X-RAY DIFFRACTION STUDIES OF CARYOPHYLLENE DERIVATIVES AND SOME OTHER MOLECULES.

A Thesis

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SUMMARY.

This thesis is divided into four parts. Part I is concerned with a brief account of some of the methods used in X-ray crystallography. The remaining parts describe the application of these methods in determining the crystal structures of six molecules.

Part II contains descriptions of the structural analyses of two caryophyllene rearrangement products. The first, the dibromo derivative of 1,5,9,9-tetramethyltricyclo-$\left[6,2,1,0^{4,11}\right]$undec-5-ene, is a product of the acid-catalysed rearrangement of isocaryophyllene. The structure of this molecule was of considerable interest in view of the number of rearrangement products already derived from caryophyllene itself. The second, the dibromo derivative of 2,6,10,10-tetramethyltricyclo $\left[7,2,0,0^{2,7}\right]$undec-5-ene, is the main product obtained from the dehydrochlorination of caryophyllene dihydrochloride. For many years attempts had been made to identify this compound but without success. The absolute stereochemistries of both derivatives have been established by means of Bijvoet's anomalous dispersion method. Fairly detailed accounts of the conformations of these molecules are given as well as discussions on how the molecules are distorted in order to relieve the strain associated with these species in their classical conformations. Suggestions and comparisons are given in regard to their mechanisms of formation.

Part III describes the structural analyses of three

natural products. The first molecule to be discussed is the methiodide derivative of the O-acetyl of a homomorphinane alkaloid isolated from the plant Colchicum cornigerum. Spectroscopic and biogenetic arguments could not distinguish between two possible structure solutions whereas the X-ray structure analysis was able to do this and establish the absolute configuration. The second of these natural products to be discussed is pancuronium bromide (3α,17β-diacetoxy-2β,16β-dipiperidino-5α-androstane dimethobromide), a steroid used as a neuromuscular blocking agent. The crystal structure was determined using the water:methylene chloride solvate and a fairly detailed account of the molecular geometry is given since the high potency and specificity of action of the agent may be associated with this and the rigidity of the molecule. The last of this group of compounds is (+) trans-chrysanthemic acid. The structure analysis of the p-bromo-anilide derivative of this molecule was carried out in order to establish the absolute configuration which had already been reported on the basis of the usual chemical-type correlations. However, chrysanthemic acid is of great importance in terpene correlations and an independent determination of the absolute stereochemistry was desirable and this was carried out using Bijvoet's anomalous dispersion method.

The fourth and final part gives an account of the structure determination of di-μ-phenylthio-bis(cyclopentadienylcarbonyliron) at -160°. This cyclopentadienylcarbonyl-

iron mercaptide contains an Fe - S - Fe - S ring which is slightly puckered and has a cis arrangement of the phenyl and carbonyl groups. Even at this low temperature there is evidence that one of the cyclopentadienyl rings is disordered. A fairly detailed discussion of the molecular parameters and geometry of the molecules is given and comparisons are made with similar compounds.

CONTENTS.

PART I

SOME ASPECTS OF THE THEORY AND METHODS OF X-RAY CRYSTALLOGRAPHY.

1.1 INTRODUCTION.

One of the main problems that has faced the chemist since the discovery of the atom has been to unfold the molecular structure of the compounds he has synthesised or isolated. Many methods have been devised to do this, particularly in recent years, and many of these involve the interaction of radiation with the molecule. X-ray crystallography is one such method and has been developed to the extent that it now is universally used in all branches of chemistry where solutions of molecular structures are required.

Von Laue's discovery in 1912 that the wavelength of x-rays was approximately the same as the distance between the atoms in a crystalline solid marked the beginning of x-ray crystallography. He showed that x-ray diffraction by crystals could be described in terms of diffraction from a three-dimensional grating and hence that there existed a relationship between diffraction patterns and the atomic arrangements within the crystal. It was Bragg (1913) who noted that diffraction was very similar to reflection and he was then able to place von Laue's observations on a physical basis.

With this fundamental knowledge equations were devised which enable us, not without inherent difficulty, to build up three-dimensional electron density maps from which the position of the atoms in space and hence the molecular structure may be inferred. Such a three-dimensional model has great value especially in determining spatial

configurations and conformations which can affect the reactivity of the molecule. With the aid of electronic computers the structures of complex natural products and, more recently, proteins can be deduced more readily and more rapidly by x-ray diffraction than by a classical chemical approach. The method also gives information regarding bond lengths, angles and non-bonded distances which can be of great significance in structural theory and in the understanding of reactivity.

1.2 CRYSTAL SYMMETRY.

The observed regularity of crystals has fascinated men for centuries. From the mid-seventeenth century onwards a mathematical theory was developed to describe their symmetry but not until the discovery of x-rays in 1895 by Rontgen and von Laue's diffraction experiments in 1912 was the theory given practical application.

An object has symmetry if some movement or operation on it produces a form indistinguishable from the original. It can be shown that the only symmetry elements allowed about a point in a crystal are 1-, 2-, 3-, 4-, and 6-fold rotation axes and their corresponding axes of rotatory inversion. Hessel (1831) and Gadolin (1867) worked out that there were 32 ways of combining these symmetry elements into mathematical groups and these form the 32 point groups. Bravais (1850) then considered the crystal, not as a geometrical figure, but as a lattice structure and showed that 14 lattice types could be derived from the 7 crystal systems. When considering a crystal as a lattice structure, movements of a translational kind must be included in order to complete the set of symmetry elements allowed in such a crystal. This means that the corresponding screw-axes and glide planes must be introduced. Fedorow (1885), Schoenflies (1891) and Barlow (1894) all showed that there were 230 possible mathematical groups made up of these symmetry elements, known as the 230 space groups.

The space group of a crystal can be determined

from the x-ray diffraction pattern but only 70 can be distinguished unambiguously. The diffraction pattern will always be centrosymmetric regardless of whether the space group is or not. All optically active compounds belong to non-centrosymmetric space groups which have no mirror or glide-planes present.

1.3 DIFFRACTION BY A CRYSTAL.

The regularity in the shape of crystals led to the belief that they were made up of groups of atoms forming a basic unit which was repeated at regular intervals with the same orientation in three dimensions. This idea was confirmed by quantitative studies of the interfacial angles. The precise scheme according to which the basic unit repeats itself in space is the space lattice or lattice of the crystal. This is the mathematical framework upon which the real structure, made of atoms, is constructed. As a consequence the lattice acts as a diffraction grating for x-rays and so, just as the angles of diffraction produced by a grating depend only on the spacing, the angles of diffraction produced by a crystal depend only on the dimensions of the lattice; the finer details are not involved.

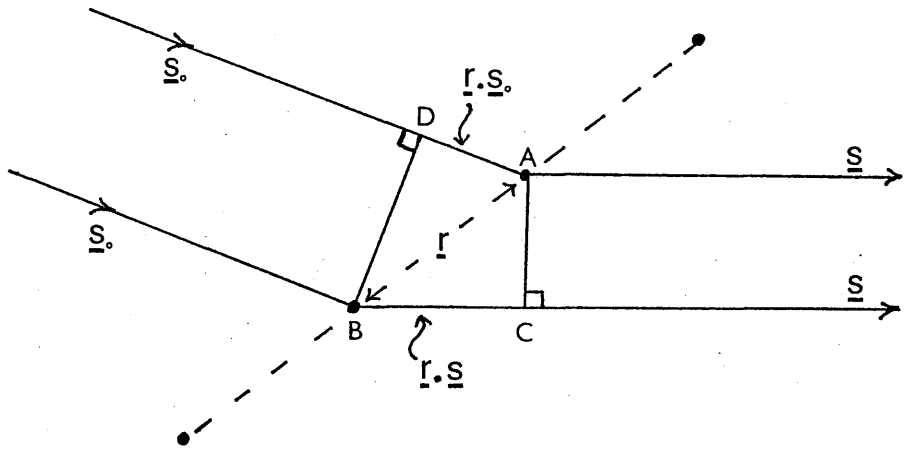
In order to diffract x-rays it is necessary to assume that each lattice point is the site of an electron. If the primitive translations of the lattice (i.e. the lattice constants or parameters) are $\underline{a}$, $\underline{b}$ and $\underline{c}$, then the positions of the electrons can be specified by the ends of vectors $\underline{r}$ such that

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

where u, v and w are integers.

If an electron lies in the path of an x-ray beam, then it is forced to vibrate by the oscillating field of the incident beam and, as a vibrating charge, will emit radiation in all directions. In order to find the total

effect of this secondary radiation the phase differences between the waves scattered in any particular direction must be considered.



In the diagram A and B are two lattice points separated by vector distance $\underline{r}$. A parallel beam of x-rays of wavelength λ, falling on the lattice in a direction defined by the vector $\underline{s}_0$ and with magnitude $1/\lambda$, is scattered in a direction defined by the vector $\underline{s}$ also having magnitude $1/\lambda$.

The path difference between the waves diffracted by successive points along the row is given by

$$BC - AD = (\underline{r}.\underline{s} - \underline{r}.\underline{s}_0) = \underline{r}.(\underline{s} - \underline{s}_0)$$
$$= \underline{r}.\underline{S}$$

where $\underline{S} = \underline{s} - \underline{s}_0$.

So that the waves scattered are in phase then this

path difference must equal a whole number of wavelengths.

Therefore $\underline{r}.\underline{S}$ = integral number,

i.e. $(u\underline{a} + v\underline{b} + w\underline{c}).\underline{S}$ = integer.

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

It follows that

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

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

$$\underline{c}.\underline{S} = \ell$$

where h, k and ℓ are integers.

These are the Laue equations and when all three are satisfied simultaneously a diffracted beam of maximum intensity is produced.

BRAGG'S LAW.

W.L. Bragg (1913), by identifying the integers h, k and ℓ of the Laue equations with the Miller indices of the lattice planes, was able to attach a physical significance to these equations. The Laue equations can be rewritten -

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

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

$$\underline{c}/\ell.\underline{S} = 1$$

Hence

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

$$(\underline{a}/h - \underline{c}/\ell).\underline{S} = 0$$

$$(\underline{b}/k - \underline{c}/\ell).\underline{S} = 0$$

This implies that $\underline{S}$ is perpendicular to vector $(\underline{a}/h - \underline{b}/k)$, and similarly is perpendicular to both $(\underline{a}/h - \underline{c}/\ell)$

and ($\underline{b}/k - \underline{c}/\ell$). These vectors are in the plane with Miller indices $hk\ell$ and thus $\underline{S}$ is perpendicular to this plane.

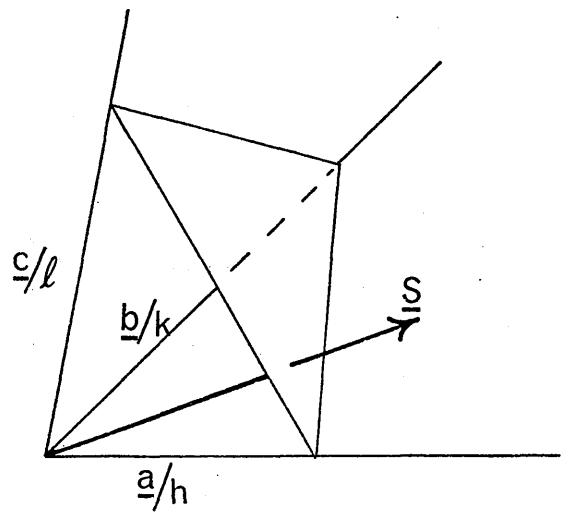


Fig. 1.

Since $\underline{S}$ is a vector in the direction of the bisector of the incident and diffracted beams, the bisector is identified with the normal to the $hk\ell$ plane. Hence diffraction can be regarded as "reflexion" of the rays from the lattice planes.

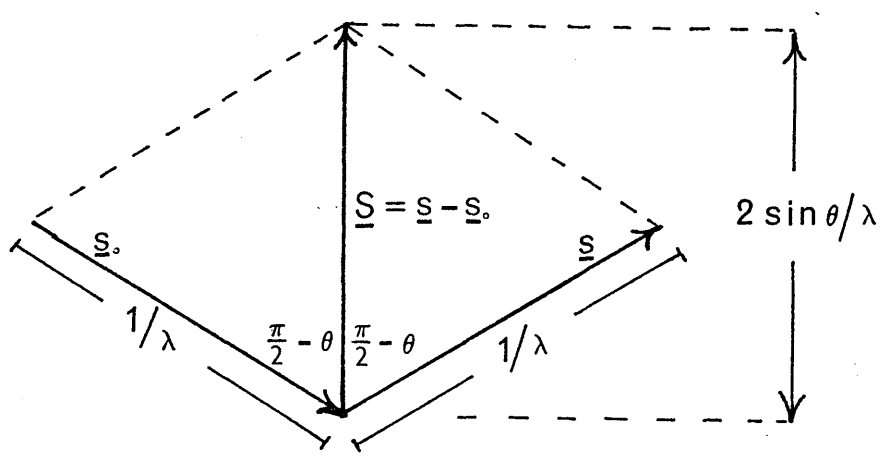


Fig. 2.

The perpendicular distance of the plane from the origin, d, is the projection of $\underline{a}/h$, $\underline{b}/k$ or $\underline{c}/\ell$ on the vector $\underline{S}$; that is,

$$d = \frac{(\underline{a}/h).\underline{S}}{|\underline{S}|}$$

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

$$d = \lambda/(2\sin\theta) \quad \text{or} \quad \lambda = 2d\sin\theta.$$

This is Bragg's Law.

1.4 RECIPROCAL LATTICE.

Mathematical methods of solving the Laue equations can be expressed in terms of the reciprocal lattice. The equation $\underline{a}.\underline{S} = h$ is equivalent to saying that the projection of vector $\underline{S}$ on $\underline{a}$ is constant for fixed values of h. In other words, the ends of the vector $\underline{S}$ lie on a plane perpendicular to $\underline{a}$. A set of planes of constant spacing is set up, each plane of the set corresponding to a particular value of h. Similarly another two sets of equidistant planes will be set up, one perpendicular to $\underline{b}$ and the other to $\underline{c}$. The intersection of these planes represents the end points of vectors that simultaneously satisfy the Laue equations. These sets of planes define a lattice of points called the reciprocal lattice and each point in the lattice is defined by the three numbers, h, k, and ℓ.

Each of the reciprocal lattice vectors, usually called $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$, is formed by the intersection of two planes perpendicular to two crystal axes; for example, $\underline{a}^*$ is perpendicular to $\underline{b}$ and $\underline{c}$,

i.e. $\underline{a}^* = p(\underline{b} \times \underline{c})$

where p is a constant to be determined.

Similarly, $\underline{b}^* = q(\underline{c} \times \underline{a})$ and $\underline{c}^* = r(\underline{a} \times \underline{b})$.

The diffraction vector $\underline{S}$ is related to the reciprocal lattice points as shown:-

$$\underline{S} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^*$$

$$= hp(\underline{b} \times \underline{c}) + kq(\underline{c} \times \underline{a}) + \ell r(\underline{a} \times \underline{b})$$

But, $\underline{a}.\underline{S} = h$

Therefore,

$$h = \underline{a}.\{hp(\underline{b} \times \underline{c}) + kq(\underline{c} \times \underline{a}) + \ell r(\underline{a} \times \underline{b})\}.$$

Since $\underline{a}.\underline{c}\times\underline{a}$ and $\underline{a}.\underline{a}\times\underline{b}$ are equal to zero then,

$$p\underline{a}.\underline{b}\times\underline{c} = 1$$

or
$$p = 1/\underline{a}.\underline{b}\times\underline{c}$$

Similarly,
$$q = 1/\underline{b}.\underline{c}\times\underline{a}$$

and
$$r = 1/\underline{c}.\underline{a}\times\underline{b}$$

However, $\underline{a}.\underline{b}\times\underline{c}$, $\underline{b}.\underline{c}\times\underline{a}$ and $\underline{c}.\underline{a}\times\underline{b}$ are all representations of the volume, V, of the unit cell of the real space lattice. Therefore,

$$p = q = r = 1/V$$

Hence,

$$\underline{a}^* = (\underline{b} \times \underline{c})/V$$
$$\underline{b}^* = (\underline{c} \times \underline{a})/V$$
$$\underline{c}^* = (\underline{a} \times \underline{b})/V.$$

We now have quantities which are characteristic of both crystal and the diffraction process.

1.5 FACTORS AFFECTING INTENSITY.

1.5.1 The Atomic Scattering Factor.

The scattering units of a crystal are its constituent atoms and the electrons of the atom are responsible for the scattering power. To a first approximation the scattering power of an atom is proportional to the number of electrons in it, that is, proportional to its atomic number, Z. Actually, the separation of the various electrons within the volume of the atom causes phase differences among the wavelets they scatter, so the scattering power of an atom is in general less than Z electrons. Thus the intensity of the resultant beam is reduced.

The electron density of the nth atom at a vector distance $\underline{r}$ relative to an origin chosen at the centre of this atom is defined as $\rho_n(\underline{r})$. The scattering power of a single atom is given by the expression

$$f_n(\underline{S}) = \int_{-\infty}^{\infty} \rho_n(\underline{r}) \exp(2\pi i\, \underline{r}.\underline{S})\, dV.$$

$f_n(\underline{S})$ is called the atomic scattering factor.

Since the atom is assumed to be spherical then $\rho_n(\underline{r})$ is a function of $|\underline{r}|$ only and as $f_n(\underline{S})$ is also spherically symmetric then it is a function of $|\underline{S}|$ which is equal to $2 \sin\theta/\lambda$. Hence the scattering factor of an atom is a function of the angle of scattering and of the distribution of electrons in the atom. For small angles of diffraction tne phase differences mentioned above are small and the scattered amplitude will approach Z. As the angle of diffraction increases, the phase differences become larger

and thus the scattered beam becomes weaker. As a result, the scattering factor becomes less than Z. For a given angle of diffraction the atomic scattering factor is constant since the atom has spherical symmetry. Approximate values of scattering factors have been calculated on the basis of quantum theory (see International Tables, vol. III).

1.5.2 Temperature Factor.

At all temperatures atoms in crystals vibrate with frequencies much lower than those of x-rays. Thus the electrons of each atom sweep out a larger volume than they would otherwise if the atom was at rest. This has the effect of modifying the atomic scattering factor of the atom by a factor $q_n(hk\ell)$ which takes into account this thermal motion.

Therefore,

$$f_T(hk\ell) = f_n(hk\ell)\ q_n(hk\ell)$$

where $f_T(hk\ell)$ is the modified atomic scattering factor and f_n is the scattering factor for the atom at rest.

When the atomic vibration is isotropic then

$$q_n(hk\ell) = \exp\{-B(\sin\theta/\lambda)^2\}$$

where θ is the Bragg angle and B, the Debye temperature factor, is a constant such that,

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

where $\bar{u}^2$ is the mean square displacement of the atoms from their mean positions.

The above expression for the modifying factor implies that all the atoms vibrate with equal amplitudes and that the thermal vibrations are equal in all directions of

the crystal. However, in most crystals the vibrations are anisotropic and so the electron density is "smeared" over an elipsoid. In this case

$$q_n(hk\ell) = \exp[-2\pi^2(U_{11}h^2\underline{a}^{*2} + U_{22}k^2\underline{b}^{*2} + U_{33}\ell^2\underline{c}^{*2} + 2U_{23}k\ell\underline{b}^*\underline{c}^* + 2U_{31}\ell h\underline{c}^*\underline{a}^* + 2U_{12}hk\underline{a}^*\underline{b}^*)]$$

where U_{ij} (i, j = 1, 2, 3) refer to the reciprocal axes a^*, b^* and c^*.

