0	24.8	22.3
1	3	1	48.6	42.1
1	3	2	13.5	-12.6
1	3	3	27.3	-29.1
1	3	4	41.5	40.6
1	3	5	12.9	15.0
1	3	6	31.5	29.1
1	3	7	35.2	33.4
1	3	8	27.5	-26.6
1	3	9	33.8	-33.9
1	3	10	27.7	30.5
1	3	11	25.3	28.7
1	3	12	1.1	1.7
1	3	13	6.6	6.5
1	3	14	19.1	-16.3
1	3	15	17.4	-15.9
1	3	16	7.5	7.9
1	3	17	22.1	20.5
1	3	18	11.0	-8.5
1	3	19	7.3	-7.8
1	3	21	3.3	3.4
1	3	-1	23.5	-22.5
1	3	-2	5.6	3.9
1	3	-3	55.8	-51.5
1	3	-4	44.0	-43.6
1	3	-5	79.0	73.8
1	3	-6	21.0	27.0
1	3	-7	54.1	-52.8
1	3	-8	12.5	-12.6
1	3	-9	19.4	19.0
1	3	-10	3.2	-3.2
1	3	-11	54.0	50.4
1	3	-12	34.1	32.9
1	3	-13	63.2	-60.7
1	3	-18	10.5	13.8
1	3	-19	8.9	-11.6
1	3	-20	10.2	-9.8
1	3	-21	8.3	9.3
1	3	-22	2.6	1.8
2	3	0	55.6	-50.3
2	3	1	81.6	-78.5
2	3	2	51.5	50.4
2	3	3	3.5	-4.9
2	3	4	7.3	6.7
2	3	5	21.8	21.1
2	3	6	14.9	-13.2
2	3	7	39.3	-34.8
2	3	8	30.0	33.3
2	3	9	19.2	16.7
2	3	10	14.2	-11.9
2	3	11	6.9	-7.6
2	3	12	5.6	-5.1
2	3	13	14.0	-15.4
2	3	14	15.8	15.8
2	3	15	29.7	26.5
2	3	16	14.2	-11.9
2	3	17	9.1	-6.6
2	3	18	3.8	2.5
2	3	20	3.8	3.4
2	3	-1	64.2	58.8
2	3	-2	15.0	16.6
2	3	-3	10.4	-12.2
2	3	-4	9.1	10.0
2	3	-5	28.6	-26.5
2	3	-6	56.1	-55.7
2	3	-7	39.1	38.4
2	3	-9	25.3	-35.5
2	3	-8	30.3	27.3
2	3	-11	16.0	-14.1
2	3	-12	6.6	-9.3
2	3	-13	4.8	4.5
2	3	-14	23.2	22.8
2	3	-15	7.1	-10.3
2	3	-16	13.0	-14.0
2	3	-19	6.7	4.1
2	3	-20	12.3	13.0
2	3	-21	12.0	-11.9
2	3	-22	11.2	-12.4
3	3	0	19.7	21.2
3	3	1	43.8	39.1
3	3	2	13.5	-9.7
3	3	3	4.0	-3.6
3	3	4	17.4	-13.3
3	3	5	40.4	-35.9
3	3	6	33.1	31.7
3	3	7	17.9	19.4
3	3	8	16.8	-14.6
3	3	9	10.9	-9.5
3	3	10	14.9	-14.1
3	3	11	13.5	-13.4
3	3	12	13.4	14.7
3	3	14	12.8	-12.0
3	3	15	9.8	-12.0
3	3	18	5.8	5.6
3	3	19	7.5	8.5
3	3	-1	59.9	-57.7
3	3	-2	39.7	-38.3
3	3	-3	38.9	36.9
3	3	-4	12.6	9.9
3	3	-5	6.9	-5.7
3	3	-6	3.9	-0.7
3	3	-7	24.2	-28.8
3	3	-8	28.1	-32.5
3	3	-9	46.7	53.5
3	3	-10	18.9	16.0
3	3	-11	26.5	-31.3
3	3	-12	10.2	-7.2
3	3	-13	13.0	-10.7
3	3	-14	21.0	-21.1
3	3	-15	24.9	26.2
3	3	-16	18.6	23.9
3	3	-17	19.2	-22.0
3	3	-18	7.9	-6.0
3	3	-19	11.7	12.7
3	3	-20	7.4	-6.7
3	3	-21	5.5	5.0
3	3	-22	5.5	5.2
4	3	0	1.9	1.3
4	3	1	39.7	40.3
4	3	2	14.6	-11.4
4	3	3	57.9	-50.9
4	3	4	20.6	19.7
4	3	5	32.0	30.0
4	3	6	22.5	-21.5
4	3	7	4.9	-3.7
4	3	8	4.5	3.6
4	3	9	17.2	-15.0
4	3	10	6.1	4.4
4	3	11	16.6	18.0
4	3	12	15.3	-15.0
4	3	13	9.4	-11.0
4	3	-1	24.2	28.0
4	3	-2	30.5	35.1
4	3	-3	24.1	-27.5
4	3	-4	28.8	-35.1
4	3	-5	34.7	40.0
4	3	-6	1.0	-5.9
4	3	-7	4.5	-4.0
4	3	-8	15.8	14.9
4	3	-9	25.5	-27.4
4	3	-10	34.4	-34.8
4	3	-11	21.6	22.2
4	3	-12	13.4	14.0
4	3	-14	9.9	9.5
4	3	-15	3.1	-3.5
4	3	-16	13.3	-16.9
4	3	-17	17.4	19.6
4	3	-18	20.0	17.4
4	3	-19	17.2	-18.3
4	3	-20	6.2	-3.6
4	3	-21	9.4	7.4
5	3	0	8.3	-3.5
5	3	1	9.0	-6.3
5	3	2	30.5	35.8
5	3	3	53.1	53.8
5	3	4	15.3	-11.5
5	3	5	12.2	-11.6
5	3	7	9.5	-8.2
5	3	8	9.6	9.2
5	3	9	17.8	15.5
5	3	10	17.2	-15.5
5	3	11	12.9	-11.4
5	3	12	2.6	2.1
5	3	15	4.9	6.4
5	[illegible]	[illegible]	13.5	-12.7
5	3	-2	2.1	-6.1
5	3	-3	18.0	19.3
5	3	-4	22.2	25.2
5	3	-5	27.3	-32.4
5	3	-6	20.5	-25.0
5	3	-7	17.3	18.3
5	3	-8	1.1	-1.8
5	3	-9	15.4	12.3
5	3	-10	14.9	16.5
5	3	-11	25.8	-22.3
5	3	-12	24.0	-26.4
5	3	-13	27.9	30.9
5	3	-14	15.8	16.3
5	3	-15	21.7	-19.6
5	3	-16	9.5	9.1
5	3	-17	5.1	-5.7
5	3	-18	11.0	-9.2
5	3	-19	14.0	15.3
5	3	-20	8.9	9.2
6	3	0	21.0	22.3
6	3	1	4.9	5.3
6	3	2	2.3	-2.8
6	3	3	6.9	-6.3
6	3	4	8.9	8.0
6	3	5	4.2	-3.4
6	3	6	7.9	7.7
6	3	7	22.8	22.8
6	3	8	8.9	-9.6
6	3	9	9.6	-12.8
6	3	10	6.3	6.4
6	3	11	6.2	6.3
6	3	-1	17.6	-22.3
6	3	-2	7.1	-2.1
6	3	-3	8.6	10.0
6	3	-4	14.9	-17.5
6	3	-5	11.7	12.4
6	3	-6	17.0	20.6
6	3	-7	28.2	-29.8
6	3	-8	14.9	-16.4
6	3	-9	15.3	14.5
6	3	-10	11.4	-12.2
6	3	-11	2.5	1.8
6	3	-12	13.8	16.5
6	3	-13	26.7	-24.7
6	3	-14	16.0	-12.9
6	3	-15	23.8	21.7
6	3	-16	7.1	5.5
6	3	-17	8.3	-11.3
6	3	-18	6.2	10.1
6	3	-19	5.6	-5.5
7	3	0	17.2	-17.9
7	3	1	13.3	-15.2
7	3	2	8.3	8.9
7	3	4	13.2	10.4
7	3	5	8.1	5.7
7	3	6	8.1	-8.3
7	3	7	9.8	-9.2
7	3	8	5.5	5.6
7	3	-1	17.3	16.8
7	3	-2	13.8	13.9
7	3	-3	17.6	-19.4
7	3	-5	4.1	-4.9
7	3	-6	17.5	-19.6
7	3	-7	21.3	19.8
7	3	-8	12.3	10.8
7	3	-9	27.8	-29.6
7	3	-10	13.4	-16.9
7	3	-11	13.7	16.0
7	3	-12	1.9	-2.6
7	3	-13	9.2	7.9
7	3	-14	10.4	13.6
7	3	-15	15.4	-14.6
7	3	-16	9.6	-8.3
8	3	0	7.5	7.4
8	3	1	4.0	-3.3
8	3	4	6.5	-6.6
8	3	5	10.5	-10.0
8	3	-1	6.7	-6.1
8	3	-2	10.7	-10.9
8	3	-3	18.8	18.8
8	3	-4	4.9	5.6
8	3	-5	11.7	-13.1
8	3	-8	12.2	-14.9
8	3	-9	21.5	21.9
8	3	-10	8.0	8.9
8	3	-11	11.5	-10.3
8	3	-12	4.2	-2.1
8	3	-13	1.6	4.3