1.6 THE STRUCTURE FACTOR EXPRESSION.

In most crystals a certain arrangement of atoms exists within each unit cell. We can 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 identical interpenetrating lattices. Each of these 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 on the atomic arrangement within the unit cell.

The position of the nth atom situated at the point (x_n, y_n, z_n), where x_n, y_n and z_n are fractions of the unit cell vectors, can be represented by the vector $\underline{r}_n$, where

$$\underline{r}_n = x_n\underline{a} + y_n\underline{b} + z_n\underline{c}$$

The path difference between the beam scattered by the nth atom relative to that scattered by an atom at the origin is $2\pi\underline{r}_n.\underline{S}$. Hence the total wave scattered by the entire contents of the unit cell is given by

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp\{2\pi i\ \underline{r}_n.\underline{S}\}$$

where $f_n(\underline{S})$ is the scattering factor of the nth atom. Including the previous expression, we have

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp\{2\pi i\ (x_n\underline{a}.\underline{S} + y_n\underline{b}.\underline{S} + z_n\underline{c}.\underline{S})\}$$

Since we have already stated that the wave scattered by the crystal will only have an appreciable amplitude when the

Laue equations are satisfied, it follows that

$$G(\underline{S}) = F(hk\ell) = \sum_{n=1}^{N} f_n(hk\ell) \exp\{2\pi i\ (hx_n + ky_n + \ell z_n)\}$$

The quantity $F(hk\ell)$ is called the structure factor and is defined only when h, k and ℓ are integers. It is a complex quantity which can be represented by a modulus $|F(hk\ell)|$ known as the structure amplitude and a phase constant, $\alpha(hk\ell)$. It can be written as

$$F(hk\ell) = A + i\,B$$

where $$A = \sum_{n=1}^{N} f_n(hk\ell) \cos\{2\pi(hx_n + ky_n + \ell z_n)\}$$

and $$B = \sum_{n=1}^{N} f_n(hk\ell) \sin\{2\pi(hx_n + ky_n + \ell z_n)\}$$

and therefore,

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

and $$\alpha(hk\ell) = \tan^{-1} B/A.$$

We therefore have a description of the amplitude and phase of the complete wave scattered by the unit cell and hence by the crystal since all the unit cells are assumed to scatter in phase (see Lonsdale, 1936).

If $\rho(x,y,z)$ is the electron density at the point (x,y,z) the amount of scattering matter in the volume element $Vdxdydz$ is $\rho Vdxdydz$ and the structure factor equation becomes

$$F(hk\ell) = \int_{x=0}^{1}\int_{y=0}^{1}\int_{z=0}^{1} V\rho(x,y,z) \exp\{2\pi i\ (hx + ky + \ell z)\}dxdydz.$$

1.7 ANOMALOUS SCATTERING OF X-RAYS.

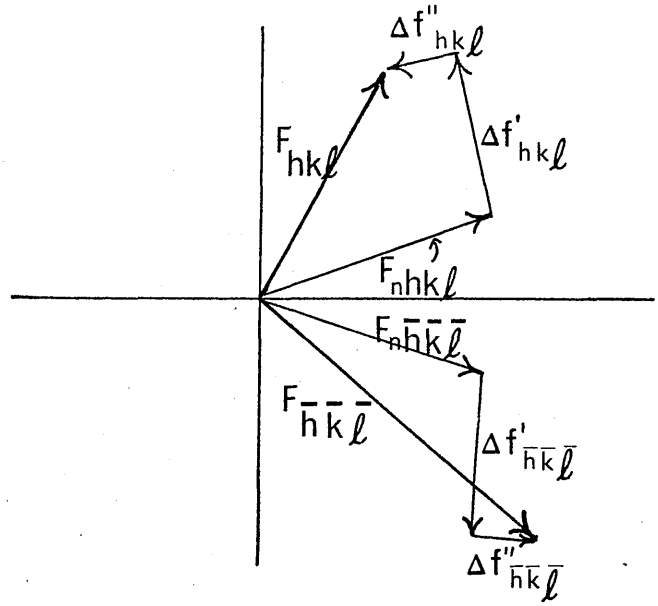
Friedel's law (1913) states that all x-ray diffraction patterns are centrosymmetric in that reflexions $hk\ell$ have the same intensity as the reflexions $\bar{h}\,\bar{k}\,\bar{\ell}$. If this was true then the structure obtained by reversing the sense of the axes used to define the original structure would still be consistent with the observed diffraction pattern and, as a result, the x-ray method would be unable to distinguish between optical enantiomorphs.

However, following work by Coster et al. (1930), it became apparent that the scattering factor of an atom is more correctly represented by the complex expression,

$$f = f_o + \Delta f' + i\Delta f'',$$

where f_o is the normal scattering factor and $\Delta f'$ and $\Delta f''$ are factors which take account of the fact that the individual electrons of an atom do not behave as free electrons during the scattering process. The scattering power of a bound electron may be greater than or less than that of a free electron and the phase of the scattered wave may be different. Since the innermost electrons are most tightly bound they will give the most significant values of $\Delta f'$ and $\Delta f''$ and as a result these two correction factors are almost independent of $\sin\theta$. Significant values of $\Delta f'$ and $\Delta f''$ arise if the frequency of the incident radiation falls near a natural absorption frequency of a scattering atom causing an anomalous phase change. This effect is known as anomalous scattering or dispersion. Since $\Delta f''$ is always positive,

the most important result of anomalous scattering is the breakdown of Friedel's law, as illustrated in the diagram below.



($F_{nhk\ell}$ is the resultant of the scattering from the atoms without dispersion.)

It was Bijvoet (1949) who first pointed out that anomalous scattering could be used in the determination of absolute configuration for molecules in non-centrosymmetric space groups. This was first carried out on sodium rubidium tartrate (Peerdeman, van Bommel, and Bijvoet, 1951). When using this method a right-handed coordinate system only must be used and the indexing of the reflexions must also be consistent with this system (Peerdeman and Bijvoet, 1956). Due to the anomalous scatter there will be pairs of reflexions present with unequal intensities. The ratios of these are then compared to the ratios of the same pairs of structure

factors calculated using complex scattering curves and the correct absolute configuration deduced.

In some non-centrosymmetric space groups in which the origins are not fixed by symmetry, errors in positional parameters of the anomalous scattering atoms can result if $\Delta f''$ is neglected. This effect has been dealt with in some detail by Cruickshank and McDonald (1967).

1.8 THE RELATION BETWEEN INTENSITY AND STRUCTURE AMPLITUDE.

The relationship between $F(hk\ell)$ and $I(hk\ell)$ depends on a number of factors, primarily geometric, which relate to the individual reflexion and to the apparatus used to measure its intensity.

Consider a crystal rotating with uniform velocity in an x-ray beam. When a set of $hk\ell$ planes passes through the reflecting position, the total energy, $E(hk\ell)$, of the diffracted beam is given by the expression,

$$E(hk\ell) = K\, L(hk\ell)\, p(hk\ell)\, |F(hk\ell)|^2$$

where K is a constant for the experiment and $L(hk\ell)$ is the Lorentz factor and $p(hk\ell)$ the polarisation factor.

The energy of the diffracted beam is directly proportional to the intensity on the photographic film. Therefore,

$$I(hk\ell) = K\, L(hk\ell)\, p(hk\ell)\, |F(hk\ell)|^2.$$

The maximum range of intensities measured on one film is 1 to 50 but a greater range is found using a single crystal and so the multiple film technique (Robertson, 1943) is used when intensities are to be measured using a calibrated step-wedge or microdensitometer. The intensities can, of course, be measured directly on either linear or four-circle diffractometers in which the diffracted photons are counted.

The Lorentz factor is a measure of the varying times crystal planes spend in the reflecting position, and varies with the type of photograph (Tunell, 1939). For equi-inclination geometry,

$$L(hk\ell) = 1/[2\cos\theta(\cos^2\mu - \cos^2\theta)^{\frac{1}{2}}]$$

where μ is the equi-inclination angle.

The polarisation factor arises because of the nature of the x-ray beam and the manner in which its reflexion efficiency varies with the reflexion angle. In all 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 where

$$p(hk\ell) = (1 + \cos^2 2\theta)/2.$$

$p(hk\ell)$ is independent of the method of data collection.

We now have

$$I(hk\ell) = \left\{K(1 + \cos^2 2\theta)/2[2\cos\theta(\cos^2\mu - \cos^2\theta)^{\frac{1}{2}}]\right\} |F(hk\ell)|^2$$

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 two further, non-geometrical factors which can arise in a less simple fashion, namely, absorption and extinction. They can both be neglected when minute crystals are used.

Absorption causes a decrease in the primary x-ray beam and is dependent on the material of the crystal and the thickness of crystal through which the beam passes. The corrections can only be applied with ease to cylindrical or spherical specimens.

The effect of extinction is to attenuate the x-ray beam as it passes through the crystal when it is in a reflecting position. Darwin, who first treated the effect mathematically, termed it extinction and recognised two

different kinds, primary and secondary extinction. Primary extinction occurs when the reflecting beam emerging from the crystal is reflected back into the crystal. This doubly reflected beam is parallel to but out of phase with the incident beam and so causes destructive interference and results in a decrease in the intensity of the primary beam. Secondary extinction occurs when the surface planes of the crystal reflect away an appreciable amount of incident radiation and so the lower planes receive a beam of much weaker intensity.

1.9 FOURIER SERIES.

Since crystals can be considered as periodic disributions of scattering material (electrons), W.H. Bragg (1915) first suggested that the electron density, $\rho(x,y,z)$ could be conveniently expressed in the form of a triple Fourier series as shown

$$\rho(x,y,z) = \sum_{h',k',\ell'=-\infty}^{\infty} A(h'k'\ell') \exp\{2\pi i\,(h'x + k'y + \ell'z)\}$$

where h', k' and ℓ' are integers and $A(h'k'\ell')$ 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 $A(h'k'\ell')$. This series for $\rho(x,y,z)$ is substituted in the general expression for the structure factor giving,

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 \sum_{h',k',\ell'=-\infty}^{\infty} A(h'k'\ell') \exp\{2\pi i\,(hx + ky + \ell z)\}$$

$$\times \exp\{2\pi i\,(h'x + k'y + \ell'z)\} V\, dxdydz.$$

The exponential functions are both periodic and so, on integrating, every term is zero except that for which $h = -h'$, $k = -k'$ and $\ell = -\ell'$ which gives

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 A(h'k'\ell')\, V\, dxdydz$$

$$= A(\bar{h}\,\bar{k}\,\bar{\ell})\, V.$$

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

$$\rho(x,y,z) = 1/V \sum_{h,\,-\infty}^{\infty} \sum_{k,\,-\infty}^{\infty} \sum_{\ell}^{\infty} F(hk\ell) \exp\{-2\pi i\,(hx + ky + \ell z)\}.$$

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

$$F(000) = V \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z)\, dxdydz$$

$$= Z \quad \text{(sum of the electrons in the unit cell).}$$

The Fourier series above can be more conveniently written as,

$$\rho(x,y,z) = \sum_{h,\,-\infty}^{\infty} \sum_{k,\,-\infty}^{\infty} \sum_{\ell}^{\infty} \left\{ \left| F(hk\ell) \right| /V \right\} \cos\{2\pi hx + 2\pi ky + 2\pi \ell z - \alpha(hk\ell)\},$$

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

The values of the structure amplitudes, $\left|F(hk\ell)\right|$, can be derived from the observed intensities but no experimental means exists for recording the phases. This constitutes the phase problem.

1.10 METHODS OF SOLVING THE PHASE PROBLEM.

1.10.1 The Trial And Error Method.

The method of trial and error consists of postulating a structure, i.e. assuming locations of the atoms in the unique part of the unit cell and finding 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 large disagreements indicate that the postulate is wrong. This procedure is continued until a set of atomic parameters are found which give good agreement.

Supplementary physical and geometrical data often help in the derivation of a satisfactory trial structure but the method can still require many calculations before the correct result is obtained. This can be avoided or, at least reduced, by making 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.

For obvious reasons this method is useful only for relatively simple molecules with rigid structures although it can be used effectively in more complex instances

if the structure of the molecule or major part of it is known. A notable example of its use is in the solution of D.N.A. and many other fibrous or semi-crystalline, helical materials have been solved with the aid of this trial and error method.

1.10.2 The Patterson Function.

A Fourier synthesis may be performed using $|F(hk\ell)|^2$ values as coefficients instead of the structure factors; these quantities are directly related to the observed intensities and so can always be measured. Patterson (1934, 1935) developed this approach and showed that the resulting synthesis was related in a simple way to the crystal structure.

The Patterson function is defined as

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\,\rho(x+u, y+v, z+w)\,dxdydz,$$

where u, v, and w are fractional coordinates. This is written in full as

$$\begin{aligned} P(uvw) = \frac{1}{V}\int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_{\ell=-\infty}^{\infty}\sum_{h'}\sum_{k'}\sum_{\ell'} & F(hk\ell) \\ & \times \exp\{-2\pi i\,(hx + ky + \ell z)\} \times F(h'k'\ell') \\ & \times \exp\{-2\pi i\,(h'x + k'y + \ell' z)\} \\ & \times \exp\{-2\pi i\,(h'u + k'v + \ell' w)\}\,dxdydz. \end{aligned}$$

As before, this function equals zero except when $h = -h'$, $k = -k'$ and $\ell = -\ell'$. Hence we have,

$$\begin{aligned} P(uvw) = \frac{1}{V}\sum_h\sum_{k=-\infty}^{\infty}\sum_\ell & F(hk\ell)\,F(\bar{h}\,\bar{k}\,\bar{\ell}) \\ & \times \exp\{-2\pi i\,(h'u + k'v + \ell' w)\}. \end{aligned}$$

But $F(hk\ell)$ and $F(\bar{h}\,\bar{k}\,\bar{\ell})$ are complex conjugates and so

the Patterson function reduces to the form,

$$P(uvw) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell}^{-\infty \; \infty} |F(hk\ell)|^2 \exp 2\pi i \, (hu + kv + \ell w).$$

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

Difficulties, however, arise when attempts are made to interpret the resulting map, for the method is subject to the inherent limitation that all the vectors arise from the origin point. Interpretation, therefore, becomes more difficult as the structure becomes more complex. If there are N atoms in the real unit cell then N^2 peaks will exist in the cell of the vector distribution:- N of them superimposed at the origin and N(N - 1)/2 related to the remaining N(N - 1)/2 by a centre of symmetry.

The maximum amount of information is usually gained from the three-dimensional synthesis but Harker (1936) showed that with space groups possessing certain symmetry elements, e.g., a two-fold screw axis, certain sections of the three-dimensional distribution - in this case, $v = \frac{1}{2}$, contain useful information about the vectors between equivalent atoms of the structure.

We can modify the map in order to pinpoint the $(N^2 - N)/2$ discrete interatomic vectors by a process known

as 'sharpening' which greatly reduces the overlap caused by peak broadening. If the atoms had all their scattering power concentrated at the nucleus, i.e., were point atoms, this broadening would not occur and the Patterson would theoretically consist of point-vector peaks. A modification factor is applied to the structure amplitudes and these new values are squared and used as the coefficients for a sharpened Patterson function.

1.10.3 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 contributing to each vector. Therefore, if a crystal contains a relatively small number of heavy atoms the height of the peaks due to these atoms will stand out against a background of overlapping smaller peaks and the coordinates of these heavy atoms may be easily evaluated.

The contributions of these atoms to the various structure factors can readily be calculated and a phase angle for each reflexion deduced. Since the contribution of the heavy atoms to the phases outweigh the contribution of the lighter atoms, the phase angles, α_H, appropriate to the heavy atom, will approximate closely to the correct phase angles based on contributions from all atoms. The Fourier synthesis computed using the observed structure amplitudes and heavy atom phases yields an approximation to the electron density which will generally indicate further atomic sites. Better approximations to the phase angles can then be

evaluated by inclusion of more atomic contributions in the calculation of phase angles, and the whole process recycled until the complete structure is revealed.

The classical example of this technique is the analysis of platinum phthalocyanine by Robertson and Woodward (1940). With one heavy atom in the asymmetric unit situated at a centre of symmetry and with this position taken as the origin, the signs of the structure factors are all positive. One two-dimensional Fourier synthesis then revealed the entire structure.

Disadvantages of this method arise because of the very reason which makes it a useful technique. Since the heavy atoms contribute most to each structure amplitude then the accuracy in determining the light atom positions is reduced. The presence of the heavy atoms can also cause high absorption errors which reduce the accuracy of the data.

The position of the heavy atom may cause difficulties. If it is located at a special position in the asymmetric unit then it may not contribute to systematic classes of reflexions. In non-centrosymmetric crystals the phase angles may vary continuously between 0° and 360° and complications can arise if the heavy atom is in such a position in the asymmetric unit that it causes higher symmetry than that possessed by the space group itself; this phenomenon is known as pseudo-symmetry. This pseudo-symmetry will appear in the Fourier synthesis based on the heavy atom positions and will lead to difficulties in interpretation.

1.10.4 Isomorphous Replacement Method.

In this approach the phase of any structure factor is determined by considering the difference between the contributions made to a particular reflexion by two isomorphous heavy atom derivatives. This method was first used by Cork (1927) and later developed independently by Robertson in his work on the phthalocyanines (Robertson, 1935, 1936; Robertson and Woodward, 1937). Its use for the solution of general organic structures has declined but until now it is the only successful method used in the solution of protein structures.

1.10.5 Minimum Function Method.

The solution of all crystal structures is contained in the Patterson function but no general method has been devised for unravelling the complexities of this function especially where a large number of atoms is present. The minimum function method (Buerger, 1951) which involves the superposition of Patterson functions attempts to solve this problem. One vector map is placed with its origin at the derived heavy atom position, while the origin of the second superimposes a symmetry-related heavy atom position. A third map is then drawn over the minimum contours of the coincident peaks. Further superpositions may be required depending on the number of heavy atoms in the unit cell, but the final composite minimum function may reveal the structure or an appreciable amount of it. Successful applications of this technique include the structure determination of Vitamin B_1 (Kraut and Reed, 1962).

1.10.6 Direct Methods.

In this method, in contrast to those discussed above, an attempt is made to obtain the structure factor phases by direct examination of the intensity data without previous knowledge of atomic positions.

It has been shown by algebraic and probability methods that certain inequality relationships exist among the phases of the structure factors (Harker and Kasper, 1948; Karle and Hauptman, 1950) and these inequalities depend only on the fact that electron density is always positive. Sayre (1952) derived a simple form of equality relation between the structure factors such that,

$$F_H = (\varphi_H/V) \sum_{H'} F_{H'} F_{H-H'} ,$$

where H is the Miller triple, $hk\ell$, for the reflecting plane and H' is a particular value of H and φ_H is a scaling factor. From this relation Zachariasen (1952) and Cochran (1952) were able to discover a probability relationship between structure factors of the type,

$$s(H) \sim s\left\{\sum_{H'} s(H')\, s(H-H')\right\} ,$$

where s means 'sign of' and $\sim$ means 'probably equals'.

This relationship is almost certainly true if the structure factors involved are sufficiently large but since the magnitudes of the structure factors fall off rapidly with $\sin\theta$ then it is often difficult to find many large enough to be used. This can be overcome if we assume that the scattering model is that of point atoms at rest for random

atomic distribution and use the normalised structure factor, E_H, defined as,

$$E_H = F_H / \epsilon^{\frac{1}{2}} \left(\sum_{i=1}^{N} f_i^2 \right)^{\frac{1}{2}},$$

where ϵ is a multiplicity factor which corrects certain zones of reflexions for systematic absences and point group symmetry and f_i is the atomic scattering factor of the ith atom in the unit cell. We can now write,

$$sE_H \sim s \sum_{H'} E_{H'} E_{H - H'} ,$$

which is termed the Σ_2 relation derived by Karle and Hauptman (1953). The probability that this equation is correct has been given by Cochran and Woolfson (1955). This is,

$$P = \tfrac{1}{2} + \tfrac{1}{2} \tanh \left\{ \left(\left| E_H E_{H'} E_{H - H'} \right| \right) / N^{\frac{1}{2}} \right\} ,$$

where N is the number of atoms in the unit cell and they are assumed equal.