PART 5

PARTIAL X-RAY ANALYSIS
OF THE STRUCTURE OF
BIS-TETRAPHENYL ARSONIUM
MERCURIC TETRABROMIDE

5.1 INTRODUCTION.

In recent years, knowledge of the structures of mercury compounds has considerably increased, mainly by x-ray work. There have been recent reviews of mercury-nitrogen compounds by Lipscomb (1957), of halogeno-mercurate (II) compounds by Deacon (1963), and a general review of the structural chemistry of mercury by Grdenic (1965).

Work on the coordination and stereochemistry of mercury as part of a broad programme has been started at this laboratory, and is continuing elsewhere. Work done on mercury in this Department includes the mercuric chloride adduct of perloline by Jeffreys et.al. (1963) and (1966), the mercuric chloride adduct of 1,6-dithiacyclo deca-cis-3, cis-8-diene (Cheung and Sim, 1965), and also a series of mercuric halide adducts of various compounds by McEwen (1965).

The analysis of bis-tetraphenyl arsonium mercuric tetrabromide described here has been undertaken as a part of this series of investigations. Mercury may be coordinated in this compound in two possible ways, either tetrahedrally or octahedrally. It is to discover which of these two possibilites that the analysis has been undertaken, and also to discover whether the coordination is regular or distorted.

The complex is prepared by adding a solution of one part of mercuric bromide in ethanol to a solution of two parts of tetraphenyl arsonium bromide in ethanol. White crystals separate out, and these are washed in ethanol, and pumped dry.

$$2(C_6H_5)_4As\ Br + HgBr_2 \longrightarrow (C_6H_5)_8As_2Hg\ Br_4.$$

The crystals were analysed for percentage composition of mercury by the method due to Rauscher (1938). The percentage mercury present was found to be 15.7%. The theoretical percentage composition of the crystals based on the formula shown gives a mercury content of 15.6%.

5.2 EXPERIMENTAL.

Bis-tetraphenyl arsonium mercuric tetrabromide has molecular formula $C_{48}H_{40}As_2HgBr_4$; the molecular weight is 1286.3, and the crystal melts at 248^o-252^o (with decomposition).

Rotation, oscillation, Weissenberg and precession photographs were taken with copper K-α (λ = 1.542 Å) and molybdenum K-α (λ= 0.7107 Å) radiation. The unit cell parameters were determined from rotation and precession photographs, and in the latter case, the unit cell edges and angles were derived from the reciprocal cell parameters by the conversion formulae for triclinic crystals as listed by Buerger (1942). From these, the following values were obtained

$a = 13.29 \pm 0.04$ Å

$b = 10.38 \pm 0.03$ Å

$c = 10.18 \pm 0.04$ Å

$\alpha = 100^o 13'$

$\beta = 94^o 15'$

$\gamma = 108^o 25'$

The volume of the unit cell was calculated using the

$\gamma =$ expression

$$V = abc\sqrt{(1-\cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)}$$

and was found to be 1298 $Å^3$.

Since the crystal is triclinic, there are no systematic absences, and so the space group may be P1 <u>or</u> P$\bar{1}$.

The density was found by flotation to be 1.64 gm/ml., and consequently, the number of molecules in the unit cell is one. This number of molecules leads to a calculated density of 1.65 gm/ml.

The calculated linear absorption coefficient for copper K-α radiation is 115.3cm^{-1}. The total number of electrons per unit cell, F(000), is 614.

The crystal is shaped like a long, narrow needle, and in order that absorption corrections might be made, the radius of the crystal was measured, and this was found to be 0.03 cm.

Equatorial and equi-inclination upper layer Weissenberg intensity data were obtained by rotating the crystal about the needle axis (c-crystal axis), the reciprocal lattice nets hk0,......,hk7 and hk$\bar{1}$,......,hk$\bar{6}$ being registered in this manner. All intensity data were collected using Robertson's multiple film technique (1943). The intensities, measured visually by comparison with a calibrated intensity strip, were corrected for Lorentz, polarisation and rotation factors appropriate to the upper

The values of the structure amplitudes were obtained by application of the mosaic crystal formulae. In all, the total number of independent observed structure amplitudes that were obtained was 3002.

The various layers of $|Fo|$ were placed on the same scale by comparison of the observed and calculated structure amplitudes obtained from the Patterson function. Throughout the refinement, the scale was adjusted by correlation with the calculated structure amplitudes, to ensure that $\sum|Fo|$ always equalled $\sum|Fc|$.

5.3 DETERMINATION OF THE SPACE GROUP.

The crystal is triclinic, and the space group must therefore be P1 or P$\bar{1}$. Since there are no systematic absences, the correct space group must be deduced by some other means. A method of discovering whether a crystal is non-centrosymmetrical or centrosymmetrical was devised by Howells, Phillips, and Rogers in 1950. They have shown that the fraction N(z) of reflections whose intensities are equal to or less than a fraction z of the local average differ in a non-centrosymmetrical and a centrosymmetrical crystal. Appropriately, this is called the "N(z) Test".

The fractions N(z) of reflections can be evaluated for the given crystal, and these can be compared with the theoretical distributions for non-centrosymmetrical and centrosymmetrical crystals. In the case of a non-centrosymmetrical crystal, the fractions N(z) are given by

$$N(z) = 1 - \exp(-z)$$

and in the case of a centrosymmetrical crystal, by the function

$$N(z) = \operatorname{erf} (\tfrac{1}{2}z)^{\frac{1}{2}}$$

The symbol 'erf' represents the error function (Lipson and Cochran, 1957). These two functions, which are shown in Table 1 differ appreciably from each other, particularly at lower values of z. These expressions apply only for a random distribution of scattering material in a unit cell. Intensities are compared only with others having about the same value of θ, and thus the intensities are divided up into various zones of θ.

TABLE 1

Values, (in%), of the two functions representing N(z).

z.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
a.	0.0	9.5	18.1	25.9	33.0	39.4	45.1	50.3	55.0	59.3	63.2
b.	0.0	24.8	34.5	41.9	47.4	52.1	56.1	59.8	62.9	65.7	68.3

where $a = 1-\exp(-z)$ and $b = \mathrm{erf}(\frac{1}{2}z)^{\frac{1}{2}}$.

In the case of bis-tetraphenyl arsonium mercuric tetrabromide, the data were divided into four ranges of $\sin\theta$. All values of $\sin\theta$ less than 0.2 and greater than 0.9 were excluded. The four ranges of $\sin\theta$ which were chosen were 0.2-0.4; 0.4-0.55; 0.55-0.7; and 0.7-0.9, and the total number of reflections in each range was 309, 554, 746, and 993 respectively.