The pairs of reflexions, $|E_{H'}|$ and $|E_{H - H'}|$, are termed "interaction pairs" for $|E_H|$. From the set of $|E_H|$ calculated from the intensity data one obtains a Σ_2 listing. A basic set of signs is then specified which includes origin-defining phases and any other signs which can be assigned with adequate probability by inequalities or by so-called Σ_1 relation,

$$sE_{2H} \sim s(E_H^2 - 1).$$

With this basic set the Σ_2 relations are used to specify the signs of unknown E_H's for which one (or more) interaction pairs have both signs known and for which P is greater than

a specified limit. When this expansion of the known group terminates because no more new E_H's can have phases specified to the set P value, a symbolic sign is assigned to a large unknown $|E_H|$ with many interaction pairs. The Σ_2 relations are then used to further expand the known set. If this expansion terminates then a second symbolic sign may be chosen and the expansion continues anew. In this manner a "known" set of E_H's is determined in a sequential process using as many symbols as necessary. For a centrosymmetric structure 10 - 15 phases per atom in the asymmetric unit should be defined.

Since many of the phases will have been determined symbolically, it is generally true that, for a set of signs determined with m symbols, there are 2^m possible mathematical solutions, only one of which is nearest the correct physical solution. Once numerical values have been assigned to the symbols, sets of phases can be evaluated for use in a Fourier synthesis with normalised structure factors as coefficients.

This method of "symbolic addition" has been used with much success for centrosymmetric space groups (Karle and Karle, 1963, 1964a, 1966a). In recent years its use has been extended to non-centrosymmetric space groups (Karle and Karle, 1964b, 1966b, 1968; Germain and Woolfson, 1968) where methods like the tangent formula refinement process have been used to help in choosing the correct solution for the phases.

1.11 METHODS OF REFINEMENT.

1.11.1 Correctness of Structure.

Once a structure has been determined by one of the above methods, it is necessary to extract the best results from the experimental data and to assess their accuracy. This involves obtaining the best possible agreement between the observed and calculated structure amplitudes and improving the phase angles. This is accomplished by adjusting the positional and thermal parameters already derived for the structure. Such a procedure is known as 'refinement'.

It is convenient to express the overall agreement between the observed and calculated structure amplitudes in terms of the agreement index or residual factor, R, where

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

The value of R will be a small fraction when the structure is correct and a large fraction when it is incorrect. The value of R is not, however, always a reliable indication of the correctness of a solution as it comes from a mixture of reflexions but in most cases is a rough quantitative guide.

1.11.2 Fourier Refinement.

The first systematic method of refinement was that of successive Fourier syntheses. The electron density distribution is calculated using the observed amplitudes $|F_o|$, and new phases calculated on the basis of the approximate trial structure. From the resulting map it should be

possible to allocate improved coordinates for atoms which can then be used to calculate a cycle of structure factors. These structure factors are then used to calculate another Fourier map and the process is repeated until there is no furtner decline in the R value.

The successive Fourier refinement of a centrosymmetrical structure has converged completely when there is no change in any of the signs as derived from the previous step. In a non-centrosymmetrical structure any change in the coordinates necessarily brings about a change in the phases so the process of Fourier refinement theoretically never ends.

The true electron density is represented by an infinite series but, in practice, the number of terms which are included in such a summation is limited due, mainly, to the wavelength of the incident radiation. As a result, diffraction ripples surround the true peaks on the Fourier map and the peaks are displaced from their correct positions. This is called the termination of series error. Booth (1946, 1947) has suggested a method of overcoming this difficulty known as the "back-shift" correction. Two Fourier syntheses are calculated, one using $|F_o|$ as coefficients, the other using $|F_c|$; both are based on the same atom positions. Both will suffer from series termination errors and both will have atomic coordinates shifted from true positions. In the $|F_c|$ synthesis the coordinates used for calculation should be deduced from it, but because of the error the two sets will

differ. If the difference between them is subtracted from the coordinates obtained from the $|F_o|$ synthesis then approximately correct atomic positions should be obtained.

The Fourier synthesis can also be used for refinement in the 'difference' synthesis which was first suggested by Booth (1948) and Cochran (1951). In this case $(|F_o| - |F_c|)$ values are used as Fourier coefficients and if the structure is correct then an almost flat featureless map will be produced; if the structure is wrong large undulations will appear. Nowadays the difference synthesis is used primarily to locate hydrogen atoms, and to check the final results after least-squares refinement.

1.11.3 Least-squares Refinement.

In this method of refinement, first employed by Hughes (1941), the discrepancies between the observed and calculated structure amplitudes are minimised by making small variations in the parameters of the atoms in the cell. The observed structure amplitudes are subject to random errors of observation, and so refinement by least-squares consists essentially of finding the most acceptable fit of the set of F_c with the set of F_o's. Legendre proposed the principle that the most acceptable values were such as to make the sum of the squares of the errors a minimum. It is this principle on which the method of least-squares is based. If we compare the $|F_o|$ and $|F_c|$ values for each reflexion then the most probable values for the atomic parameters are such that make $\sum(||F_o| - |F_c||)^2$ a minimum.

The function which is most commonly used for minimisation is,

$$M = \sum_{hk\ell} w(|F_o| - |F_c|)^2 = \sum_{hk\ell} w\Delta^2, \qquad (1)$$

where the summation is over all the structure amplitudes from independent observations. Since the $|F_o|$ values of each reflexion cannot be determined with the same accuracy there should be a weighting function for each observation. From a statistical viewpoint the best weight is equal to the inverse of the square of the standard deviation of the observation but it is not always feasible to estimate a standard deviation for each reflexion and various methods have been devised to overcome this difficulty. Cruickshank and Smith's least-squares program (1965), currently in use at the University of Glasgow, outputs an analysis of the weighting scheme after each cycle of refinement. The structure amplitudes are batched according to magnitude and $\sin\theta/\lambda$, and if the average values of $w\Delta^2$ in each batch are approximately constant then the weighting scheme is considered to be satisfactory.

The calculated structure factor is a function of the parameters $p_1, p_2, \ldots p_n$, which may be coordinates, thermal parameters or scale factors, and the problem in the least-squares technique is to determine the values of these parameters which minimise M. For M to be a minimum we must have,

$$\frac{dM}{dp_j} = 0 \qquad (j = 1,2,\ldots n) \qquad (2)$$

Applying this condition to (1) we obtain,

$$\sum_{hk\ell} w \Delta \frac{\partial |F_c|}{\partial p_j} = 0 \qquad (j = 1,2,\ldots n). \quad (3)$$

The parameters must be varied until these n conditions are satisfied. For a set of p_j close to the correct values, Δ may be expanded as a function of the parameters by a first order Taylor series,

$$\Delta(\underline{p} + \underline{\epsilon}) = \Delta(\underline{p}) - \sum_{i=1}^{n} \epsilon_i \frac{\partial |F_c|}{\partial p_i}, \quad (4)$$

where ϵ_i is a small change in p_i, and $\underline{p}$ and $\underline{\epsilon}$ stand for the whole set of parameters and changes. Hence, on substituting (4) in (3) we obtain,

$$\sum_{i=1}^{n} \left(\sum_{hk\ell} w \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j}\right) \epsilon_i = \sum_{hk\ell} w \Delta \frac{\partial |F_c|}{\partial p_j}. \quad (5)$$

This gives a set of n equations called the normal equations which are linear in the correction terms and thus soluble for them. They may be written in matrix form as,

$$\sum_{i=1}^{n} a_{ij} \epsilon_i = b_j, \quad (6)$$

where $a_{ij} = \sum_{hk\ell} w \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j}$ and $b_j = \sum_{hk\ell} w \Delta \frac{\partial |F_c|}{\partial p_j}$,

and their solution is given by,

$$\epsilon_i = \sum_{i} (a^{-1})_{ij} b_j,$$

where $(a^{-1})_{ij}$ is the matrix inverse of a_{ij}.

Even with modern computers it is often impracticable to calculate all the terms of the normal equation matrix, a_{ij}, in (6). It is therefore necessary to consider approximations

in which many off-diagonal elements of a_{ij} $(i \neq j)$ are neglected. The simplest approximation is to neglect all off-diagonal elements but this requires many cycles of refinement for convergence. A better approximation is the block-diagonal form in which the off-diagonal elements involving correlations between scale and thermal parameters and among parameters of the same atom are retained. This results in a matrix whose non-zero elements are blocks about the diagonal.

Since high-order terms of the Taylor series are neglected in the least-squares method, several successive cycles of refinement are necessary before a true minimum has been attained. Convergence is reached when the atomic parameters after two successive cycles are not significantly different. The progress of the least-squares refinement may be followed by observing changes in $\Sigma w\Delta^2$ and R' where,

$$R' = \sum_{hk\ell} w \Delta^2 / \sum_{hk\ell} wF_o^2 .$$

Cochran (1948) and Cruickshank (1952) have shown that the results from the Fourier and least-squares methods of refinement are in close agreement. The coordinates found for an atom in a Fourier series corrected for series-termination errors are the same as those given by minimising the function $\Sigma(1/f)\Delta^2$. Hence if a weighting function 1/f is used in least-squares refinement tne resulting coordinates will be the same as those from a difference or corrected F_o synthesis.

1.12 ACCURACY.

In the least-squares refinement of a structure it is possible to solve the normal equations by matrix methods and obtain both the new values of the parameters varied and their standard deviations, σ. These σ values give us an assessment of the accuracy of the parameters; if σ is small then the parameter has been determined relatively accurately.

If correctly chosen relative weights have been used in the least-squares refinement, then the variance (σ^2) of a parameter, p_i, is given by,

$$\sigma^2(p_i) = (a^{-1})_{ii}(\Sigma w \Delta^2)/(m - n),$$

where $(a^{-1})_{ii}$ is a diagonal element of the inverse matrix, and m and n are respectively the number of observations and refined parameters. If there is a correlation between the parameters then the covariance of the parameters p_i and p_j for relative weights can be estimated as,

$$\mathrm{cov}(p_i,p_j) = (a^{-1})_{ij}(\Sigma w \Delta^2)/(m - n).$$

Having obtained the best possible atomic coordinates, various molecular parameters can be calculated. These bond lengths and angles and non-bonded contacts will in most cases deviate from the standard accepted values and it is necessary to determine if these differences are due to experimental error or if they are significant. The standard deviation in a bond length AB between atoms A and B is given by the expression,

$$\sigma(AB) = \left\{\sigma^2(A) - 2\mathrm{cov}(A,B) + \sigma^2(B)\right\}^{\frac{1}{2}},$$

where $\sigma^2(A)$ and $\sigma^2(B)$ are the variances of A and B in the

direction AB. When there is no correlation between the atoms, cov(A,B) = 0. The standard deviation in tne angle between the bonds AB and BC is,

$$\sigma(\beta) = \left\{ \frac{\sigma^2(A)}{AB^2} + \frac{AC^2\sigma^2(B)}{AB^2BC^2} + \frac{\sigma^2(C)}{BC^2} \right\}^{\frac{1}{2}},$$

where $\sigma^2(A)$ and $\sigma^2(C)$ are the variances of A and C in the plane of the three atoms and perpendicular to AB and BC respectively, and $\sigma^2(B)$ is the variance of B in the direction of the centre of the circle passing through atoms A, B and C (Darlow,1960).

Before conclusions can be drawn from a comparison of two different experimental measurements of a bond length or angle, proper statistical significance tests should be applied (Cruickshank and Robertson, 1953). As a general rule, if the difference between two bond lengths or angles is greater than about three times the estimated standard deviation, then this difference is probably significant.

PART II

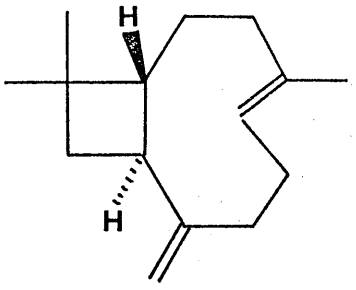
CRYSTAL STRUCTURE ANALYSES OF TWO CARYOPHYLLENE REARRANGEMENT PRODUCTS.

INTRODUCTION.

Caryophyllene (I) is the major constituent of oil of cloves and was one of the first sesquiterpenes to be studied by the organic chemist. However, it has taken many years to clarify this early work and X-ray crystallography has proved to be one of the most successful techniques for unravelling the mysteries.

The bicyclic skeleton of caryophyllene is unique and can rearrange under suitable treatment to numerous different tricyclic systems. The structures and stereochemistry of many of these rearrangement products have been confirmed or illucidated by X-ray diffraction methods and work of this kind began in 1955 with caryolan-1-ol (II) (Robertson and Todd, 1955) which is obtained by treating caryophyllene with sulphuric acid. Since then there have been many examples of crystal structure analyses of caryophyllene rearrangement products reported in the literature, for example, isoclovene (III) (Clunie and Robertson, 1961) and pseudoclovene-A (IV) (Ferguson et al., 1967), both of which are products of the dehydration of caryolan-1-ol.

The second part of this thesis describes in detail the crystal structure analyses of dibromo derivatives of 1,5,9,9-tetramethyltricyclo $\left[6,2,1,0^{4,11}\right]$ undec-5-ene (V), a rearrangement product of isocaryophyllene (VI), and 2,6,10,10-tetramethyltricyclo $\left[2,7,0,0^{2,7}\right]$ undec-5-ene (VII), which is formed by the removal of hydrogen chloride from caryophyllene dihydrochloride (VIII).



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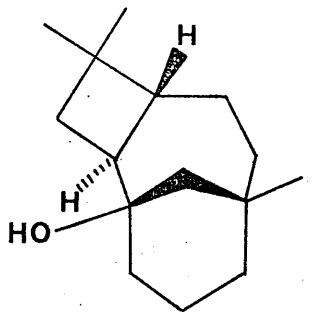

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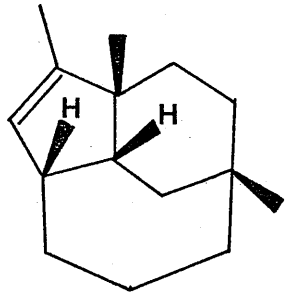

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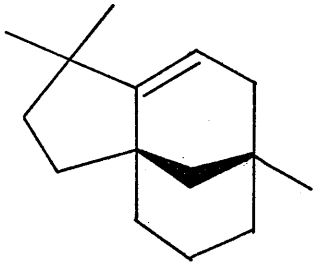

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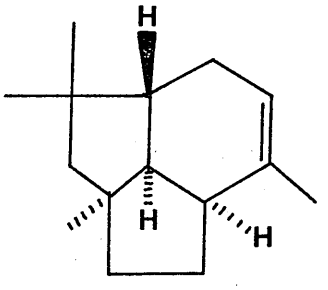

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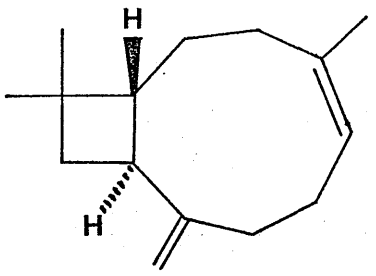

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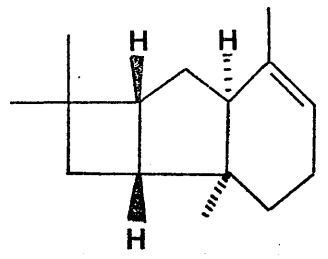

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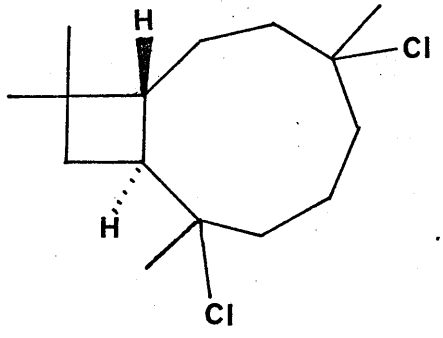

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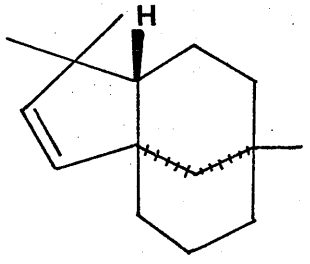
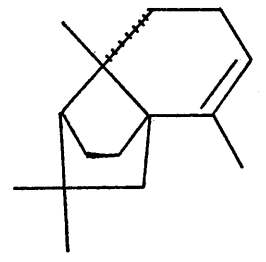


IX



X

THE STRUCTURE AND ABSOLUTE STEREOCHEMISTRY OF 1,5,9,9-TETRAMETHYLTRICYCLO [6,2,1,$0^{4,11}$] -UNDEC-5-ENE: AN X-RAY ANALYSIS OF THE DIBROMO DERIVATIVE.

1.1 INTRODUCTION.

The acid-catalysed rearrangement of caryophyllene has been shown (Nickon, 1954; Barton and de Mayo, 1957; Nickon et al., 1968) to produce three major products, caryolan-1-ol, clovene (IX) and neoclovene (X) (Parker et al., 1965; McKillop et al., 1967). The same reaction has now been carried out on isocaryopnyllene by Gollnick and Schade (1970) and they have found that pure (-)-isocaryophyllene, on treatment with sulphuric acid in ether, yields a complex mixture of hydrocarbons. Two main components (each 35%) were able to be isolated in a pure state by fractional distillation and preparative g.l.c. In agreement with the findings of Nickon et al. (1968), neither caryolan-1-ol nor clovene which were formed by caryophyllene under the same conditions, were detected in the crude reaction mixture.

The first major hydrocarbon, $C_{15}H_{24}$, was shown to be identical to neoclovene by chemical means. The second major hydrocarbon, $C_{15}H_{24}$, was shown by various spectrochemical techniques to be tricyclic with a tri-substituted double bond but no furtner information was readily obtainable. A crystalline dibromo derivative was prepared by addition of bromine to an ice-cold solution of the hydrocarbon in carbon tetrachloride so that an X-ray structure analysis

by the phase-determining heavy-atom method could be carried out. The presence of the bromine atoms in the compound also enabled the absolute configuration to be determined.

1.2 EXPERIMENTAL.

Crystal Data.

The dibromo derivative of 1,5,9,9-tetramethyltricyclo-$[6,2,1,0^{4,11}]$undec-5-ene, $C_{15}H_{24}Br_2$, M = 364.2.

Orthorhombic,

$\underline{a} = 6.63 \pm 0.02$, $\underline{b} = 8.96 \pm 0.01$, $\underline{c} = 26.35 \pm 0.01$ Å.

$\underline{U} = 1565.2$ Å^3, $\underline{D}_m = 1.51$ (by flotation), $\underline{Z} = 4$, $\underline{D}_c = 1.53$.

F(000) = 736. Space group $P2_12_12_1$ (D_2^4, No. 19).

Linear absorption coefficient for X-rays ($\lambda = 1.5418$ Å), $\mu = 71.0$ cm^{-1}.

The derivative was recrystallised from benzene in the form of needles which were sensitive to light.

Crystallographic Measurements.