The N(z) tests were carried out on the $|Fo|^2$ terms, and values for N(z) were evaluated for each range, for z = 0.1 to z = 1.0, where z is the average value of $|Fo|^2$ for each range of sin θ. The results obtained for these zones of sin θ are shown in Tables 2, 3, 4 and 5. The average values of N(z) for these four ranges, weighted according to the number of reflections in each range, are shown in Table 6.

TABLE 6

Values, (in%), of N(z) for the crystal.

z.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
N(z)	0.0	8.3	19.2	29.0	37.2	42.6	47.7	51.7	54.9	58.2	61.3

A comparison of these values of N(z) with the theoretical distributions for non-centrosymmetrical and centrosymmetrical crystals is shown in fig. 1. This comparison indicates that the crystal is probably non-centrosymmetrical, and thus the space group of bis-tetraphenyl arsonium mercuric tetrabromide is P1.

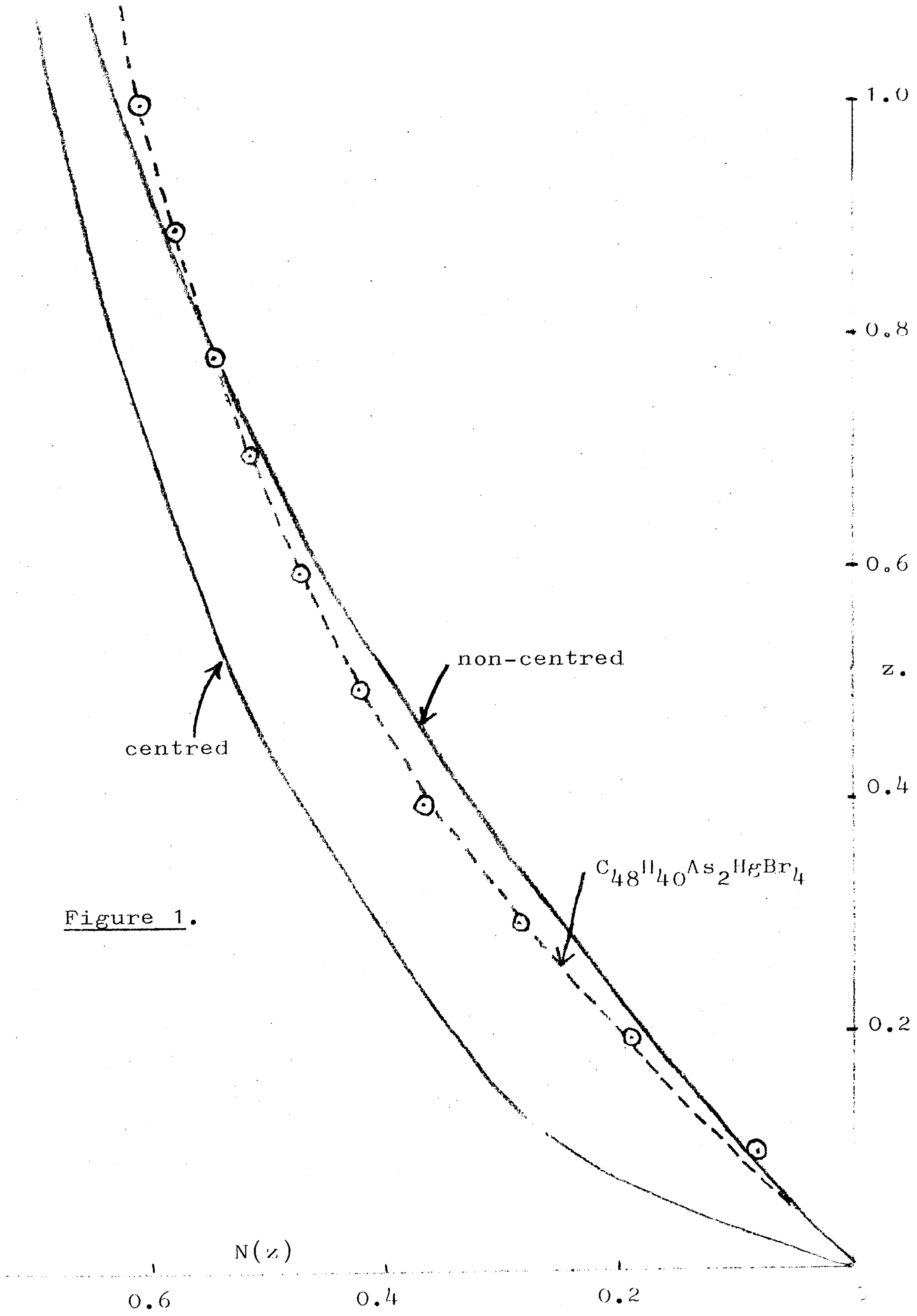
1.0
0.8
0.6
z.
0.4
0.2
non-centred
centred
$C_{48}H_{40}As_2HgBr_4$
N(z)
0.6
0.4
0.2
0

Figure 1.

The figures given for N(z) in these four tables are actual numbers of reflections.

TABLE 2 ($\sin\theta$ from 0.2-0.4)

z.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
N(z)	0	62	85	106	125	139	154	165	173	187	195

TABLE 3 ($\sin\theta$ from 0.4-0.55)

z.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
N(z)	0	100	177	207	237	266	289	317	322	334	351

TABLE 4 ($\sin\theta$ from 0.55-0.7)

z.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
N(z)	0	46	166	231	304	348	365	385	396	416	433

TABLE 5 ($\sin\theta$ from 0.7-0.9)

z.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
N(z)	0	7	72	211	302	356	432	479	538	578	616

5.4 PARTIAL SOLUTION OF THE STRUCTURE.

The three dimensional Patterson function was calculated, and the resulting map was drawn up. Because the mercury atom is located at the origin, peaks will appear on the Patterson map, which correspond to the actual positions of the bromine atoms in the crystal. A complication is that peaks related by a centre of symmetry at the origin will also appear. That is, for each bromine atom, peaks will appear at (x_{Br}, y_{Br}, z_{Br}) and $(\bar{x}_{Br}, \bar{y}_{Br}, \bar{z}_{Br})$. If the mercury-bromine coordination is tetrahedral, then eight single weight peaks in the shape of a cube will be produced, whereas, if the mercury-bromine coordination is square-coplanar (i.e. if the overall coordination for mercury is octahedral), then four double weight peaks in the shape of a square will be produced.

Examination of the three dimensional Patterson map revealed eight peaks, approximately the same distance from the origin, and in the shape of a cube. Four of these peaks which formed a tetrahedron round the origin were selected. The coordinates of the four bromine atoms thus determined are shown below, with the mercury atom (which can be arbitrarily placed at the origin).

	x/a	y/b	z/c
Mercury (1)	0.0000	0.0000	0.0000
Bromine (1)	-0.1970	-0.0607	0.0337
Bromine (2)	0.0752	-0.2019	0.0727
Bromine (3)	0.1397	0.2426	0.1138
Bromine (4)	0.0270	-0.0857	-0.2596

The positions of the interatomic vector peaks between these four bromine atoms were calculated, and these show up clearly in the three dimensional Patterson map.

Structure factors calculated employing these coordinates, and isotropic temperature factors of $U = 0.04 \text{Å}^2$, led to an overall agreement index of 42.7%. A three dimensional Fourier synthesis was evaluated using the observed structure amplitudes and phase constants appropriate to these five atoms, and improved atomic coordinates were obtained for the four bromine atoms.

The crystal used to record the intensity data was quite large, having a diameter of 0.06 cm., and therefore it is possible that absorption of the x-rays by the crystal was fairly high. Corrections for this absorption, assuming that the crystal was a cylinder of radius 0.03 cm., were now carried out in the manner detailed in International Tables for X-Ray Crystallography, Volume III. The value obtained for μR was 3.5.