Oscillation and Weissenberg photographs were taken with Cu-K_α ($\lambda = 1.5418$ Å) radiation. The unit cell parameters were measured from oscillation and zero-layer Weissenberg photographs using the Aluminium-wire technique to calculate the standard deviations. The space group was established uniquely from the systematic absences (h00, 0k0, and 00ℓ absent when h, k, and ℓ are odd) as $P2_12_12_1$. A crystal, coated in varnish to prevent decomposition, was

mounted about the needle axis, a, and used in the collection of the intensity measurements. The three-dimensional intensity data were obtained from a non-integrating equi-inclination Weissenberg camera using the multiple-film technique (Robertson, 1943). The reciprocal lattice nets $0k\ell$ - $5k\ell$ were surveyed and the intensities of the 860 reflexions were measured visually by comparison with a calibrated step-wedge. The intensities were corrected for Lorentz, polarisation and rotation factors (Tunell, 1939) but no allowance was made for unobserved reflexions and absorption corrections were neglected. Initially the data were put on a common scale by ensuring that $k\Sigma|F_o| = \Sigma|F_c|$ for each layer. The layer scale factors were later refined by least-squares methods.

Structure Determination.

The equivalent positions for the space group $P2_12_12_1$ are

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

The vectors to be expected between the same bromine atoms and their symmetry-related positions are,

$$\tfrac{1}{2} + 2x, \quad 2y, \quad \tfrac{1}{2};$$
$$\tfrac{1}{2}, \quad \tfrac{1}{2} + 2y, \quad 2z;$$
$$2x, \quad \tfrac{1}{2}, \quad \tfrac{1}{2} + 2z.$$

Maxima corresponding to vectors between non-symmetry related bromine atoms will occur at -

$$(x_1 - x_2), \quad (y_1 - y_2), \quad (z_1 - z_2);$$
$$\tfrac{1}{2} + (x_1 + x_2), \quad (y_1 + y_2), \quad \tfrac{1}{2} + (z_1 - z_2);$$
$$\tfrac{1}{2} + (x_1 - x_2), \quad \tfrac{1}{2} + (y_1 + y_2), \quad (z_1 + z_2);$$
$$(x_1 + x_2), \quad \tfrac{1}{2} + (y_1 - y_2), \quad \tfrac{1}{2} + (z_1 + z_2).$$

Initial coordinates for the two bromine atoms were derived from the Harker sections at $u = \frac{1}{2}$, $v = \frac{1}{2}$, and $w = \frac{1}{2}$ (Figure 1.1) and the vectors expected between these two bromine atoms were found in the three-dimensional Patterson synthesis.

Structure factors based on these coordinates were calculated and resulted in a discrepancy factor, R, of 0.32. In the subsequent Fourier synthesis the structure factors were weighted in order to reduce phase angle errors and so improve the resolution of the light atoms (Sim, 1961). Maxima corresponding to eight carbon atoms of the structure were revealed in the ensuing electron-density map. Inclusion of these atoms in a structure factor calculation lowered R to 0.26. In the following electron-density map the remaining carbon atoms were found and with all the atoms included the residual, R, fell to 0.21. Two further rounds of structure factor and Fourier calculations reduced R to 0.19. An overall isotropic temperature factor of 0.06 Å^2 was used in the above calculations and the values of the atomic scattering factors were taken from "International Tables for X-ray Crystallography", Vol.III. A difference synthesis was computed at this point in order to ensure that all the atoms present in the asymmetric unit had been located.

Structure Refinement.

The positional and thermal parameters of the atoms and the individual layer scale factors were refined by least-squares methods minimising the expression

$$M = \sum w (|F_o| - |F_c|)^2.$$

The course of the refinement is outlined in Table 1.1.

A weighting scheme of the form,

$$\sqrt{w} = \left\{[1 - \exp(-p_1(\sin\theta/\lambda)^2]/[1 + p_2|F_o| + p_3|F_o|^2]\right\}^{\frac{1}{2}},$$

was applied during refinement. Initially p_1 was set at 500 and p_2 and p_3 at zero, but the parameters were adjusted so that constant averages for $w\Delta^2$, for reflexions batched according to $|F_o|$ and $\sin\theta/\lambda$, were obtained. The final values of p_1, p_2, and p_3 were 100, 0.001 and 0.0001 respectively.

A total of six cycles of full-matrix least-squares refinement were carried out. Before anisotropic refinement of the bromine atoms the data were placed on a common scale by use of the layer scale factors obtained at the end of the isotropic refinement. After the sixth cycle R was reduced to its final value of 0.096 and the agreement between the observed and calculated structure amplitudes at the conclusion of the refinement is shown in Table 1.2; the phase angles are also given.

During the course of the refinement it was noticed that C(2) (see Fig. 1.3) was moving appreciably in the x-direction from its position in the electron density maps. This gave rise to an abnormally long C(1) - C(2) bond distance (see Fig. 1.4). Since there is no chemical reason

for this bond lengthening, it is probably due to the absence of absorption corrections which, because the molecule contains two heavy bromine atoms, could cause large systematic errors in the data.

The final fractional coordinates and e.s.d.s for the non-hydrogen atoms with their thermal parameters are given in Table 1.3. The anisotropic temperature parameters are values of U_{ij} in the expression,

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)].$$

The final three-dimensional electron density distribution over one molecule was calculated from the observed structure amplitudes and phase angles based on the final atomic parameters and is shown in Figure 1.2 as superimposed contour sections drawn parallel to (100); an explanation of the atomic arrangement corresponding to the electron density distribution and of the atom numbering system is shown in Figure 1.3. Figures 1.4 and 1.5 give details of intramolecular bonded distances and valence angles respectively. Some intramolecular non-bonded distances and all intermolecular contacts <4.0 A are listed in Table 1.4. Table 1.5 contains the displacements of atoms from various planes in the molecule and the equations of these planes. The packing arrangement of the molecules in the crystal projected down the a axis is illustrated in Figure 1.6.

Absolute Configuration.

The absolute configuration of the dibromo derivative of 1,5,9,9-tetramethyltricyclo $[6,2,1,0^{4,11}]$-undec-5-ene was established using Bijvoet's anomalous-dispersion method (1949). The bromine atoms in the molecule scatter the X-rays anomalously which results in a breakdown of Friedel's Law. Consequently, for the space group $P2_12_12_1$ we have,

$$I(hk\ell) = I(\bar{h}\bar{k}\ell) = I(h\bar{k}\bar{\ell}) = I(\bar{h}k\bar{\ell})$$
$$\neq I(\bar{h}\bar{k}\bar{\ell}) = I(\bar{h}k\ell) = I(h\bar{k}\ell) = I(hk\bar{\ell}).$$

The reflexions were indexed in a right-handed system in a manner described by Peerdeman and Bijvoet (1956). The intensities of a number of Bijvoet pairs were measured visually and structure factors calculated with the anomalous dispersion corrections included, i.e., $\Delta f'$ and $\Delta f''$ Since the correction terms for bromine with Cu-K_α radiation are not very large, it proved difficult to find the Bijvoet pairs. However, of the 17 found, 15 showed differences in the same direction as the observed structure factors. Hence, the molecule chosen (Figure 1.3) is the one with the correct absolute configuration.

The results are shown in Table 1.6. Reflexions marked with an asterisk are those in which calculated structure factors show small differences in the opposite direction to the observed structure factors. Values of $\Delta f'$ and $\Delta f''$ for bromine were taken from "International Tables for X-ray Crystallography", Vol.III.

Table 1.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-3}$	Final R′
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, full-matrix.	1-4	0.125	1.74	0.024
x,y,z,Uij(i,j=1,2,3) for Br atoms; x,y,z,Uiso for carbon atoms; one scale factor, full-matrix.	5-6	0.096	0.73	0.014

Table 1.2

Observed and calculated structure amplitudes with phase angles.

Table 1.3

Fractional coordinates and thermal parameters ($Å^2$) with estimated standard deviations.

	x/a	y/b	z/c	Uiso
Br(1)	0.13822±56	0.44291±38	0.26258±12	*
Br(2)	-0.40001±63	0.22278±39	0.34688±15	*
C(1)	-0.0972 ±46	0.7182 ±29	0.4031 ±10	0.067 ±07
C(2)	-0.3383 ±67	0.7574 ±44	0.3818 ±13	0.123 ±13
C(3)	-0.3689 ±53	0.6303 ±32	0.3413 ±11	0.079 ±08
C(4)	-0.1503 ±49	0.5877 ±31	0.3223 ±10	0.077 ±08
C(5)	-0.1383 ±44	0.4396 ±30	0.2965 ±09	0.072 ±07
C(6)	-0.1146 ±53	0.2962 ±32	0.3290 ±11	0.076 ±08
C(7)	0.0038 ±48	0.3148 ±33	0.3748 ±11	0.077 ±09
C(8)	-0.0837 ±43	0.4535 ±29	0.4034 ±09	0.061 ±07
C(9)	0.0118 ±47	0.5021 ±37	0.4583 ±11	0.071 ±09
C(10)	-0.0885 ±60	0.6652 ±35	0.4589 ±12	0.080 ±10
C(11)	-0.0321 ±41	0.5903 ±28	0.3698 ±10	0.055 ±07
C(12)	0.0387 ±49	0.8619 ±33	0.3979 ±11	0.090 ±09
C(13)	-0.2806 ±46	0.4204 ±36	0.2492 ±11	0.083 ±09
C(14)	0.2418 ±66	0.4983 ±49	0.4566 ±15	0.106 ±13
C(15)	-0.0817 ±64	0.3982 ±39	0.4992 ±13	0.097 ±11

* Anisotropic thermal parameters Uij ($Å^2$) with e.s.d.s.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br(1)	0.094 2	0.089 2	0.091 2	-0.038 4	0.017 4	-0.007 4
Br(2)	0.099 3	0.086 2	0.140 3	-0.013 4	0.009 5	-0.045 4

Table 1.4

a) Some intramolecular non-bonded distances (Å).

Br(1)...C(4)	2.80	C(4) ...C(7)	2.99
Br(1)...C(6)	2.76	C(4) ...C(9)	3.82
Br(1)...C(7)	3.29	C(4) ...C(10)	3.69
Br(1)...C(8)	3.99	C(4) ...C(12)	3.40
Br(1)...C(11)	3.32	C(4) ...C(13)	2.59
Br(2)...C(3)	3.66	C(5) ...C(8)	2.84
Br(2)...C(4)	3.72	C(6) ...C(9)	3.96
Br(2)...C(5)	2.92	C(6) ...C(11)	2.90
Br(2)...C(7)	2.90	C(6) ...C(13)	2.62
Br(2)...C(8)	3.30	C(7) ...C(10)	3.89
Br(2)...C(13)	3.22	C(7) ...C(13)	3.92
C(1) ...C(5)	3.77	C(7) ...C(14)	3.14
C(1) ...C(7)	3.75	C(7) ...C(15)	3.41
C(1) ...C(14)	3.30	C(8) ...C(14)	2.61
C(1) ...C(15)	3.83	C(8) ...C(15)	2.57
C(2) ...C(5)	3.86	C(9) ...C(12)	3.60
C(2) ...C(8)	3.25	C(10)...C(12)	2.53
C(2) ...C(9)	3.83	C(10)...C(14)	2.65
C(2) ...C(10)	2.75	C(10)...C(15)	2.62
C(2) ...C(12)	2.70	C(11)...C(12)	2.59
C(3) ...C(5)	2.58	C(11)...C(13)	3.89
C(3) ...C(6)	3.45	C(11)...C(14)	3.04
C(3) ...C(7)	3.86	C(11)...C(15)	3.84
C(3) ...C(8)	2.96	C(12)...C(14)	3.85
C(3) ...C(10)	3.63	C(14)...C(15)	2.58
C(3) ...C(13)	3.12		

Table 1.5

Distances (Å) of atoms from various planes in the molecule.

Atoms included in calculation of planes.

Plane 1	Plane 2	Plane 3
C(11)....-0.025	C(1) 0.025	C(8) ....-0.127
C(1) 0.039	C(2) ....-0.024	C(11).... 0.125
C(10)....-0.038	C(3) 0.018	C(6) 0.127
C(9) 0.023	C(11)....-0.019	C(5) ....-0.125

Atoms not included in calculation of planes.

C(8) ....-0.776	C(4) ....-0.599	C(7) 0.726
	C(12)....-1.194	C(4) ....-0.490
	C(8) 1.487	

Plane Equations.

Plane 1:	0.925X + 0.379Y + 0.034Z	=	-2.160 Å
Plane 2:	-0.351X - 0.627Y + 0.695Z	=	-3.551
Plane 3:	0.981X - 0.155Y - 0.120Z	=	2.323

X, Y and Z are coordinates in Å referred to the orthogonal axes a, b and c.

Table 1.6

Bijvoet pairs used in the anomalous-dispersion calculation.

h	k	l	$I_{\ell}/I_{\bar{\ell}}$	$F^2_{\ell}/F^2_{\bar{\ell}}$	
1	1	12	1.45	1.17	
1	1	2	1.23	1.06	
1	1	3	1.88	1.30	
1	1	5	1.40	1.04	
1	1	6	1.45	1.06	
1	2	3	1.60	1.04	
1	2	7	3.00	2.25	
1	2	11	1.23	1.04	
1	2	12	1.14	1.06	
1	3	2	1.14	0.96	*
1	4	17	1.50	1.06	
1	5	15	1.33	1.23	
2	1	4	1.18	1.19	
2	1	6	1.50	1.19	
2	1	7	1.18	1.02	
2	1	10	1.14	1.02	
2	2	4	1.33	0.90	*

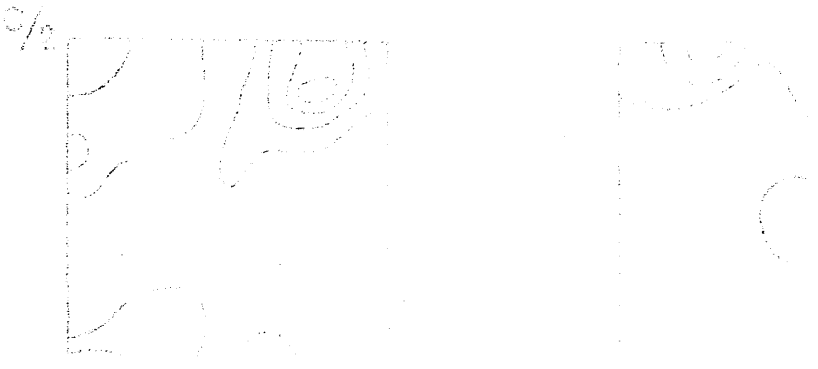


Figure 1.1

Harker sections at u = 1/2, v = 1/2, and w = 1/2 through the three-dimensional Patterson distribution. Contour levels are at equal arbitrary intervals.

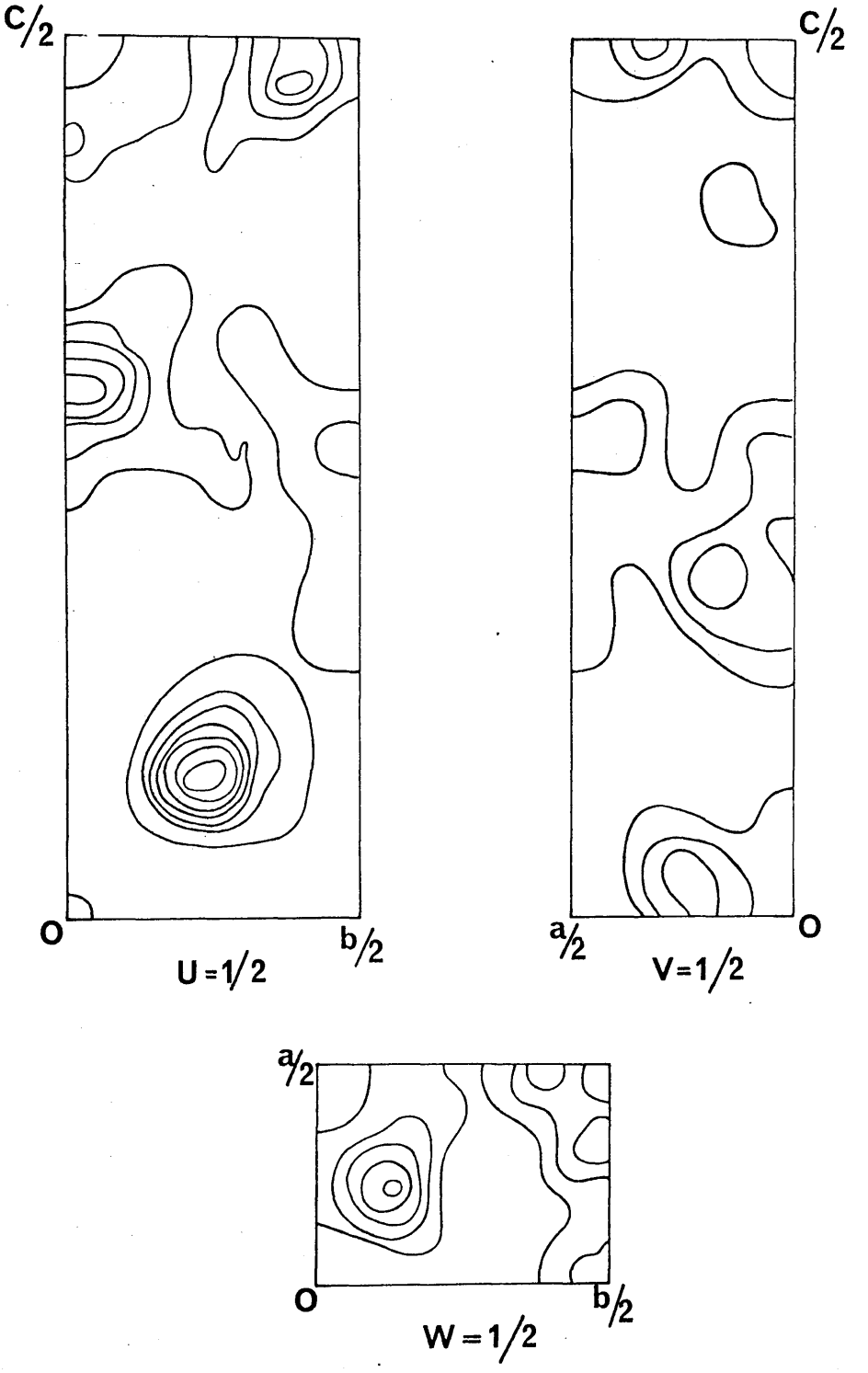

c/2
O
b/2
U=1/2
c/2
a/2
O
V=1/2
a/2
O
b/2
W=1/2

Figure 1.2

Superimposed sections parallel to the (100) plane of the three-dimensional electron-density distribution over one molecule. The contours start at 1e $Å^{-3}$ and are drawn at intervals of 1e $Å^{-3}$ except around the bromine atoms, where the intervals are 10e $Å^{-3}$.

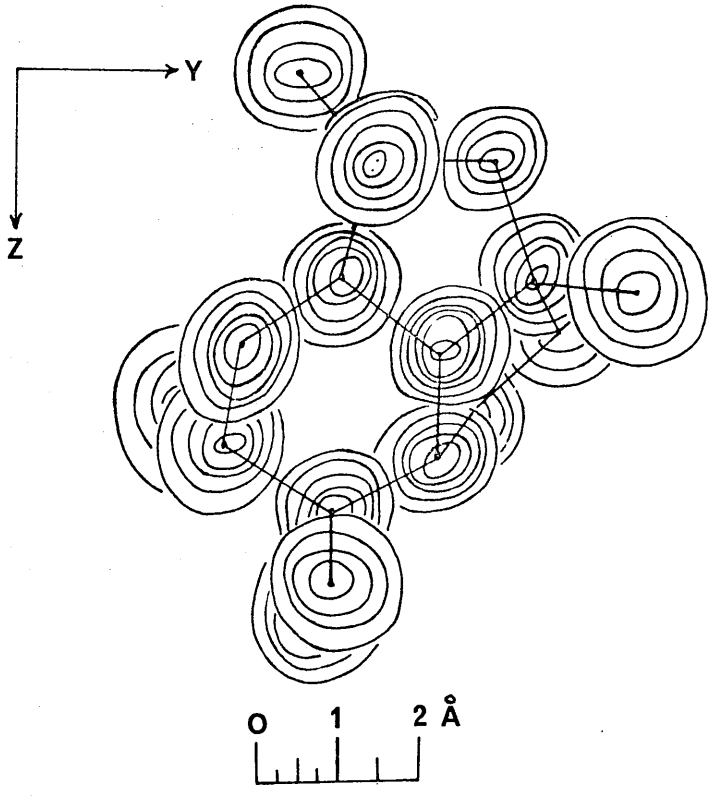
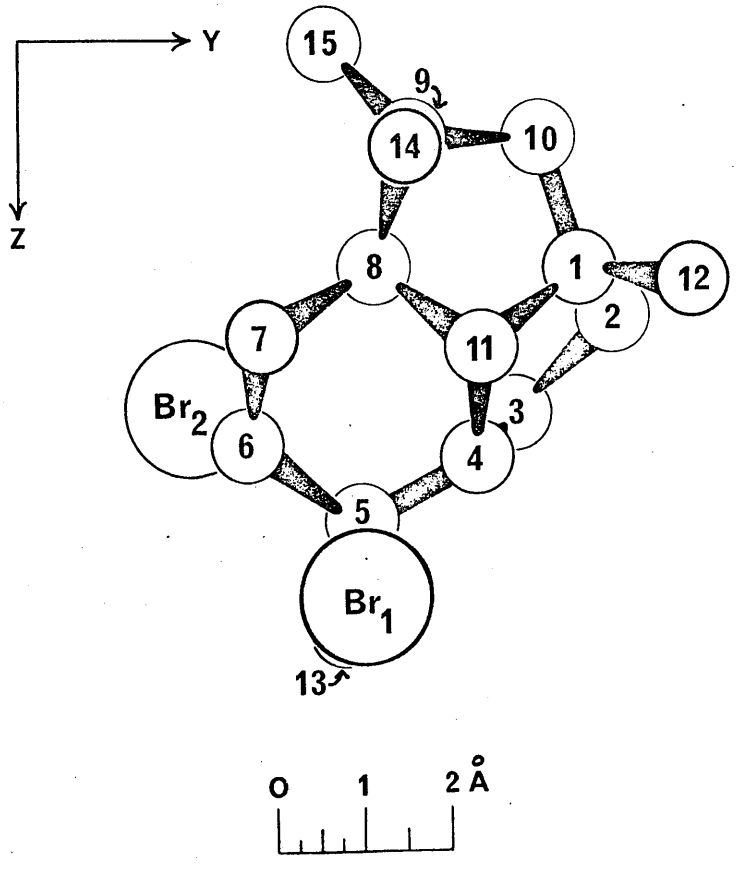
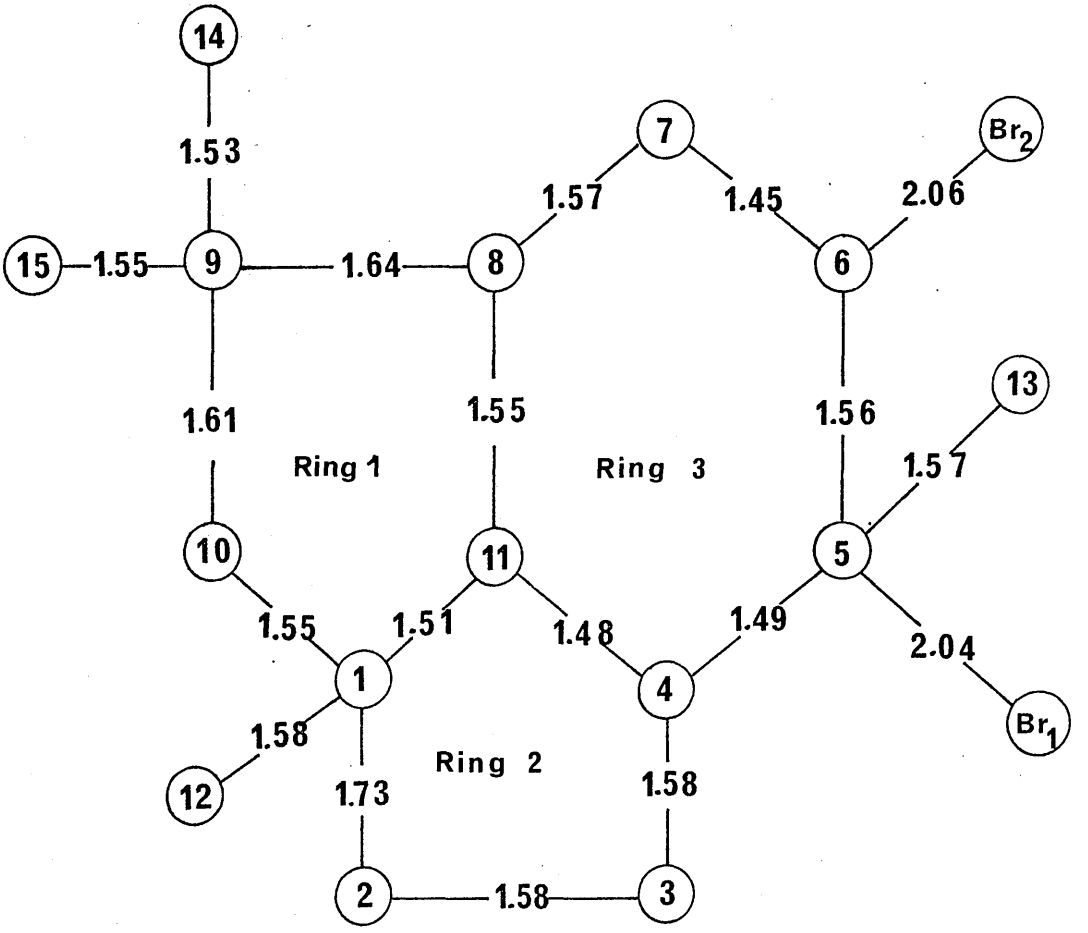

Y
Z
0 1 2 Å

Figure 1.3

The arrangement of the atoms corresponding to the electron-density distribution in Figure 1.2 with an explanation of the numbering scheme adopted in the analysis.


Y
Z
15
9
14
10
8
1
12
2
7
11
3
Br2
6
4
5
Br1
13
0
1
2 Å

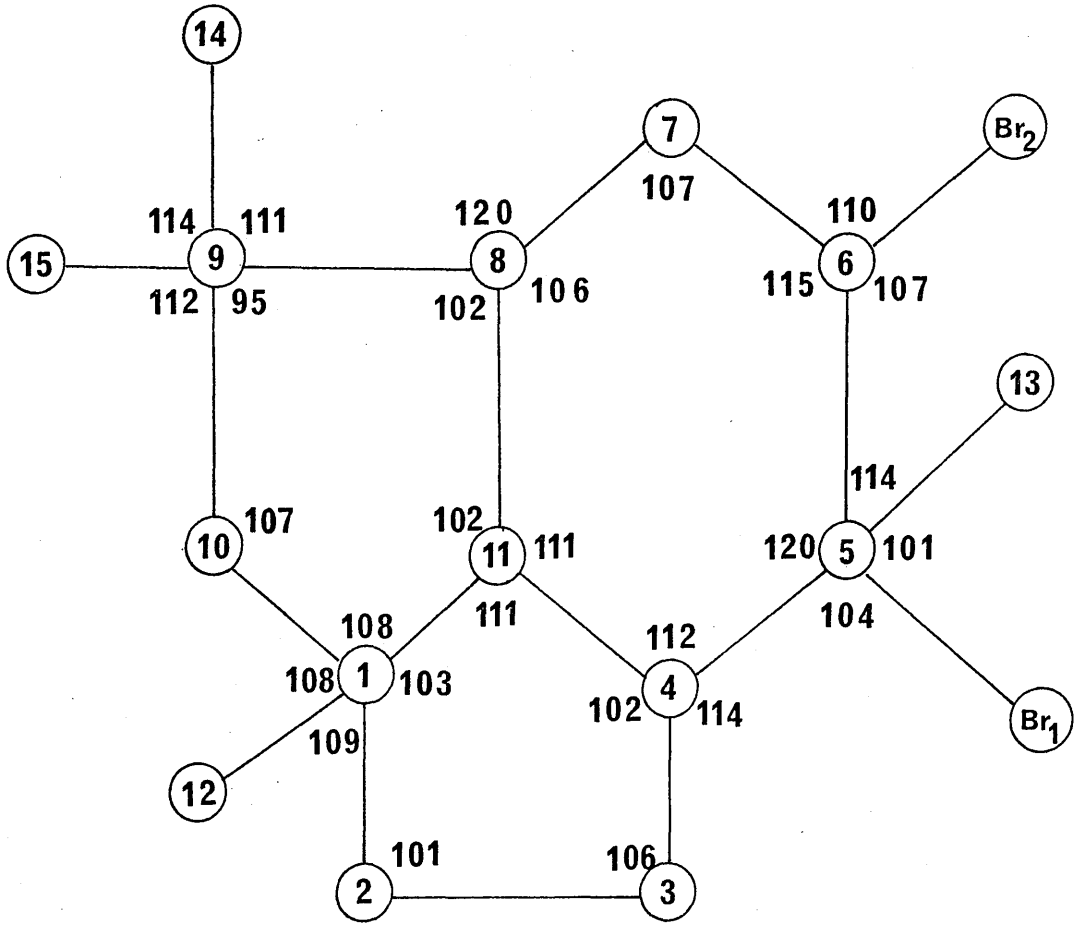


The average e.s.d. for C - C bond length is 0.05 Å

The average e.s.d. for C - Br bond length is 0.03 Å.

Figure 1.5

Bond angles (degrees).

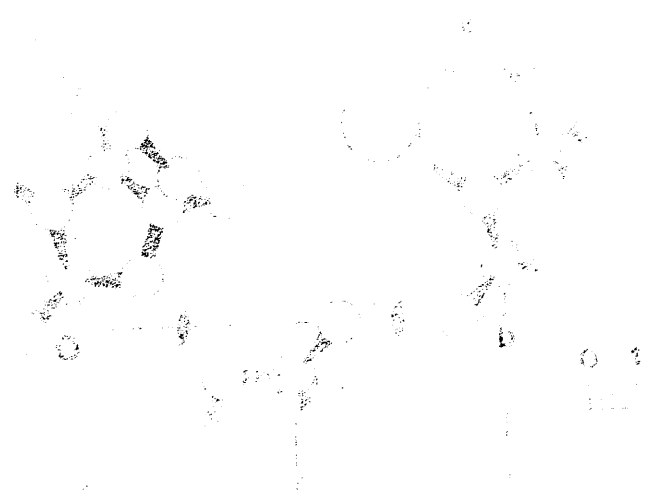


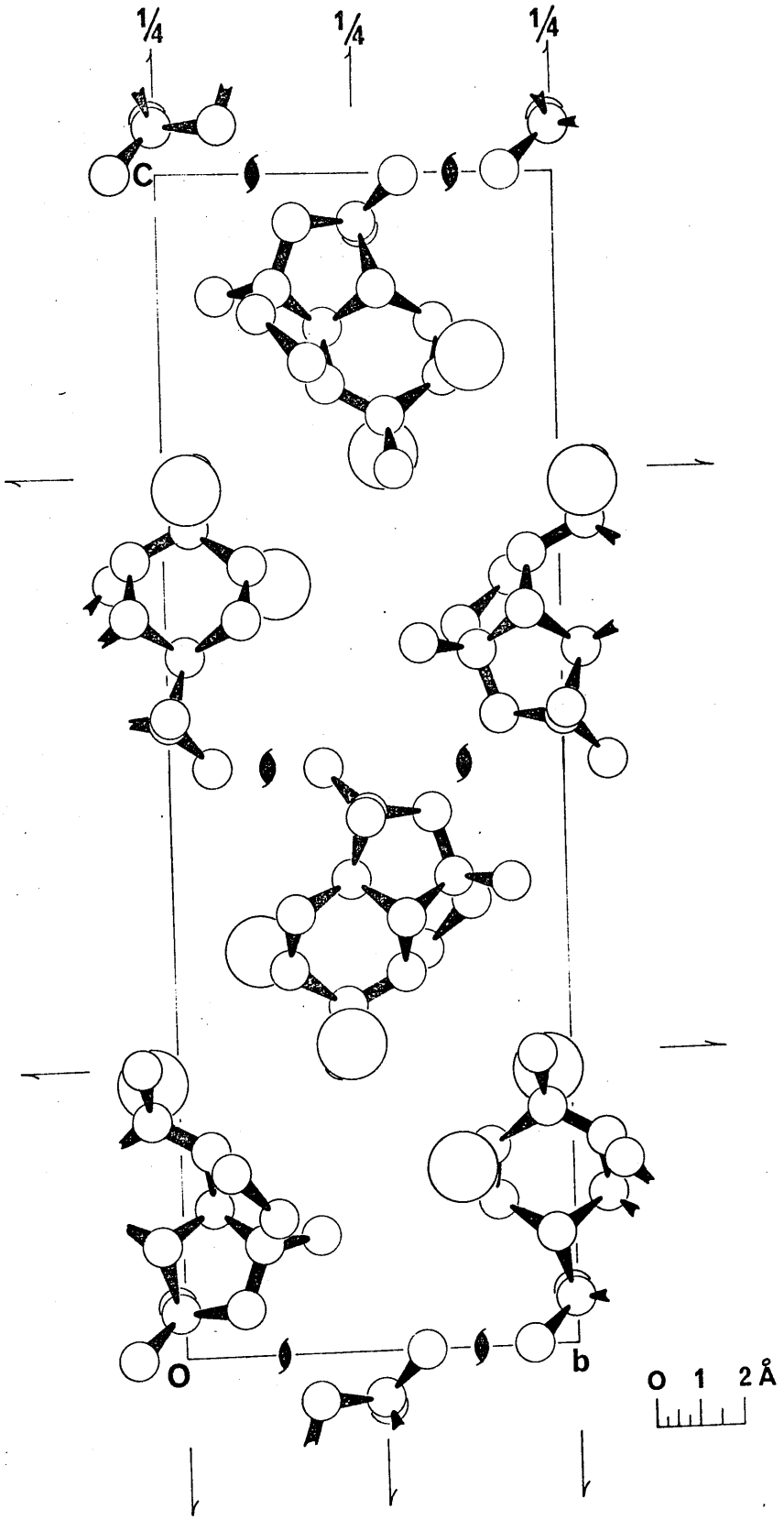
The average e.s.d. for C-C-C bond angle is 2°.

The average e.s.d. for C-C-Br bond angle is 1.8°.

Figure 1.6

A molecular-packing diagram viewed along the a axis.



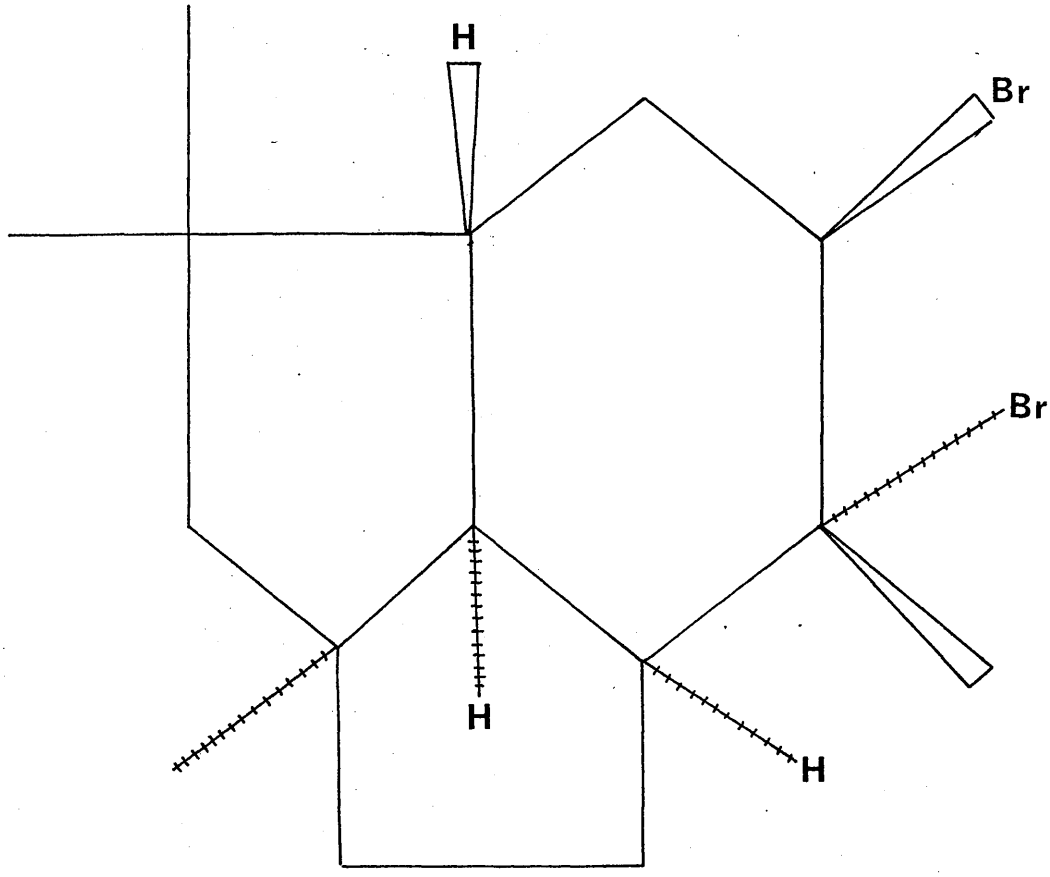

1/4
1/4
1/4
C
O
b
0 1 2Å

1.3 DISCUSSION.

This X-ray analysis has established the structure and absolute stereochemistry of the dibromo derivative of 1,5,9,9-tetramethyltricyclo $\left[6,2,1,0^{4,11}\right]$ undec-5-ene as (XI); it follows that (V) represents the structure and absolute stereochemistry of the parent hydrocarbon itself.

The accuracy of the molecular parameters is not high as might be expected in view of the presence of two heavy bromine atoms in the molecule. Such atoms dominate the structure factor and hence make it difficult to determine the positions of the light atoms with a high degree of accuracy. The neglect of applying absorption corrections and the decomposition of the crystals in light also contributed to the low accuracy of the structure analysis.

Bond lengths do not differ significantly from the expected values. The average carbon - carbon bond length is 1.56 Å, or 1.55 Å if the anomalously high value for the C(1) - C(2) bond is omitted, which is in good agreement with the value of 1.545 Å for diamond. The average standard deviation for these bond lengths is 0.05 Å. The carbon - bromine bond lengths are 2.06 Å and 2.04 Å with standard deviations of 0.03 Å. Both of these are significantly longer than the expected value of 1.94 Å for bromoalkanes (Sutton, 1958). The lengthening may well be a result of the uncertainty in the positions of C(5) and C(6) caused by the diffraction effects emanating from the adjacent bromine atoms. However a similar carbon - bromine bond lengthening



XI

has been found in the molecule cadinol dihydrobromide (Hanic).

The average internal valency bond angle in the six-membered ring system C(4), C(5), C(6), C(7), C(8), and C(11), (Ring 3), is $111.6^{\circ} \pm 2.3^{\circ}$. The average bond angles in the two cyclopentane rings are $103.0^{\circ} \pm 2.3^{\circ}$ and $104.5^{\circ} \pm 2.3^{\circ}$ which is similar to the usual mean angle of 105° associated with cyclopentane rings (Sim, 1965). The C(8) - C(9) - C(10) angle of 95.3° is distinctly smaller than the other valence angles in these five-membered rings. This effect has been observed in pseudo-clovene-A-diol (98.8°) (Hawley et al., 1969) and in ring D of numerous steroids, e.g., 4-bromo-estradiol (98.5°) (Norton et al., 1964) and 3-keto-4,4-dimethyl-5α-androstane-17β-iodoacetate (97.7°) (Macaulay, 1968). The contraction is probably due to the steric interaction between the C(9) and C(8) substituents.