Using the absorption corrected intensity data, with the coordinates for the mercury and the four bromine atoms obtained from the first Fourier synthesis, a second cycle of structure factors was calculated; the agreement index obtained was 35.9%.

The second Fourier synthesis took the form of an $|Fo| - |Fc|$ map, and the coordinates obtained from this were included in a third structure factor calculation, leading to an agreement index of 33.8%. In both of these structure factor calculations, overall isotropic temperature factors of $U = 0.04 \text{ Å}^2$ were employed.

From a third Fourier synthesis, based upon the observed structure amplitudes, coordinates for the mercury and four bromine atoms were obtained. Three cycles of least squares refinement of the positional and thermal parameters were then carried out, using anisotropic temperature factors. This led to an agreement index of 28.9%.

Several attempts were made to locate the two arsenic atoms, but these met with no success. Since the purpose of the analysis was to discover how the mercury atom and four bromine atoms were coordinated, and to examine this coordination for any distortion, it was decided at this stage to postpone further work on this project. A diagrammatic representation of the course of the analysis up to this stage is given in Table 7.

For the structure factor calculations, the theoretical atomic scattering factors of Thomas-Fermi (1935) for bromine and mercury were used.

The weighting scheme used in the least squares refinement was that of Cruickshank et.al. (1961b); in this

$$\sqrt{w} = 1/(p_1+F+p_2.F^2)^{\frac{1}{2}}$$

The values which were used for the constant terms were

$p_1 = 2 \cdot F \min = 6.70$

$p_2 = 2/F \max = 0.014$

TABLE 7

COURSE OF THE ANALYSIS

OPERATION	ATOMS INCLUDED	R(%)
3D Patterson Synthesis	- - - -	- -
1st 3D Fourier Synthesis	Hg + 4(Br)	42.7
2nd " " (and absorption correction)	"	35.9
3rd 3D Fourier Synthesis	"	33.8
1st Least Squares Cycle	"	31.1
2nd " "	"	29.7
3rd " "	"	28.9

5.5 RESULTS OF THE ANALYSIS.

The final atomic coordinates and anisotropic temperature factors given by the least squares refinement are listed in Tables 8 and 9 respectively. The standard deviations of the final atomic coordinates, given in Table 10, were derived from the least squares totals as shown in Section 1.9.

The mercury-bromine bond lengths and interbond angles are listed in Tables 11 and 12, and the intramolecular non-bonded contacts between the bromine atoms are listed in Table 13. The standard deviation for a typical bond length is 0.02 Å, and the standard deviation for a bond angle is 1°.

The observed and calculated structure amplitudes are listed in Table 14, these being the values obtained from the last least squares cycle. The final agreement index, calculated over 3002 observed structure amplitudes, is 28.9%.

5.6 DISCUSSION OF THE RESULTS.

Six ions of the atoms of groups IA and IIA of the periodic table, namely Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{+}, Ag^{+} and Au^{+}, have complete d-shells. This spherically symmetrical arrangement may be expected to lead to simple stereochemistry; that is, the configurations corresponding to one-, two-, three-, four-, five- and six-fold coordination. In the case of mercury, a marked preference is displayed for two-fold coordination, although four-fold coordination is also common.

In addition to this preference for a certain type of coordination, mercury also tends to adopt configurations which are distorted in some manner from the regular pattern.

The object of the present structure analysis was to discover whether the mercuric ion was octahedrally or tetrahedrally coordinated, and also to discover whether any distortion had occurred, and if so, to what degree, Although the analysis has not been completed, sufficient work has been done on the project to determine the answer to this problem. From an examination of the results, it can be seen that in the case of bis-tetraphenyl arsonium mercuric tetrabromide, the mercuric ion adopts a distorted tetrahedral configuration, and consequently this discussion will be devoted to the four-fold coordination of mercury in general, with particular reference to mercury-bromine distances and angles.

Almost completely regular tetrahedral coordination of the mercuric ion has been reported in two cases. These are the mercurichloride derivative of the alkaloid perloline (Jeffreys et.al., 1963 and 1966), in which the $HgCl_4^{2-}$ anion is sufficiently isolated from the rest of the molecule to resist distortion, and red mercuric iodide (Huggins and Magill, 1927). In the mercuric iodide, the crystal structure is composed of an infinite array of fully "corner-linked" tetrahedra. In most other structures containing four-fold mercury coordination, the tetrahedron is extremely irregular. This distorted tetrahedral arrangement round the mercury atom is very clearly illustrated in the structure $HgCl_2.2\left[(C_6H_5)_3AsO\right]^-$, reported by Brändén, (1963), and in the structure $\left[HgCl_2.(C_6H_5)_3AsO\right]_2$, also investigated by Brändén, (1964).

The bonds in tetrahalomercurates can be regarded as being formed by mercury sp^3-hybrid orbitals. Once these orbitals have been used for σ-bonding, there is a possibility that π-bonding may occur between filled metal orbitals and empty ligand orbitals. Formation of π-bonding will be instrumental in reducing the length of a mercury-ligand bond, and varying amounts of π-bonding in a complex will lead to different bond lengths between the central mercury atom and the different ligands [(Orgel, 1960) and (Cotton, 1960)].

In the case of bis-tetraphenyl arsonium mercuric tetrabromide, the mercury-bromine bond lengths fall into two distinct categories -- short and long. The Hg-Br(1) and the Hg-Br(3) distances are 2.54 Å and 2.56 Å respectively, while the Hg-Br(2) and the Hg-Br(4) distances are 2.80 Å and 2.74 Å respectively. The variation in these interbond distances may be explained by assuming that differences in the π-bond order of the various bonds have occurred, and examination of the interbond angles (see later in this section) seems to provide a measure of confirmation for this hypothesis. Mercury-bromine bond lengths in the region of 2.45 Å-2.55 Å have been reported in the structure of $(CH_3)_4N.HgBr_3$ which contains recognisable planar $HgBr_3^-$ ions (White, 1963), where the reported value was 2.52 Å. Longer mercury-bromine distances in the region of 2.75 Å-2.85 Å have been found by McEwen (1965) in the structure of dibromobisthioureamercury (II), in which one of the mercury-bromine distances is 2.81 Å.

Four of the six Br-Hg-Br interbond angles approximate to the tetrahedral value of 109°28', but the remaining two deviate significantly from this figure. The Br(1)-Hg-Br(3) angle is 121.9° and the Br(2)-Hg-Br(4) angle is 90.4°. If variations in the π-bond order in the different mercury-bromine bonds are assumed (see this section-page 130) then it would be expected that repulsion between the interbond electron clouds would vary in magnitude. Therefore, the angle between the two shorter bonds might be expected to be greater than tetrahedral, and the angle between the two longer bonds to be less than tetrahedral. This type of distortion, in which four angles round a mercury atom are approximately the same and one is significantly smaller, and one is significantly larger has been observed by Brändén in 1963 and 1964.

Although only a limited amount of work has been done on this compound, nevertheless, the estimated standard deviations of the bromine atoms are quite small, and thus a discussion of the irregularities of the coordination of the mercuric ion is permissible. Further discussion of the complex must be postponed until more detailed information concerning the molecular geometry has been obtained.

TABLE 8.

BIS-TETRAPHENYL ARSONIUM MERCURIC TETRABROMIDE.

FINAL ATOMIC COORDINATES.

ATOM	x/a	y/b	z/c
Hg(1)	0.0000	0.0000	0.0000
Br(1)	-0.1974	-0.0582	0.0258
Br(2)	0.0748	-0.2035	0.0752
Br(3)	0.1386	0.2376	0.1096
Br(4)	0.0255	-0.0846	-0.2624

TABLE 9.

BIS-TETRAPHENYL ARSONIUM MERCURIC TETRABROMIDE.

FINAL ANISOTROPIC TEMPERATURE FACTORS. (Å^2).