The dibromo derivative is a substituted tricyclo-$\left[6,2,1,0^{4,11}\right]$ undecane system; the two cyclopentane rings adopt envelope conformations and are fused to a cyclohexane ring which assumes a distorted chair conformation. The two cyclopentane rings (Rings 1 and 2 in Figure 1.4) are cis-fused to each other and the cyclohexane ring (Ring 3) is cis-fused to ring 1 and trans-fused to ring 2.

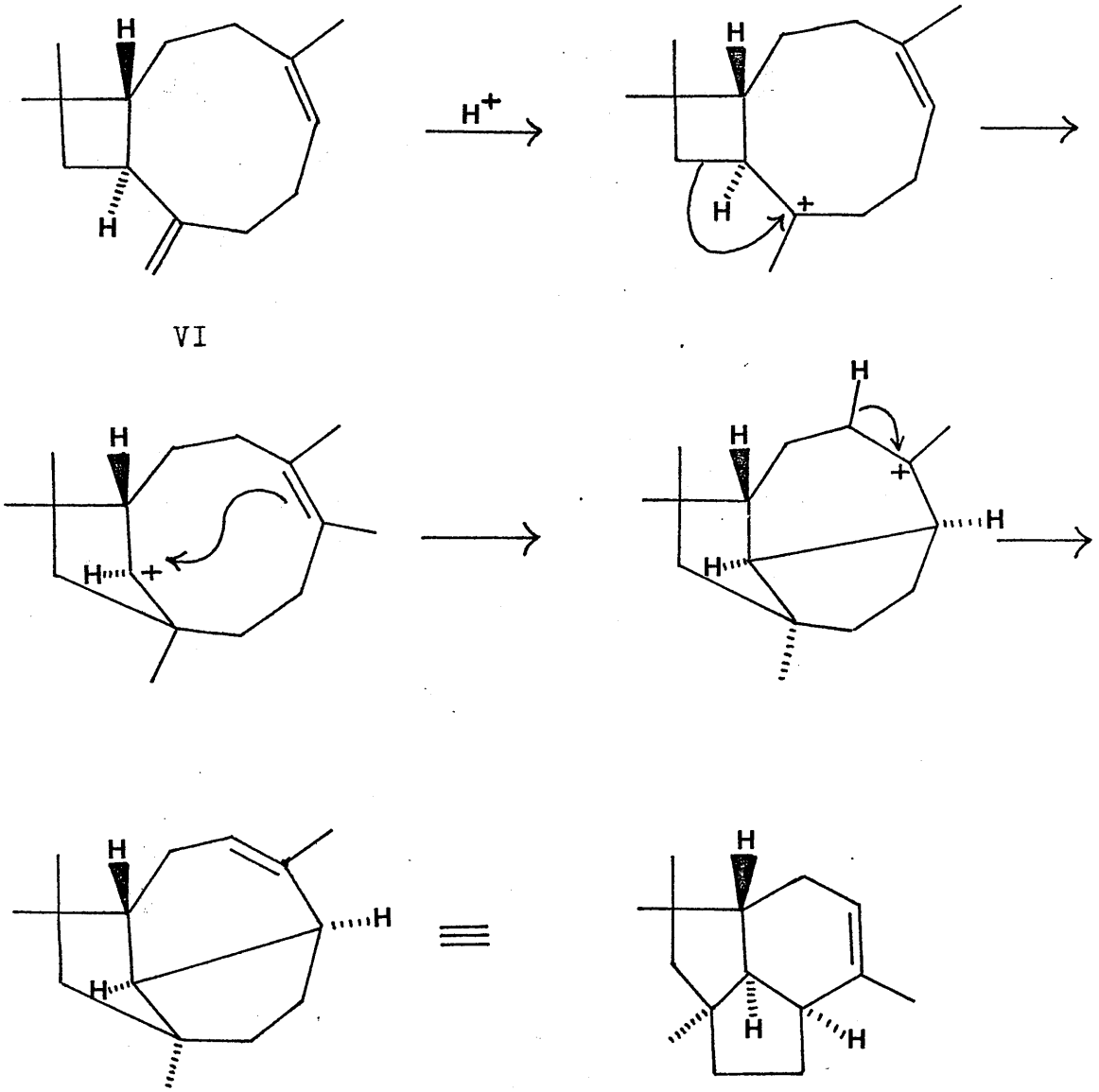
The cyclopentane ring (Ring 1) has an envelope conformation with C(8) displaced 0.78 Å from the best plane through carbon atoms 1, 11, 9, and 10. The second cyclopentane ring (Ring 2) also adopts an envelope conformation with C(4) displaced 0.60 Å from the plane containing carbon

atoms 1, 11, 3, and 2. The torsion angle C(3),C(2) - C(1),C(11) is 4° which is close to the value expected for a perfect envelope conformation. The six-membered ring (Ring 3) assumes a distorted chair conformation. The carbon atoms 8, 11, 6, and 5 are alternately above and below the mean plane through them by an average value of 0.13 Å. C(7) lies above this plane by 0.73 Å but C(4) is displaced below this plane by only 0.49 Å which is significantly shorter than the 0.73 Å expected for an ideal chair conformation (Brown, Martin, and Sim, 1965). As a consequence of this ring flattening the valence angles C(4) - C(5) - C(6) and C(5) - C(6) - C(7) are increased to 119° and 115° respectively.

The rigidity of the structure depends on the conformation of the cyclohexane ring (Ring 3). If the two bromine atoms were in equatorial positions and C(13), therefore, in an axial position, the ring would adopt a boat conformation and the system would be more flexible. This, however, is not a favourable situation due to the severe steric interactions which would arise between the C(13) methyl group, the C(8) hydrogen atom and the C(14) methyl group which together with C(2) and C(3) would all lie on one side of the molecule. With the ring in a chair conformation, the bromine atoms adopt axial positions and the C(13) methyl group lies well clear of any of the other atoms. As a result, the molecule adopts the more rigid conformation despite the distortions in the valency angles that it requires.

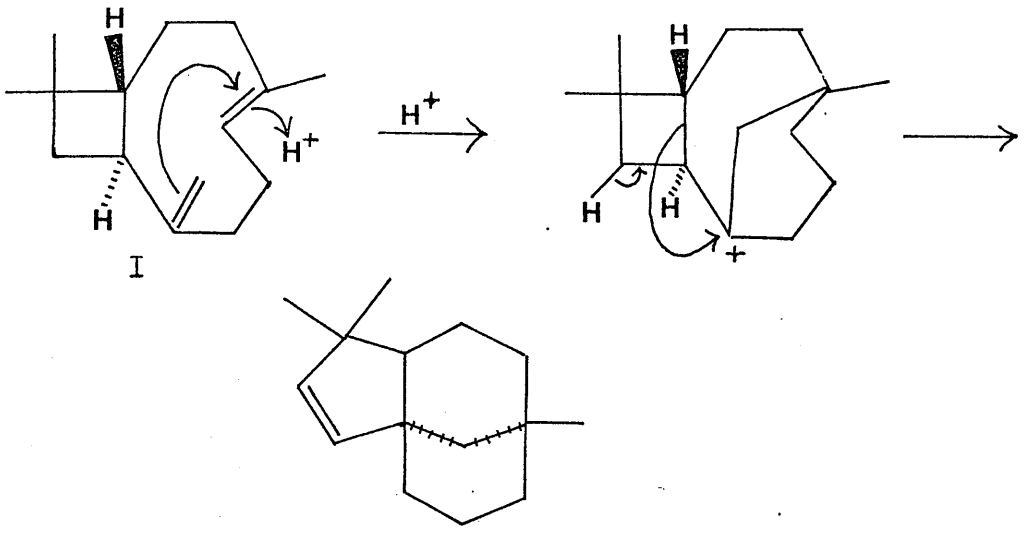
There are no abnormally short intermolecular contacts, and the molecules are thus held in the crystal by van der Waals' forces.

In reconciling the final structure with that of its known precursor, isocaryophyllene, we have considered the possible mechanism of formation. The scheme proposed is shown below:-



It is interesting to note that the formation of clovene and caryolan-1-ol from caryophyllene can only be explained if it is assumed that the exo- and endo- double bonds are in close proximity which is possible in caryophyllene but not so in isocaryophyllene. This would appear to explain why neither of these two products are found in the hydrocarbon mixture formed from the acid-catalysed rearrangement of isocaryophyllene. The formation of neoclovene, however, does not require this close proximity of the two double bonds and so we find that both forms of caryophyllene will rearrange under the same conditions to give neoclovene. The mechanisms involved are shown below.

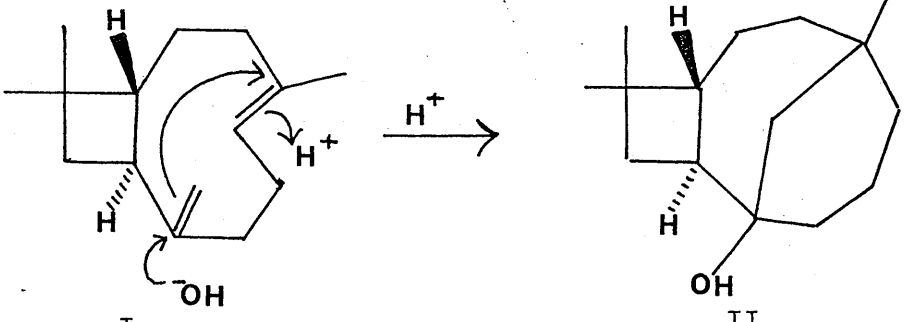
a)



I

IX

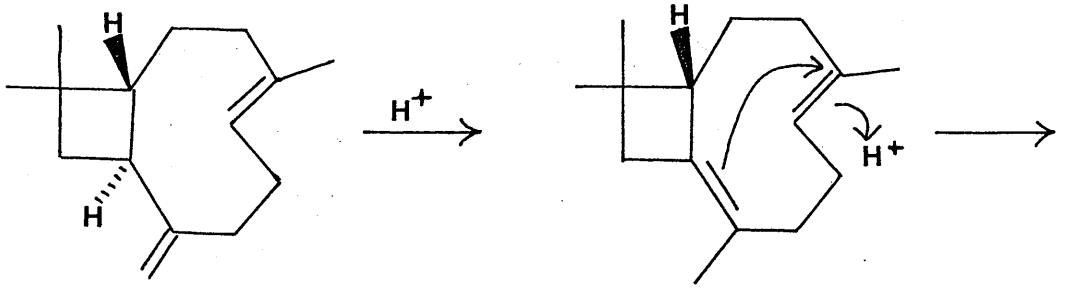
b)



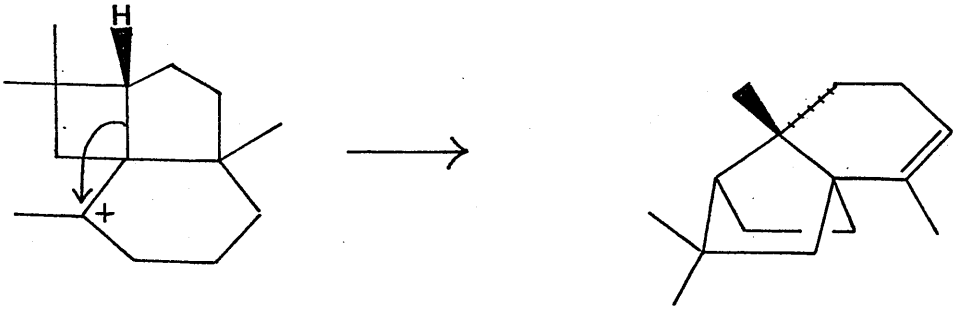
I

II

c)



I



X

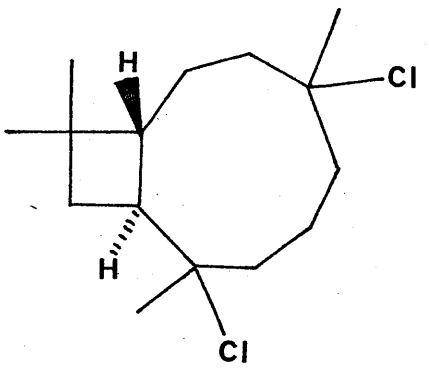
THE STRUCTURE AND ABSOLUTE STEREOCHEMISTRY OF 2,6,10,10-TETRAMETHYLTRICYCLO [7,2,0,$0^{2,7}$]-UNDEC-5-ENE: AN X-RAY ANALYSIS OF THE DIBROMO DERIVATIVE.

2.1 INTRODUCTION.

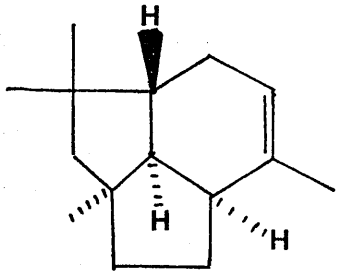
During early investigations into the chemistry of caryophyllene a number of workers used the dihydrochloride (VIII) as suitable crystalline derivative. In an effort to elucidate the structure of caryophyllene and unaware of the complexities inherent in the caryophyllene nucleus, these early workers submitted this dihydrochloride to various mild and severe dehydrochlorination conditions (Schreiner and Kremers, 1901; Semmler and Mayer, 1910; Henderson et al., 1929). A great deal of confusion then ensued as to the identity of the derived hydrocarbons because of the limited methods of comparison with other bicyclic and tricyclic hydrocarbons derived from caryophyllene and caryolan-1-ol.

This dehydrochlorination, using one of the earliest procedures (Schreiner and Kremers, 1901), viz., refluxing with sodium acetate in acetic acid for one hour, has now been carried out by Gollnick and Schade (1971). They found a complex mixture of hydrocarbons from which two main components could be isolated by fractional distillation and preparative g.l.c. Neither clovene nor the tricyclic hydrocarbon (V) (Gollnick and Schade, 1970), each derived from caryophyllene and isocaryophyllene respectively, were identified as minor components. One of the major hydrocarbons (34%), however, was identified as neoclovene (X).

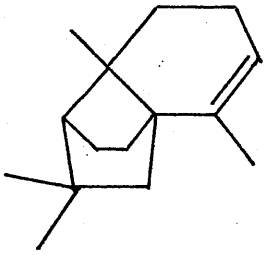
The major hydrocarbon (46%), $C_{15}H_{24}$, was shown by various chemical techniques to be tricyclic with a trisubstituted double bond but no further information was readily obtainable. Addition of bromine to an ice-cold solution of the hydrocarbon in carbon tetrachloride yields a crystalline dibromide suitable for analysis by X-ray methods.



VIII



V



X

2.2 EXPERIMENTAL.

Crystal Data.

The dibromo derivative of 2,6,10,10-tetramethyltricyclo-$[7,2,0,0^{2,7}]$undec-5-ene, $C_{15}H_{24}Br_2$, M = 364.2.

Orthorhombic,

a = 15.47 ± 0.02, b = 14.02 ± 0.01, c = 7.01 ± 0.01 Å.

U = 1520.8 Å^3, D_m = 1.60 (by flotation), Z = 4, D_c = 1.59.

F(000) = 736. Space group $P2_12_12$ (D_2^3, No. 18).

Linear absorption coefficient for X-rays (λ = 1.5418 Å), μ = 71.0 cm^{-1}.

The derivative crystallised from benzene to form crystals which were sensitive to light but decomposition was slow.

Crystallographic Measurements.

The unit cell dimensions were measured using oscillation and zero-layer Weissenberg photographs taken with Ni-filtered Cu-K_α radiation (λ = 1.5418 Å) and standard deviations calculated using the Aluminium-wire technique. Precession photographs were taken with Zr-filtered Mo-K_α radiation (λ = 0.7107 Å) and the space group was determined uniquely from the systematic absences (h00 and 0k0 absent when h and k are odd). The intensity data were collected

on a non-integrating Weissenberg camera with the multiple-film technique (Robertson, 1943). A small crystal, rotating about the c-axis, was used and the reciprocal lattice nets hk0 - hk6 were surveyed. 1336 reflexions were measured visually using a calibrated step wedge.

The intensities were corrected for Lorentz, polarisation and rotation factors but because of the small size of the crystal absorption corrections were ignored. No allowance was made for unobserved reflexions. Initially the data were put on a common scale by ensuring that $k \Sigma |F_o| = \Sigma |F_c|$ for each layer. The layer scale factors were later refined by least-squares methods.

Structure Determination.

A three-dimensional Patterson synthesis was computed with the data sharpened to point atom at rest with respect to the bromine atoms. For space group $P2_12_12$ the Harker sections occur at $u = \frac{1}{2}$, $v = \frac{1}{2}$, and $w = 0$; the sections at $u = \frac{1}{2}$ and $v = \frac{1}{2}$ are shown in Figure 2.1. Some difficulties arose in finding a solution for the Patterson synthesis since a large number of possible Harker peaks appeared on the map. Only by a process of elimination were the correct positions of the two bromine atoms found. The set of structure factors phased on one bromine atom position alone gave a discrepancy factor, R, of 0.64, whereas the set derived from the two bromine atoms gave an R-factor of 0.75. This was due to the special relationship between the two bromine atom positions shown below;

Br(1)	0.04665	0.13159	0.25014
Br(2)	0.04688	0.36775	0.74969.

The structure factors calculated using the two bromine atom coordinates were weighted in order to reduce phase angle errors (Sim, 1961) and these weighted structure factors were used in the first Fourier synthesis. Six carbon atoms were clearly revealed in the ensuing electron-density distribution and after two further rounds of structure factor and Fourier calculations coordinates for all 17 non-hydrogen atoms in the asymmetric unit were obtained. Another two cycles of Fourier refinement led to improved coordinates for these atoms and the R-factor was reduced to 0.18. In all the structure factor calculations values for the atomic scattering factors were taken from "International Tables for X-ray Crystallography", Vol. III.

Structure Refinement.

Nine cycles of full-matrix least-squares refinement reduced R to its final value of 0.107. During the first five cycles positional and thermal parameters were refined, but thereafter the anisotropic vibration of the bromine atoms was taken into account. Before commencing anisotropic refinement the data were placed on a common scale using the layer scale factors obtained at the end of isotropic refinement. The weighting scheme used in the refinement was of the form,

$$\sqrt{w} = \left\{ [1 - \exp(-p_1(\sin\theta/\lambda)^2]/[1 + p_2|F_o|] \right\}^{\frac{1}{2}}.$$

Initially p_1 was set at 500 and p_2 at zero but the parameters

were adjusted so that constant averages for $w\Delta^2$ for reflexions batched according to $|F_o|$ and $\sin\theta/\lambda$ were obtained; the final values of p_1 and p_2 were 100 and 0.1 respectively. At convergence the shifts in the coordinates were all less than one fifth of the estimated standard deviations. The shifts in the scale factor and thermal parameters were also insignificant. The process of refinement is outlined in Table 2.1 while the agreement between the observed and final calculated structure amplitudes can be seen in Table 2.2. The phase angles are also included in this table.

The final fractional coordinates, thermal parameters and standard deviations for non-hydrogen atoms are in Table 2.3. The anisotropic temperature factors are values of U_{ij} in the expression,

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)] .$$

The final electron-density distribution for one molecule is shown in Figure 2.2 as superimposed contour sections drawn parallel to (001) and the atomic arrangement corresponding to this and the atom numbering scheme are shown in Figure 2.3. Figures 2.4 and 2.5 give details of intramolecular bonded distances and valence angles. Some intermolecular non-bonded contacts <4.0 Å are in Table 2.4. Table 2.5 contains the displacements of atoms from various planes in the molecule and the equations of these planes. The packing arrangement of the molecules in the crystal projected down the c axis is illustrated in Figure 2.6.