ATOM.	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Hg(1)	0.0221	0.0183	0.0142	-0.0045	-0.0009	0.0103
Br(1)	0.0248	0.0423	0.0181	0.0176	0.0172	0.0131
Br(2)	0.0578	0.0434	0.0404	0.0371	0.0086	0.0403
Br(3)	0.0366	0.0190	0.0360	-0.0127	0.0042	0.0047
Br(4)	0.0554	0.0494	0.0311	0.0070	0.0041	0.0299

TABLE 10.

BIS-TETRAPHENYL ARSONIUM MERCURIC TETRABROMIDE.

STANDARD DEVIATIONS OF THE FINAL ATOMIC COORDINATES. (Å).

ATOM.	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Hg(1)	0.000	0.000	0.000
Br(1)	0.012	0.013	0.016
Br(2)	0.012	0.014	0.016
Br(3)	0.012	0.013	0.016
Br(4)	0.012	0.013	0.015

TABLE 11.

BIS-TETRAPHENYL ARSONIUM MERCURIC TETRABROMIDE.

BOND LENGTHS. (Å).

Hg(1) - Br(1)	2.54		Hg(1) - Br(3)	2.56
Hg(1) - Br(2)	2.80		Hg(1) - Br(4)	2.74

TABLE 12.

BIS-TETRAPHENYL ARSONIUM MERCURIC TETRABROMIDE.

BOND ANGLES. (°).

Br(1) - Hg(1) - Br(2)	109.6
Br(1) - Hg(1) - Br(3)	121.9
Br(1) - Hg(1) - Br(4)	111.0
Br(2) - Hg(1) - Br(3)	107.7
Br(2) - Hg(1) - Br(4)	90.4
Br(3) - Hg(1) - Br(4)	111.7

TABLE 13.

BIS-TETRAPHENYL ARSONIUM MERCURIC TETRABROMIDE.

NON-BONDED CONTACTS BETWEEN BROMINE ATOMS. (Å).

Br(1).....Br(2)	4.37	Br(2).....Br(3)	4.33
Br(1).....Br(3)	4.47	Br(2).....Br(4)	4.33
Br(1).....Br(4)	4.36	Br(3).....Br(4)	4.39

TABLE 14 (Overleaf).

BIS-TETRAPHENYL ARSONIUM MERCURIC TETRABROMIDE.

THE OBSERVED AND CALCULATED

STRUCTURE AMPLITUDES.

H	K	L	Fo	Fc
0	9	0	40.2	45.7
0	10	0	13.9	29.3
0	11	0	22.0	23.5
1	2	0	160.3	102.5
1	3	0	17.9	68.9
1	4	0	36.5	57.2
1	6	0	27.5	21.6
1	7	0	19.3	23.9
1	8	0	39.8	47.4
1	9	0	19.3	26.4
1	10	0	44.9	41.3
1	11	0	62.7	50.3
1	-2	0	40.9	33.8
1	-3	0	177.3	80.8
1	-4	0	333.1	137.5
1	-5	0	39.2	52.7
1	-6	0	57.6	50.1
1	-7	0	50.3	45.4
1	-8	0	27.4	23.5
1	-9	0	65.7	52.5
1	-10	0	67.1	53.7
1	-12	0	9.2	9.4
2	0	0	110.2	119.6
2	1	0	183.6	125.3
2	2	0	155.7	124.4
2	3	0	43.2	20.8
2	4	0	74.1	86.3
2	5	0	16.2	30.2
2	6	0	12.9	9.9
2	7	0	69.9	66.0
2	8	0	32.8	41.2
2	9	0	30.3	24.5
2	10	0	34.8	42.5
2	11	0	32.9	47.0
2	-1	0	38.4	64.7
2	-2	0	149.0	98.5
2	-3	0	29.8	45.2
2	-4	0	43.0	59.4
2	-5	0	14.1	86.8
2	-6	0	56.7	54.7
2	-8	0	19.8	39.5
2	-9	0	32.8	53.5
2	-10	0	39.3	64.2
2	-11	0	18.0	31.2
2	-12	0	14.1	4.9
3	0	0	123.0	138.3
3	1	0	176.3	128.3
3	2	0	33.7	93.4
3	3	0	85.7	72.9
3	4	0	79.6	53.4
3	5	0	27.1	38.1
3	6	0	30.0	64.9
3	7	0	32.2	53.2
3	9	0	18.3	26.7
3	11	0	26.2	32.7
3	-1	0	65.7	62.8
3	-2	0	111.2	96.9
3	-3	0	103.1	65.6
3	-4	0	19.7	25.3
3	-5	0	134.8	45.7
3	-6	0	152.7	69.6
3	-7	0	94.0	41.9
3	-8	0	102.8	65.9
3	-9	0	56.7	73.7
3	-10	0	55.9	53.1
3	-11	0	26.9	35.6
3	-12	0	14.7	27.4
4	0	0	102.4	76.8
4	1	0	143.1	128.2
4	2	0	225.4	162.1
4	3	0	51.6	75.4
4	4	0	26.0	16.7
4	5	0	73.9	76.1
4	6	0	56.9	74.6
4	7	0	19.4	16.8
4	8	0	20.4	28.2
4	9	0	34.6	33.3
4	-1	0	77.0	86.7
4	-2	0	79.4	74.3
4	-3	0	74.6	79.6
4	-4	0	67.8	31.9
4	-5	0	76.0	18.3
4	-6	0	85.0	44.4
4	-7	0	12.8	37.3
4	-8	0	69.3	61.9
4	-9	0	40.1	62.4
4	-10	0	39.7	49.8
4	-11	0	27.2	27.8
4	-12	0	50.9	47.6
5	0	0	27.7	32.4
5	1	0	198.0	153.6
5	2	0	216.6	158.9
5	3	0	56.4	62.6
5	5	0	55.3	71.6
5	6	0	28.0	33.0
5	-1	0	113.3	72.3
5	-2	0	140.1	132.7
5	-3	0	104.3	76.1
5	-4	0	71.8	50.8
5	-5	0	29.3	39.0
5	-6	0	26.4	19.0
5	-7	0	41.0	52.6
5	-8	0	44.3	53.4
5	-10	0	19.2	26.2
5	-11	0	13.2	25.1
5	-12	0	36.4	38.1
6	0	0	40.1	49.6
6	1	0	94.8	107.7
6	2	0	72.4	76.6
6	3	0	23.9	55.3
6	4	0	54.2	54.8
6	5	0	18.8	23.8
6	6	0	23.2	34.2
6	7	0	20.3	16.2
6	8	0	13.0	7.1
6	9	0	28.7	33.9
6	-1	0	110.7	70.4
6	-2	0	110.5	104.2
6	-3	0	88.8	93.8
6	-4	0	108.7	59.2
6	-5	0	82.9	61.1
6	-6	0	60.8	34.2
6	-7	0	53.8	43.0
6	-8	0	128.1	89.7
6	-9	0	59.6	41.7
6	-11	0	31.5	34.7
6	-12	0	41.8	35.3
7	0	0	81.2	66.2
7	1	0	26.0	35.3
7	2	0	39.2	64.9
7	3	0	85.3	79.8
7	4	0	38.6	39.7
7	5	0	51.6	42.3
7	6	0	38.5	41.3
7	7	0	21.5	19.7
7	8	0	15.4	26.2
7	9	0	41.9	39.9
7	-1	0	33.6	54.8
7	-2	0	42.8	26.2
7	-3	0	17.0	57.2
7	-4	0	64.4	57.4
7	-5	0	26.6	61.6
7	-7	0	37.3	52.2
7	-8	0	106.0	81.8
7	-9	0	46.5	62.0
7	-11	0	25.9	30.0
7	-12	0	50.2	49.8
8	0	0	33.2	39.3
8	1	0	63.2	56.3
8	2	0	66.6	72.2
8	5	0	40.1	39.2
8	6	0	18.4	27.0
8	7	0	27.6	31.3
8	-1	0	67.5	79.9
8	-2	0	18.3	21.6
8	-3	0	32.1	14.0
8	-4	0	77.1	54.4
8	-6	0	120.2	74.6
8	-7	0	69.7	71.9
8	-8	0	72.4	62.6
8	-10	0	38.6	47.3
8	-11	0	16.7	34.0
8	-12	0	24.4	36.4
9	0	0	20.9	52.6
9	1	0	22.1	40.2
9	2	0	22.5	49.7
9	3	0	83.9	80.6
9	4	0	59.5	70.1
9	5	0	19.9	26.1
9	7	0	41.0	44.7
9	-1	0	52.1	71.7
9	-2	0	28.3	45.8
9	-3	0	34.8	18.9
9	-5	0	36.6	35.9
9	-6	0	56.4	45.7
9	-7	0	58.4	60.7
9	-8	0	59.6	49.1
9	-10	0	55.7	58.3
9	-11	0	40.6	47.6
9	-12	0	15.1	21.7
10	0	0	70.1	70.9
10	1	0	71.8	48.1
10	3	0	84.1	79.7
10	4	0	44.6	54.2
10	5	0	18.3	21.9
10	6	0	22.1	25.6
10	7	0	22.0	29.0
10	-1	0	68.7	65.6
10	-2	0	19.3	50.1
10	-3	0	30.5	41.1
10	-6	0	39.4	59.2
10	-7	0	23.2	33.9
10	-9	0	20.2	21.4
10	-10	0	18.7	35.0
10	-11	0	21.4	39.0
11	0	0	32.7	51.6
11	1	0	40.2	39.5
11	2	0	19.2	35.2
11	3	0	27.1	40.3
11	4	0	11.2	24.5
11	5	0	21.7	27.4
11	-1	0	58.9	55.0
11	-2	0	32.1	33.6
11	-3	0	71.4	62.7
11	-4	0	32.2	32.3
11	-6	0	59.6	75.0
11	-7	0	73.0	65.1
11	-8	0	14.4	8.0
11	-9	0	21.7	24.3
11	-10	0	39.3	46.0
12	0	0	12.6	17.5
12	1	0	22.6	41.4
12	4	0	29.2	35.2
12	5	0	30.6	38.0
12	-2	0	19.4	32.4
12	-3	0	23.2	37.1
12	-4	0	20.8	47.2
12	-5	0	32.9	34.8
12	-6	0	40.0	52.6
12	-7	0	45.5	65.7
12	-8	0	13.9	28.3
12	-9	0	18.2	25.0
12	-10	0	38.3	49.5
12	-11	0	29.2	37.9
13	0	0	26.7	30.8
13	1	0	51.0	48.7
13	3	0	29.0	25.2
13	4	0	32.2	40.3
13	-2	0	20.4	23.5
13	-3	0	22.9	27.4
13	-4	0	39.6	34.7
13	-5	0	45.4	54.1
13	-6	0	31.6	41.2
13	-8	0	28.9	46.8
13	-9	0	26.3	38.8
13	-10	0	17.4	29.8
14	0	0	32.5	39.2
14	1	0	29.8	35.5
14	2	0	13.0	24.5
14	-2	0	18.9	7.7
14	-3	0	26.2	27.2
14	-5	0	30.0	39.9
14	-6	0	20.7	32.9
14	-8	0	31.6	34.6
14	-9	0	39.5	49.7
15	1	0	23.2	32.0
15	-1	0	42.5	37.1
15	-2	0	18.3	19.4
15	-5	0	23.0	34.6
15	-6	0	11.5	16.6
16	-1	0	23.6	33.0
16	-2	0	22.5	32.0
16	-4	0	26.8	33.1
16	-5	0	40.4	51.7
16	-6	0	16.0	19.6
0	1	1	25.5	98.5
0	2	1	30.4	69.1
0	3	1	55.7	58.4
0	4	1	80.8	78.6
0	6	1	32.2	42.9
0	7	1	83.3	67.4
0	9	1	75.2	47.6
0	10	1	49.9	41.9
0	11	1	41.0	26.3
1	0	1	148.4	169.2
1	1	1	128.0	121.7
1	2	1	89.5	57.9
1	3	1	131.9	75.4
1	4	1	38.2	15.3
1	5	1	53.7	49.8
1	6	1	60.5	60.0
1	7	1	66.5	57.1
1	8	1	38.5	28.4
1	9	1	66.3	45.6
1	10	1	29.6	36.6
1	11	1	37.5	31.4
1	-1	1	117.9	122.5
1	-2	1	71.9	118.5
1	-3	1	111.2	133.7
1	-4	1	154.2	139.0
1	-5	1	156.0	114.9
2	0	1	157.7	81.8
2	1	1	12.1	75.5
2	2	1	77.5	60.0
2	3	1	35.3	34.4
2	4	1	49.8	41.5
2	5	1	31.1	39.7
2	6	1	44.6	55.7
2	7	1	55.6	66.8
2	10	1	38.9	39.8
2	11	1	54.4	51.9
2	-1	1	150.8	97.3
2	-2	1	109.4	98.3
2	-3	1	167.8	172.2
2	-4	1	153.9	137.6
2	-5	1	85.0	80.9
2	-6	1	124.8	74.9
3	0	1	32.2	29.8
3	1	1	137.6	97.1
3	2	1	61.1	76.4
3	3	1	69.7	43.7
3	4	1	20.7	50.2
3	5	1	48.7	38.0
3	6	1	41.7	58.4
3	7	1	80.2	88.1
3	8	1	46.8	46.3