Absolute Configuration.

The absolute configuration of the dibromo derivative of 2,6,10,10-tetramethyltricyclo $\left[7,2,0,0^{2,7}\right]$ undec-5-ene was determined by the anomalous dispersion method (Bijvoet, 1949). Values of $\Delta f'$ and $\Delta f''$ for bromine were taken from "International Tables for X-ray Crystallography", Vol.III. The intensities of 28 Bijvoet pairs ($hk\ell$ and $h\bar{k}\ell$) were estimated visually from equi-inclination Weissenberg photographs taken with Cu-K_α radiation. With the anomalous-dispersion corrections included, structure factors were calculated and the ratios $I_o(hk\ell)/I_o(h\bar{k}\ell)$ and $F_c^2(hk\ell)/F_c^2(h\bar{k}\ell)$ determined. The results are shown in Table 2.6 and show that for each Bijvoet pair, the ratios of intensities and the squares of the calculated structure factors are either both greater or both smaller than unity with the exception of 7 pairs of reflexions which are marked with an asterisk. It follows, therefore, that Figure 2.3 correctly represents the absolute stereochemistry of the dibromo derivative of 2,6,10,10-tetramethyltricyclo $\left[7,2,0,0^{2,7}\right]$ undec-5-ene.

Table 2.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-3}$	Final R'
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, full-matrix, unit weights.	1-2	0.15	38.7	0.023
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, full-matrix, $p_1 = 100$, $p_2 = 0.1$.	3-5	0.15	9.2	0.039
x,y,z,Uij (i,j = 1,2,3) for Br atoms, x,y,z,Uiso for C atoms, one scale factor, full-matrix.	6-9	0.107	3.8	0.019

Table 2.2

Observed and calculated structure amplitudes with phase angles.

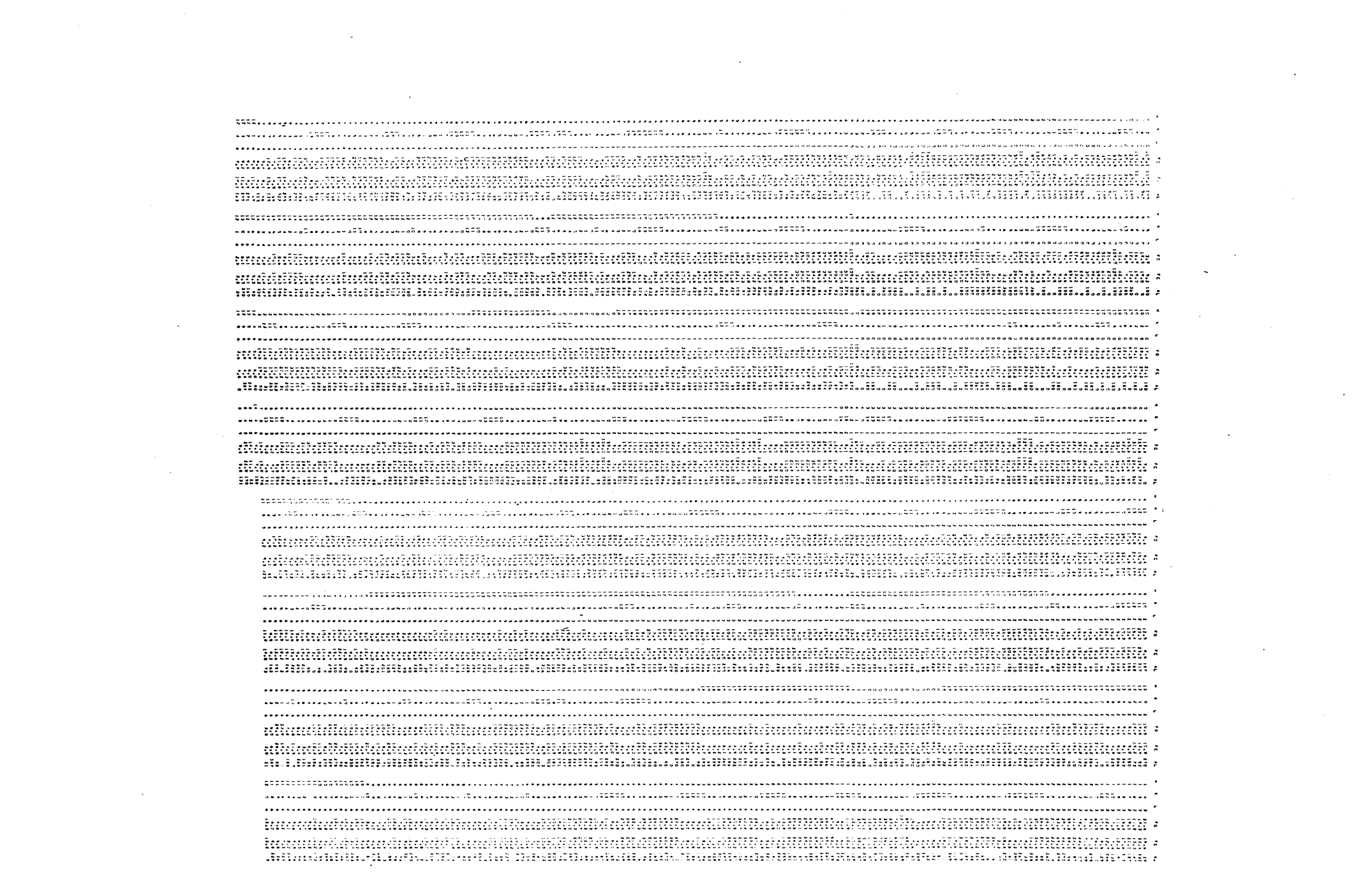


Table 2.3

Fractional coordinates and thermal parameters ($Å^2$) with estimated standard deviations.

	x/a	y/b	z/c	Uiso
Br(1)	0.54523±15	0.37107±16	0.74427±36	*
Br(2)	0.55060±14	0.13156±17	0.29422±34	*
C(1)	0.2789 ±11	0.1901 ±13	0.6538 ±29	0.055±4
C(2)	0.3525 ±10	0.2575 ±12	0.6055 ±25	0.047±4
C(3)	0.3687 ±11	0.2569 ±13	0.3860 ±29	0.054±4
C(4)	0.4535 ±12	0.3078 ±13	0.3335 ±30	0.063±5
C(5)	0.5295 ±11	0.2550 ±13	0.4317 ±28	0.055±4
C(6)	0.5204 ±11	0.2382 ±13	0.6496 ±28	0.055±4
C(7)	0.4282 ±09	0.2113 ±11	0.7139 ±24	0.043±3
C(8)	0.4140 ±10	0.1021 ±11	0.6944 ±26	0.046±4
C(9)	0.3184 ±10	0.0859 ±12	0.6772 ±29	0.051±4
C(10)	0.2625 ±11	0.0778 ±13	0.8653 ±29	0.054±4
C(11)	0.2448 ±11	0.1871 ±13	0.8549 ±29	0.053±4
C(12)	0.3305 ±11	0.3613 ±14	0.6652 ±30	0.061±4
C(13)	0.5919 ±11	0.1760 ±13	0.7265 ±30	0.059±4
C(14)	0.1788 ±14	0.0203 ±16	0.8176 ±38	0.075±6
C(15)	0.3079 ±14	0.0400 ±16	1.0471 ±36	0.072±6

* Anisotropic thermal parameters Uij ($Å^2$) with e.s.d.s.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br(1)	0.0844 14	0.0746 14	0.0851 17	-0.0276 24	-0.0102 24	-0.0433 24
Br(2)	0.0773 13	0.0850 15	0.0713 15	-0.0214 24	0.0494 22	0.0065 24

Table 2.4

a) Some intramolecular non-bonded distances (Å).

Br(1)...C(2)	3.52	C(4) ...C(8)	3.89
Br(1)...C(4)	3.33	C(4) ...C(12)	3.10
Br(1)...C(5)	2.74	C(4) ...C(13)	3.95
Br(1)...C(7)	2.89	C(5) ...C(8)	3.34
Br(1)...C(13)	2.83	C(5) ...C(11)	3.97
Br(1)...C(15)	3.87	C(5) ...C(12)	3.79
Br(2)...C(3)	3.38	C(6) ...C(8)	2.54
Br(2)...C(4)	2.90	C(6) ...C(9)	3.79
Br(2)...C(6)	2.94	C(6) ...C(12)	3.41
Br(2)...C(7)	3.67	C(7) ...C(10)	3.35
Br(2)...C(8)	3.54	C(7) ...C(11)	3.02
Br(2)...C(13)	3.16	C(7) ...C(12)	2.61
C(1) ...C(3)	2.52	C(7) ...C(13)	2.58
C(1) ...C(4)	3.88	C(7) ...C(15)	3.83
C(1) ...C(6)	3.80	C(8) ...C(10)	2.65
C(1) ...C(12)	2.53	C(8) ...C(11)	3.09
C(1) ...C(14)	3.06	C(8) ...C(12)	3.86
C(1) ...C(15)	3.50	C(8) ...C(13)	2.95
C(2) ...C(5)	3.00	C(8) ...C(14)	3.91
C(2) ...C(10)	3.41	C(8) ...C(15)	3.09
C(2) ...C(11)	2.61	C(9) ...C(12)	3.87
C(2) ...C(13)	3.97	C(9) ...C(14)	2.55
C(3) ...C(6)	3.00	C(9) ...C(15)	2.68
C(3) ...C(8)	3.14	C(11)...C(12)	3.08
C(3) ...C(9)	3.24	C(11)...C(14)	2.57
C(3) ...C(11)	3.93	C(11)...C(15)	2.65
C(3) ...C(12)	2.51	C(14)...C(15)	2.58
C(4) ...C(7)	3.02		

b) Some intermolecular distances < 4.0 Å.

$Br(1)\ldots Br(1)^{I}$	3.88
$C(1)\ldots C(5)^{II}$	3.98
$C(3)\ldots C(15)^{III}$	3.97
$C(4)\ldots C(14)^{IV}$	3.77
$C(5)\ldots C(11)^{V}$	3.97
$C(8)\ldots C(8)^{VI}$	3.91
$C(8)\ldots C(13)^{VI}$	3.91
$C(9)\ldots C(13)^{VI}$	3.94
$C(12)\ldots C(15)^{VII}$	3.86
$C(15)\ldots Br(2)^{VIII}$	3.68

The subscripts refer to the following equivalent positions:

I	1 - x,	1 - y,	z;
II	-1/2 + x,	1/2 - y,	1 - z;
III	x,	y,	z - 1;
IV	1/2 - x,	1/2 + y,	1 - z;
V	1/2 + x,	1/2 - y,	1 - z;
VI	1 - x,	-y,	z;
VII	1/2 - x,	1/2 + y,	2 - z;
VIII	1 - x,	-y,	1 + z;

Table 2.5

Distances (Å) of atoms from various planes in the molecule.

Atoms included in calculation of planes.

Plane 1	Plane 2	Plane 3
C(1) ....-0.088	C(1) ....-0.033	C(2) ....-0.029
C(9) 0.084	C(9) 0.052	C(7) 0.028
C(10)....-0.086	C(8) ....-0.053	C(5) ....-0.028
C(11).... 0.090	C(7) 0.034	C(4) 0.028

Atoms not included in calculation of planes.

C(14)....-1.562	C(2) ....-0.528	C(3) 0.698
C(15).... 0.931	C(12)....-0.096	C(6) 0.453
	C(10).... 1.486	
	C(11).... 1.441	

Plane Equations.

Plane 1: $0.845X + 0.287Y + 0.451Z = -6.566$ Å

Plane 2: $-0.150X - 0.010Y + 0.989Z = -3.890$

Plane 3: $0.219X + 0.857Y + 0.467Z = -6.293$

X, Y and Z are coordinates in Å referred to the orthogonal axes a, b and c.

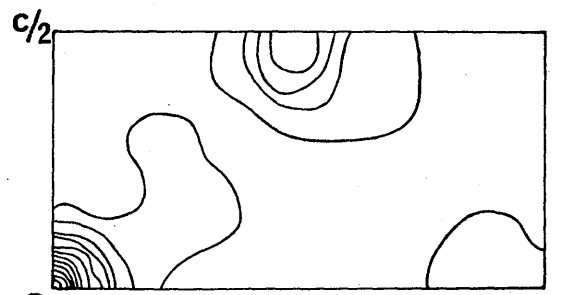
Table 2.6

Bijvoet pairs used in the anomalous-dispersion calculation.

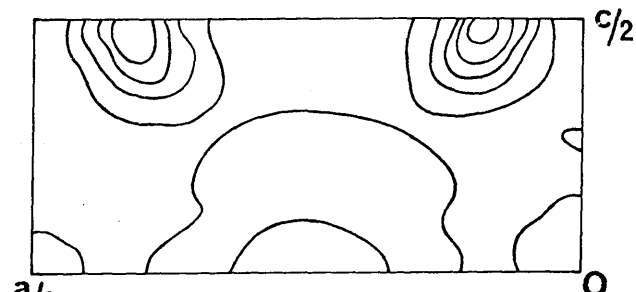
h	k	l	$I_k/I_{\bar{k}}$	$F_k^2/F_{\bar{k}}^2$		h	k	l	$I_k/I_{\bar{k}}$	$F_k^2/F_{\bar{k}}^2$	
1	3	2	1.45	0.90	*	3	1	3	1.45	0.81	*
1	8	2	1.50	1.19		3	2	3	1.40	1.44	
2	5	2	1.33	0.96	*	3	4	3	1.33	1.13	
2	6	2	0.80	0.87		6	3	3	0.83	0.90	
2	7	2	1.33	1.16		9	3	3	0.80	0.65	
4	4	2	0.80	0.94		12	3	3	0.86	1.08	*
4	5	2	0.82	0.98		2	1	4	1.25	1.08	
6	7	2	0.63	1.10	*	2	8	4	1.29	1.18	
8	4	2	0.80	0.96		3	6	4	1.25	0.81	*
10	4	2	0.81	1.07	*	3	10	4	2.00	1.33	
12	4	2	0.75	0.91		2	3	5	0.81	0.86	
1	4	3	1.18	1.12		3	1	5	1.67	2.31	
2	1	3	1.45	1.13		4	1	5	1.25	1.10	
2	2	3	1.22	1.03		7	1	5	0.88	0.83	

Figure 2.1

Harker sections at u = 1/2 and v = 1/2 through the three-dimensional Patterson distribution. Contour levels are at equal arbitrary intervals.



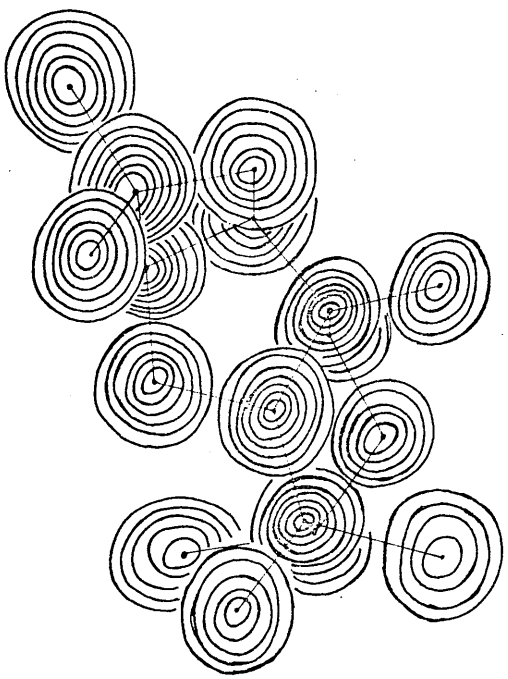
U = 1/2



V = 1/2

Figure 2.2

Superimposed sections parallel to the (001) plane of the three-dimensional electron-density distribution over one molecule. The contours start at 1e $\mathring{A}^{-3}$ and are drawn at intervals of 1e $\mathring{A}^{-3}$ except around the bromine atoms, where the intervals are 10e $\mathring{A}^{-3}$.


0
1
2 Å

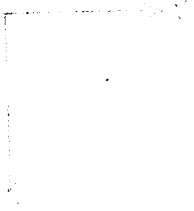


Figure 2.3

The arrangement of the atoms corresponding to the electron-density distribution in Figure 2.2 with an explanation of the numbering scheme adopted in the analysis.

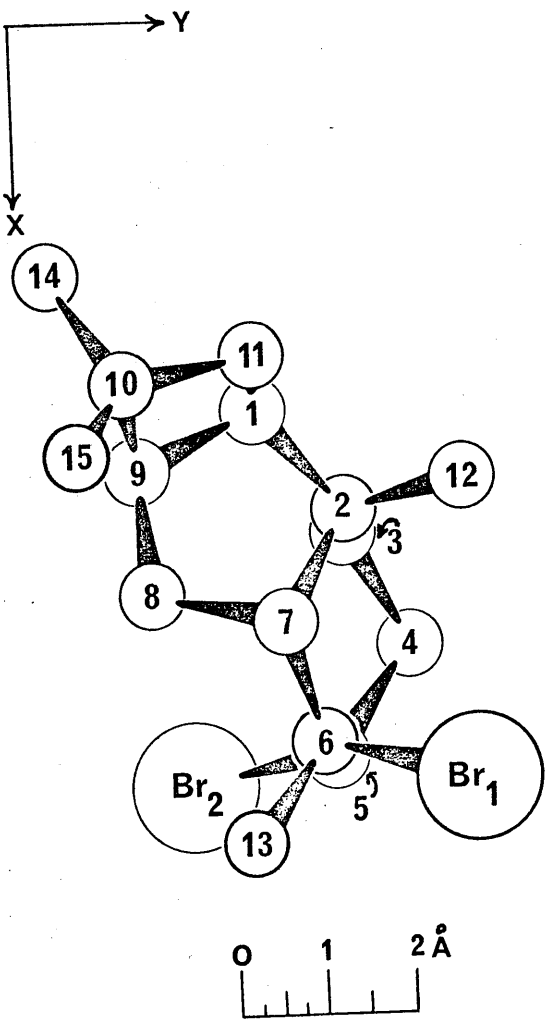
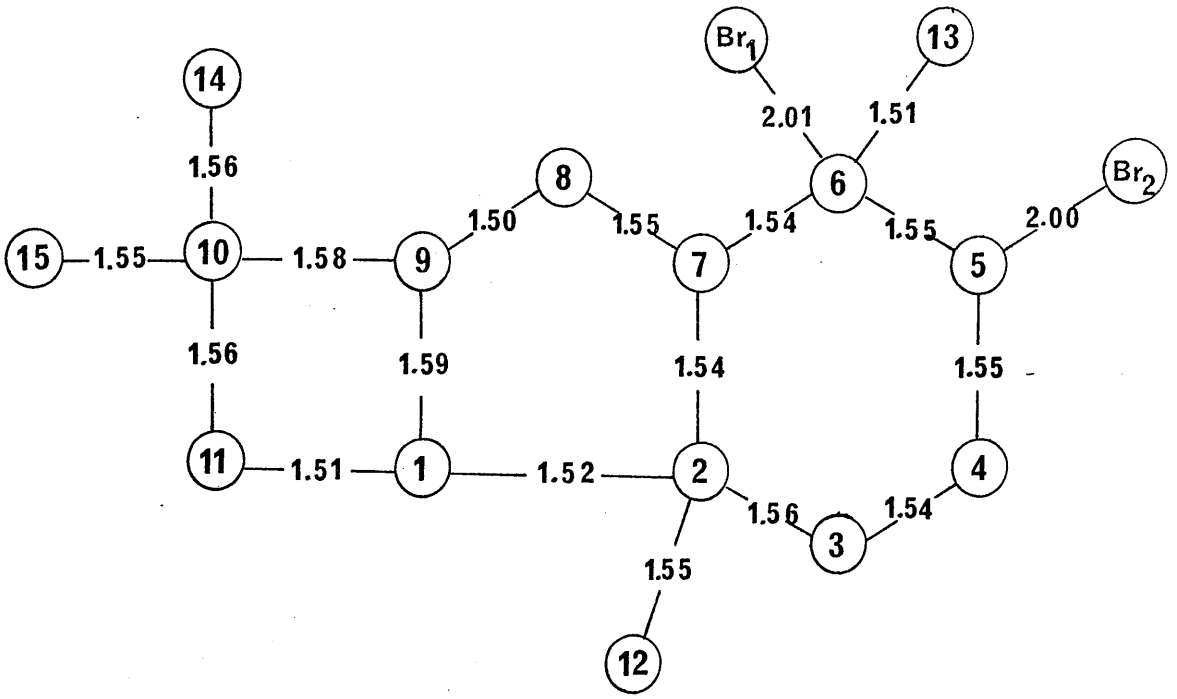

Y
X
14
11
10
1
15
9
12
2
3
8
7
4
6
Br2
Br1
5
13
0
1
2 Å

Figure 2.4

Bond lengths (Å).