3	9	1	12.9	14.0
3	10	1	67.9	45.8
3	-1	1	71.6	21.0
3	-2	1	75.4	98.8
3	-3	1	119.7	113.5
3	-4	1	16.1	71.4
3	-5	1	54.6	55.8
3	-6	1	61.8	38.6
3	-7	1	84.7	82.5
4	0	1	79.0	81.2
4	1	1	246.7	144.1
4	2	1	14.6	63.9
4	3	1	59.2	49.8
4	4	1	57.2	56.4
4	5	1	63.1	38.4
4	6	1	55.5	61.2
4	7	1	57.2	53.8
4	9	1	24.7	28.1
4	10	1	22.1	27.0
4	-1	1	53.4	18.3
4	-2	1	98.7	116.6
4	-3	1	149.8	149.6
4	-5	1	27.6	36.8
4	-6	1	29.9	40.9
4	-7	1	19.2	33.4
4	-8	1	53.1	51.4
5	0	1	100.4	72.2
5	1	1	152.7	98.9
5	2	1	22.8	80.2
5	5	1	54.2	46.0
5	6	1	14.0	27.9
5	8	1	38.2	35.8
5	9	1	45.2	34.2
5	-1	1	13.1	50.7
5	-2	1	111.1	99.4
5	-3	1	182.4	171.1
5	-4	1	108.0	89.1
5	-5	1	27.9	12.4
5	-6	1	30.7	43.2
5	-7	1	61.3	51.3
5	-8	1	54.2	28.2
6	0	1	39.5	67.8
6	1	1	93.6	81.6
6	2	1	101.1	76.7
6	3	1	89.6	61.4
6	4	1	29.3	24.9
6	5	1	56.2	40.6
6	6	1	22.3	8.0
6	7	1	33.0	26.7
6	8	1	49.7	45.4
6	9	1	25.2	24.3
6	-1	1	125.2	131.3
6	-2	1	107.5	113.4
6	-3	1	110.2	110.2
6	-4	1	19.4	94.1
6	-5	1	37.8	45.8
6	-6	1	15.4	27.2
6	-7	1	62.8	55.2
6	-8	1	19.1	38.8
6	-9	1	27.2	30.9
7	0	1	10.8	30.3
7	1	1	46.4	48.5
7	2	1	27.2	40.3
7	3	1	20.6	30.2
7	4	1	26.6	38.7
7	5	1	22.3	18.6
7	6	1	18.2	18.2
7	8	1	36.8	36.3
7	-1	1	120.8	119.2
7	-2	1	119.2	112.5
7	-3	1	94.0	72.0
7	-4	1	53.7	45.4
7	-5	1	103.0	96.2
7	-6	1	49.4	39.3
7	-7	1	17.2	23.3
7	-8	1	30.7	66.2
7	-9	1	38.6	44.4
8	0	1	15.7	45.2
8	1	1	12.4	5.8
8	2	1	18.5	37.5
8	3	1	55.7	68.0
8	4	1	14.1	25.7
8	5	1	31.1	29.8
8	6	1	43.6	36.3
8	7	1	37.6	24.8
8	8	1	41.8	35.4
8	-1	1	84.7	77.2
8	-2	1	21.9	64.2
8	-3	1	18.0	34.8
8	-4	1	16.5	13.2
8	-5	1	60.3	67.5
8	-6	1	28.5	57.7
8	-7	1	21.2	17.0
8	-8	1	31.1	45.2
8	-9	1	57.2	59.2
9	0	1	28.8	47.3
9	1	1	36.5	10.7
9	2	1	68.7	73.0
9	3	1	70.0	67.7
9	4	1	18.5	20.3
9	5	1	29.5	30.2
9	6	1	41.3	37.7
9	7	1	18.1	18.9
9	-1	1	113.1	111.3
9	-2	1	78.7	64.9
9	-3	1	23.8	4.4
9	-4	1	17.7	26.8
9	-5	1	17.0	31.7
9	-6	1	36.4	38.8
9	-7	1	30.8	35.8
9	-9	1	18.5	31.3
9	-10	1	29.7	47.0
10	0	1	48.2	47.8
10	1	1	31.2	47.8
10	2	1	49.6	58.0
10	3	1	56.5	42.5
10	4	1	17.5	31.2
10	5	1	42.1	28.6
10	6	1	18.4	19.5
10	-1	1	98.9	92.6
10	-2	1	97.6	89.8
10	-3	1	13.2	14.9
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10	-5	1	67.2	57.0
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10	-7	1	31.4	42.8
10	-8	1	22.2	19.2
10	-9	1	18.1	6.4
10	-10	1	44.9	45.1
11	0	1	80.9	68.4
11	1	1	69.9	65.4
11	2	1	19.5	19.1
11	3	1	34.7	35.7
11	4	1	46.0	35.4
11	5	1	24.0	12.4
11	6	1	24.8	25.4
11	-1	1	56.8	50.3
11	-3	1	56.2	56.0
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11	-5	1	31.2	36.8
11	-6	1	22.2	44.6
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12	0	1	56.4	66.5
12	1	1	47.6	38.2
12	2	1	32.0	18.2
12	3	1	18.4	22.0
12	4	1	18.5	19.9
12	-1	1	31.4	36.9
12	-3	1	70.1	61.0
12	-4	1	49.6	50.5
12	-5	1	18.6	16.0
12	-6	1	22.1	40.8
12	-7	1	63.8	51.3
12	-9	1	24.0	34.7
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13	0	1	20.5	39.0
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13	4	1	22.7	32.5
13	-2	1	18.1	9.4
13	-3	1	13.8	24.8
13	-4	1	19.5	46.1
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13	-6	1	19.0	26.3
13	-7	1	46.1	42.9
13	-9	1	35.7	42.9
14	0	1	69.2	49.5
14	1	1	51.0	48.3
14	2	1	13.7	18.6
14	-2	1	16.6	20.4
14	-5	1	24.6	29.3
14	-7	1	16.8	11.6
14	-8	1	15.6	30.3
14	-9	1	26.7	37.0
15	0	1	54.6	45.9
15	1	1	24.2	33.7
15	-1	1	13.3	22.7
15	-2	1	29.4	28.0
15	-3	1	43.1	34.2
15	-4	1	30.8	25.3
15	-5	1	14.8	23.5
15	-6	1	22.9	28.7
15	-8	1	25.1	18.8
15	-9	1	31.7	40.8
0	1	2	73.3	78.2
0	2	2	97.3	127.3
0	3	2	118.8	93.5
0	4	2	76.9	70.4
0	5	2	94.2	95.6
0	6	2	81.3	86.3
0	7	2	49.2	46.1
0	8	2	28.4	35.9
0	9	2	12.4	16.8
1	0	2	52.4	23.1
1	1	2	60.1	57.8
1	2	2	74.9	104.9
1	3	2	69.5	51.2
1	4	2	24.5	41.0
1	5	2	13.5	30.2
1	6	2	46.3	62.3
1	7	2	50.2	64.0
1	9	2	12.2	23.0
1	10	2	42.7	37.0
1	11	2	15.9	21.1
1	-1	2	158.8	101.9
1	-2	2	42.8	110.7
1	-3	2	80.7	79.5
1	-4	2	137.8	118.4
1	-5	2	197.6	150.1
1	-6	2	88.3	51.0
2	0	2	46.3	20.0
2	1	2	114.6	51.7
2	2	2	95.6	51.8
2	3	2	96.2	75.8
2	4	2	15.0	2.8
2	5	2	29.3	40.3
2	6	2	106.8	101.9
2	7	2	51.1	66.6
2	9	2	34.6	34.5
2	10	2	52.2	42.7
2	11	2	8.8	20.7
2	-1	2	63.6	9.0
2	-2	2	127.4	113.3
2	-3	2	184.7	149.2
2	-4	2	97.8	93.8
2	-5	2	113.4	93.4
2	-6	2	21.6	83.4
2	-7	2	80.2	73.2
3	0	2	45.6	41.6
3	1	2	28.2	8.6
3	2	2	129.8	107.7
3	3	2	104.3	67.7
3	4	2	14.3	9.5
3	5	2	39.7	64.3
3	6	2	110.5	93.0
3	7	2	34.8	57.5
3	8	2	17.5	37.6
3	9	2	14.6	34.8
3	10	2	30.5	30.5
3	-1	2	13.0	29.3
3	-2	2	54.1	41.7
3	-3	2	161.4	159.3
3	-4	2	101.0	99.9
3	-6	2	26.5	72.2
3	-7	2	98.1	107.6
3	-8	2	32.6	55.4
4	0	2	19.7	23.8
4	1	2	31.9	83.6
4	2	2	64.5	81.0
4	3	2	72.0	48.6
4	4	2	79.9	68.7
4	5	2	48.1	63.0
4	6	2	51.1	54.4
4	7	2	51.5	62.1
4	8	2	76.4	57.9
4	9	2	21.4	19.8
4	10	2	45.8	29.0
4	-1	2	15.2	20.5
4	-2	2	91.5	36.8
4	-3	2	97.1	92.1
4	-4	2	106.6	93.6
4	-5	2	14.0	14.0
4	-6	2	40.1	32.8
4	-7	2	98.9	98.8
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4	-9	2	28.2	17.2
5	0	2	109.4	77.6
5	1	2	144.5	89.1
5	2	2	9.6	19.9
5	3	2	42.9	55.4
5	4	2	120.3	91.9
5	6	2	51.7	39.1
5	7	2	33.9	47.9
5	8	2	39.2	40.5
5	9	2	8.9	17.9
5	-1	2	57.4	49.5
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5	-5	2	46.1	42.4
5	-6	2	10.2	34.2
5	-7	2	45.3	54.8
5	-8	2	48.9	53.0
5	-9	2	17.9	8.6
6	0	2	82.6	85.2
6	1	2	62.3	32.7
6	2	2	23.5	5.3
6	3	2	16.1	51.0
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6	8	2	38.7	41.6
6	9	2	19.5	25.9
6	-1	2	43.5	72.8
6	-2	2	100.0	102.0
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6	-4	2	123.1	92.0
6	-5	2	88.6	65.9
6	-6	2	95.7	89.1
6	-7	2	84.4	79.6
6	-8	2	16.2	35.1
6	-9	2	24.6	37.7
7	0	2	27.7	31.5
7	1	2	37.7	9.9
7	2	2	56.7	29.0
7	3	2	33.1	19.0
7	4	2	72.4	52.3
7	5	2	28.4	36.3
7	7	2	36.0	37.8
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7	-2	2	86.3	88.4
7	-3	2	21.5	58.0
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7	-5	2	76.9	79.7
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7	-9	2	34.9	40.8
7	-10	2	39.4	41.3
8	0	2	30.3	14.3
8	1	2	40.8	21.4
8	2	2	49.3	31.4
8	3	2	62.6	36.8
8	4	2	63.3	61.0
8	5	2	19.5	32.4
8	7	2	27.5	42.5
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8	-1	2	78.9	70.9
8	-2	2	77.4	96.2
8	-3	2	16.6	14.2
8	-4	2	68.4	35.4
8	-5	2	100.3	94.2
8	-6	2	57.8	75.6
8	-7	2	27.2	35.7
8	-9	2	24.6	36.7
9	0	2	16.9	24.4
9	1	2	19.5	30.6
9	2	2	51.3	37.7
9	5	2	38.4	32.1
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9	-8	2	28.5	35.2
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10	3	2	33.8	31.5
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10	-1	2	61.3	73.1
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10	-10	2	15.2	19.2
11	0	2	63.3	34.6
11	2	2	27.2	34.9
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11	-10	2	10.8	15.5
12	0	2	33.8	49.4
12	1	2	23.0	34.1
12	2	2	14.6	0.5
12	4	2	26.9	20.9
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13	2	2	19.8	12.9
13	3	2	26.8	26.6
13	-1	2	18.7	27.0
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13	-3	2	47.5	42.8
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14	0	2	26.4	35.1
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0	1	3	132.4	123.5
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1	3	3	120.8	85.4
1	4	3	10.4	12.6
1	5	3	86.8	56.0
1	6	3	95.8	68.6
1	7	3	21.8	10.9
1	8	3	30.8	26.4
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3	1	3	60.1	73.1
3	2	3	83.5	98.3
3	3	3	42.4	73.6
3	4	3	58.2	53.0
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3	6	3	78.7	80.6
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4	1	3	82.8	66.4
4	2	3	136.2	122.6
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5	1	3	75.2	68.4
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7	2	3	25.0	9.0
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7	4	3	49.0	47.7
7	5	3	18.1	10.5
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7	7	3	29.4	31.8
7	-1	3	17.6	38.4
7	-2	3	98.4	76.4
7	-3	3	80.4	65.0
7	-4	3	45.4	27.2
7	-5	3	74.6	75.8
7	-6	3	111.4	118.4
7	-7	3	64.9	64.1
7	-8	3	26.4	32.9
7	-9	3	13.9	49.9
7	-10	3	30.3	42.3
8	0	3	12.6	12.1
8	1	3	17.3	9.5
8	3	3	43.9	47.0
8	4	3	37.6	49.8
8	5	3	45.8	45.8
8	6	3	33.6	28.3
8	7	3	44.2	32.7
8	-1	3	33.3	37.5
8	-2	3	37.6	32.7
8	-3	3	16.8	55.8
8	-4	3	17.0	27.6
8	-5	3	34.0	47.1
8	-6	3	95.2	106.9
8	-7	3	66.8	76.6
8	-9	3	38.0	46.7
8	-10	3	54.1	69.2
9	0	3	17.7	20.4
9	1	3	55.7	56.6
9	2	3	38.1	42.0
9	3	3	37.7	40.3
9	4	3	79.6	56.8
9	5	3	62.9	56.5
9	6	3	17.9	25.3
9	-2	3	28.7	53.5
9	-3	3	16.9	13.9
9	-4	3	64.0	47.9
9	-5	3	41.4	48.2
9	-6	3	42.5	57.3
9	-8	3	22.0	29.4
9	-9	3	18.1	28.5
9	-10	3	35.4	50.7
9	-11	3	18.2	36.6
10	0	3	43.8	39.3
10	1	3	79.9	62.7
10	2	3	30.6	31.2
10	3	3	25.2	27.5
10	5	3	38.4	40.6
10	6	3	18.6	30.9
10	-2	3	42.9	50.3
10	-3	3	42.7	47.7
10	-4	3	30.2	31.7
10	-5	3	37.4	55.2
10	-6	3	37.8	64.8
10	-8	3	26.7	43.9
10	-9	3	21.1	32.1
11	0	3	37.8	47.2
11	1	3	21.3	32.5
11	2	3	35.1	32.5
11	3	3	39.2	23.1
11	4	3	13.2	12.3
11	5	3	38.7	39.3
11	-1	3	31.1	35.2
11	-2	3	22.0	24.8
11	-3	3	22.0	48.4
11	-4	3	26.9	57.7
11	-5	3	31.1	49.7
11	-6	3	56.5	50.9
11	-7	3	30.8	38.7
11	-8	3	21.3	30.2
11	-9	3	24.7	39.5
11	-10	3	22.4	23.8
12	0	3	46.2	25.0
12	1	3	27.7	26.2
12	2	3	25.2	25.3
12	3	3	20.0	15.9
12	4	3	21.0	20.1
12	-1	3	67.1	49.4
12	-2	3	30.6	19.7
12	-4	3	68.6	78.1
12	-5	3	53.2	65.0
12	-8	3	28.5	49.0
12	-9	3	18.7	33.0
13	1	3	14.0	17.3
13	3	3	10.6	20.2
13	-1	3	12.4	27.3
13	-3	3	13.0	14.3
13	-4	3	46.3	49.2
13	-5	3	54.5	63.0
13	-7	3	33.8	28.0
13	-8	3	48.7	55.8
13	-9	3	28.9	39.1
14	0	3	22.9	28.0
14	-1	3	21.8	25.4
14	-2	3	23.9	18.1
14	-3	3	29.1	28.0
14	-6	3	22.2	27.3
14	-8	3	13.4	29.0
14	-9	3	16.5	34.0
15	-1	3	28.0	34.8
15	-3	3	28.3	33.8
15	-4	3	34.9	37.9
15	-5	3	27.0	25.5
15	-6	3	15.9	22.3
15	-7	3	24.5	32.5
0	0	4	182.4	96.5
0	1	4	200.8	149.0
0	2	4	134.6	132.4
0	3	4	36.8	41.8
0	4	4	60.3	53.0
0	5	4	58.9	51.5
0	6	4	28.0	23.8
0	7	4	55.4	57.0
0	8	4	20.5	26.0
0	9	4	15.5	1.8
0	10	4	31.7	27.1
1	0	4	94.8	77.4
1	1	4	185.0	142.5
1	2	4	118.6	100.1
1	4	4	23.6	37.3
1	7	4	25.5	24.3
1	8	4	17.9	17.2
1	9	4	30.5	23.6
1	-1	4	33.8	34.0
1	-2	4	228.8	149.9
1	-3	4	178.6	152.2
1	-4	4	74.8	48.0
1	-5	4	14.3	27.3
1	-6	4	101.9	72.0
1	-7	4	22.5	19.6
2	0	4	95.2	62.2
2	1	4	96.6	75.6
2	2	4	129.7	94.4
2	3	4	51.1	51.7
2	4	4	57.5	19.8
2	5	4	51.7	44.6
2	6	4	29.1	28.7
2	7	4	29.3	30.0
2	8	4	43.3	40.1
2	9	4	65.5	37.7
2	10	4	11.2	19.2
2	-1	4	55.1	60.8
2	-2	4	106.7	97.1
2	-3	4	75.0	124.8
2	-4	4	11.0	58.5
2	-6	4	100.3	59.1
2	-7	4	59.5	62.1
2	-8	4	34.4	44.2
3	0	4	59.3	27.6
3	1	4	125.8	96.1
3	2	4	123.0	80.8
3	3	4	44.8	34.3
3	4	4	22.7	32.4
3	5	4	101.0	54.7
3	6	4	17.4	23.6
3	7	4	24.9	29.5
3	8	4	25.9	41.4
3	9	4	32.8	33.8
3	-1	4	89.3	89.3
3	-2	4	88.5	88.2
3	-3	4	58.2	53.0
3	-4	4	106.3	63.9
3	-5	4	29.2	41.6
3	-6	4	23.2	17.9
3	-7	4	48.7	65.0
3	-8	4	64.7	75.4

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