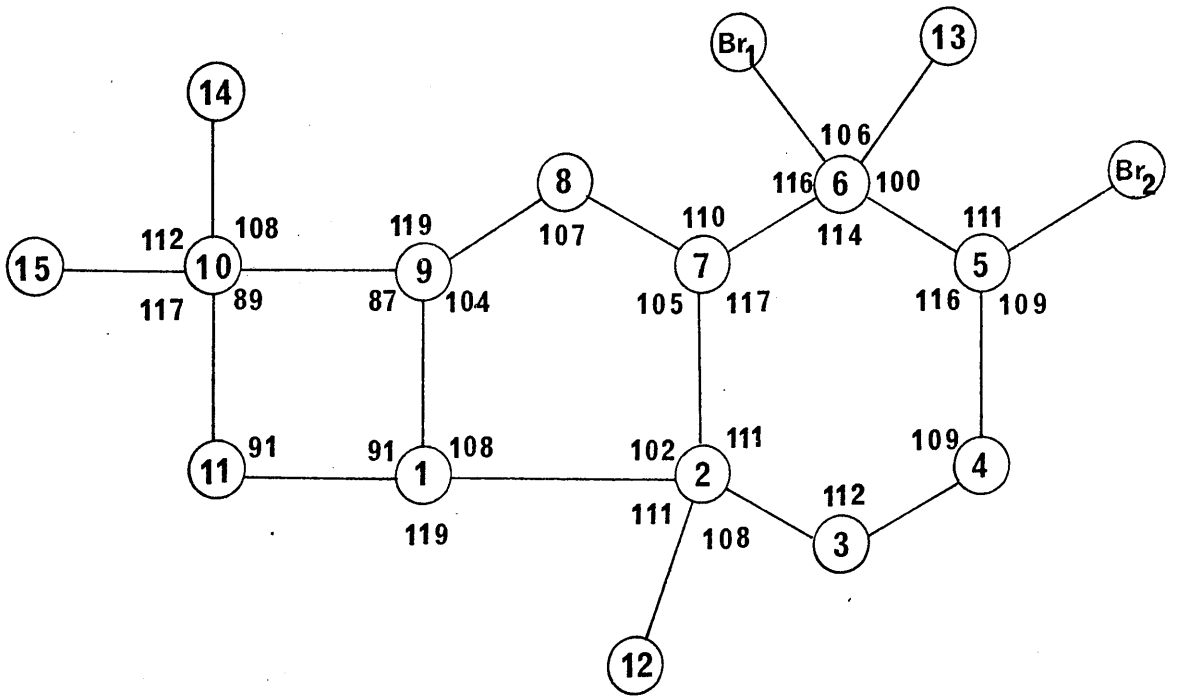
Figure 2.5

Bond angles (degrees).



The average e.s.d. for the C - C bond length is 0.03 Å.

The average e.s.d. for the C - Br bond length is 0.02 Å.

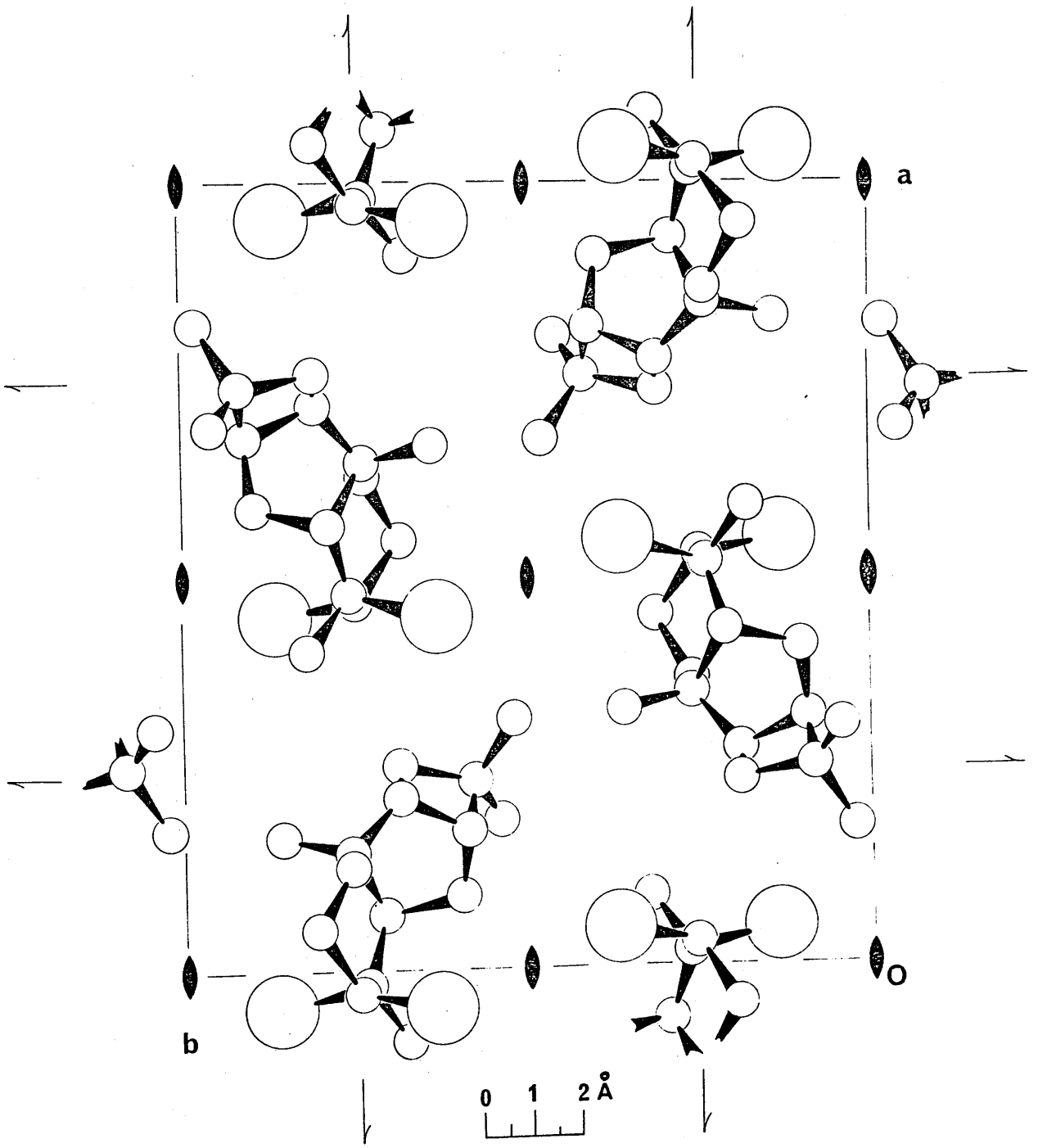


The average e.s.d. for C-C-C bond angle is 1.4°.

The average e.s.d. for C-C-Br bond angle is 1.2°.

Figure 2.6

A molecular-packing diagram viewed along the c axis.

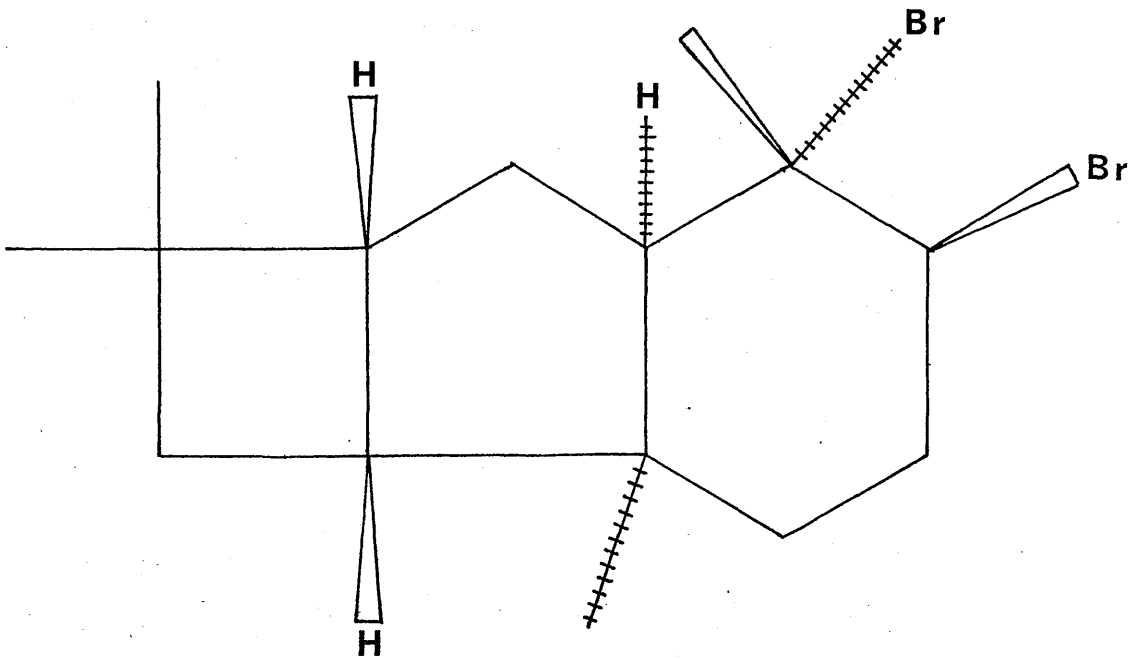

a
b
O
0 1 2 Å

2.3 DISCUSSION.

The results of this analysis establish that the dibromo derivative of 2,6,10,10-tetramethyltricyclo - $\left[2,7,0,0^{2,7}\right]$ undec-5-ene has the structure and absolute stereochemistry shown in (XII) and Figure 2.2. The molecule is tricyclic with one cyclobutane ring, one cyclopentane ring and one cyclohexane ring. Both the cyclobutane and cyclohexane rings are cis-fused to the cyclopentane ring but project from opposite sides of the central ring in a cis-anti-cis conformation. The structure and absolute stereochemistry of 2,6,10,10-tetramethyltricyclo $\left[7,2,0,C^{2,7}\right]$ - undec-5-ene itself must therefore be as shown in (VII).

The average carbon - carbon bond length is 1.55 ± 0.03 Å which is good agreement with the usual value of 1.537 Å (Sutton, 1958). The carbon - bromine bond lengths are 2.01 ± 0.02 Å and 2.00 ± 0.02 Å, which are just significantly greater than the expected value of 1.94 Å for bromoalkanes (Sutton, 1958). The discrepancy may be due to the uncertainty in the positions of the carbon atoms, C(5) and C(6), caused by the diffraction effects emanating from the adjacent bromine atoms.

The cyclobutane ring is non-planar with each atom lying alternately above and below the mean plane through the four ring atoms by 0.09 Å. The dihedral angle between the planes containing atoms C(9), C(10), and C(11), and C(11), C(1), and C(9) is 162° which confirms a measurable deviation from planarity. The conformation of the highly strained cyclobutane



XII

ring in organic compounds is of considerable interest. Greenberg and Post (1968) have surveyed a number of crystallographic studies of compounds containing cyclobutane rings and it appears that the ring is buckled in some cases (e.g., caryophyllene iodonitrosite, Hawley et al., 1968; cis-cyclobutane-1,3-dicarboxylic acid, Adman and Margulis, 1967) and planar in others (e.g., tetra-phenyl-cyclobutane, Dunitz, 1949, Margulis, 1965); there seems to be no clear-cut conditions favouring one conformation over the other. The average internal angle in the ring is 89.3°, which is in close agreement with those observed in caryophyllene iodonitrosite, 87.4° (Hawley et al., 1968), octachloro-cyclobutane, 88° (Owen et al., 1951) and anemonin, 88.3° (Karle et al., 1966).

The cyclopentane ring adopts a flattened envelope conformation with C(2) displaced only 0.55 Å from the plane containing C(7), C(8), C(9), and C(1). Because of the strain caused by the cis-fusion of the cyclobutane and cyclohexane rings, the five-membered ring is tending towards a planar arrangement. The average internal bond angle in the cyclopentane ring is $105.2^{\circ} \pm 1.4^{\circ}$ which is very close to the mean angle of 105° usually associated with cyclopentane rings (Sim, 1965). The C(1) - C(2) - C(7) angle is 101.5° which is distinctly less than the other valence angles in this ring but similar to the C(8) - C(9) - C(10) angle in the dibromo derivative of 1,5,9,9-tetramethyltricyclo $\left[6,2,1,0^{4,11}\right]$undec-5-ene.

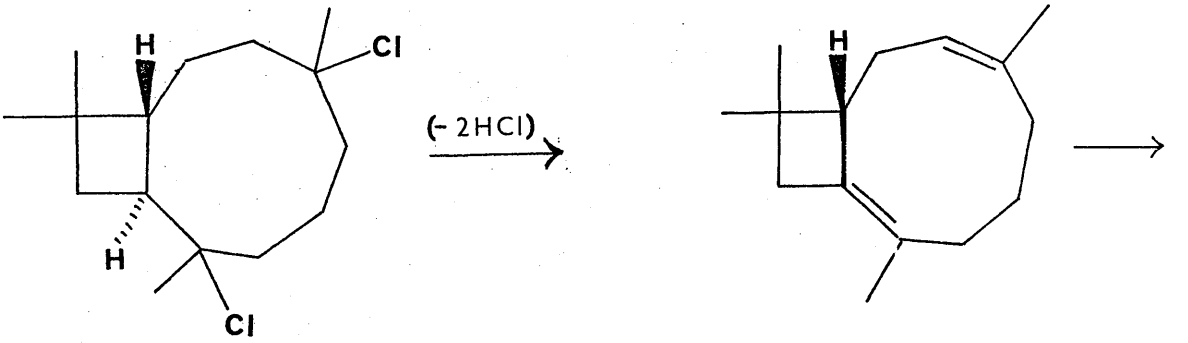
The cyclohexane ring adopts a distorted chair

conformation with C(6) and C(3) displaced above and below the plane containing the atoms C(2), C(4), C(5), and C(7) by 0.45 Å and 0.70 Å respectively. This is very similar to the situation found in the cyclohexane ring in the dibromo derivative of 1,5,9,9-tetramethyltricyclo $\left[6,2,1,0^{4,11}\right]$ undec-5-ene; the reasons for the distortion are also similar. The C(6) displacement is significantly smaller than the normal value of 0.73 Å (Brown, Martin, and Sim, 1965) found in a cyclohexane ring of ideal chair geometry and a necessary consequence of the ring flattening is the increase in the valency angles C(4) - C(5) - C(6), C(5) - C(6) - C(7), and C(2) - C(7) - C(6) from the tetrahedral value.

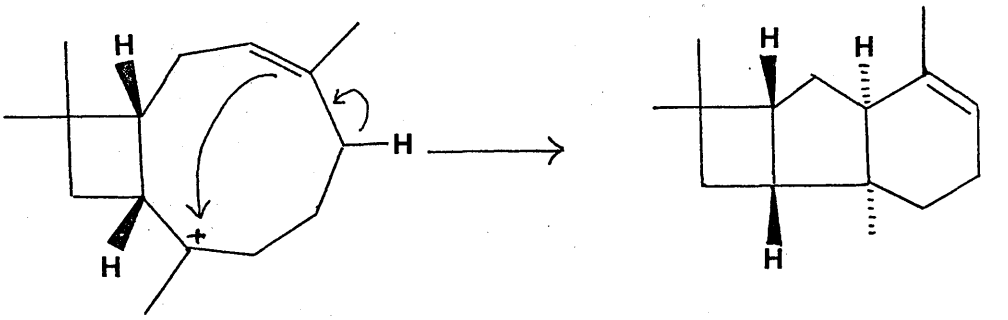
The two bromine atoms are in axial positions which in the general case of 1,2-dibromo-cyclohexane is the less sterically favoured conformation. If, however, in the dibromo derivative of 2,6,0,0-tetramethyltricyclo $\left[2,7,0,0^{2,7}\right]$-undec-5-ene the two bromine atoms are in equatorial positions then, as a result of the cis-fusion of the five-membered ring, the cyclohexane ring would tend to adopt a boat conformation. This would set up an impossible 'bow-sprit - flagpole' interaction between the C(13) methyl group and the C(3) hydrogen atom. The methyl group, C(13), therefore flips through to an equatorial position and thereby removes the interaction between it and the C(3) hydrogen atom.

There are no unusually short intermolecular contacts and the molecules are thus held in the crystal by van der Waals' forces.

Drs. J.S.Roberts and K.Gollnick have considered the possible mechanism of formation and have proposed the scheme shown below:-



VIII



VII

In caryophyllene (I) the cyclobutane ring is trans-fused to the nine-membered ring, whereas in 2,6,10,10 - tetramethyltricyclo $\left[2,7,0,0^{2,7}\right]$undec-5-ene (VII) the cyclobutane ring is cis-fused to the rest of the molecule. The above mechanism assumes that this inversion takes place during the elimination of hydrogen chloride but since the structure of caryophyllene dihydrochloride has never been examined closely, it is impossible to say whether this is correct or not.

PART III

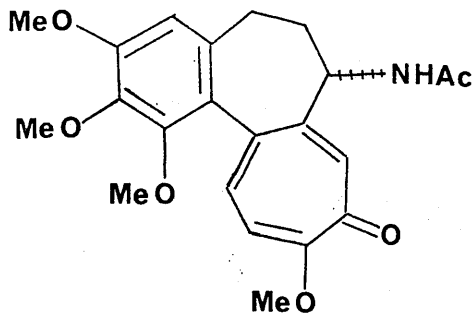
CRYSTAL STRUCTURE ANALYSES OF THREE NATURAL PRODUCTS.

THE STRUCTURE AND ABSOLUTE STEREOCHEMISTRY OF A HOMOMORPHINALE ALKALOID: X-RAY ANALYSIS OF THE METHIODIDE DERIVATIVE.

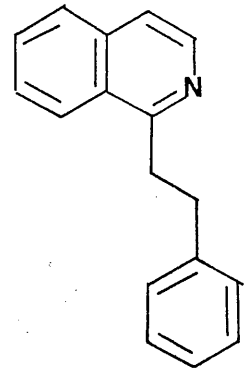
1.1 INTRODUTION.

Professor Battersby and his coworkers have been investigating the structures of the rare alkaloids of Colchicum cornigerum. The main alkaloids had earlier been shown to be tropolones and seven had been isolated including colchicene (I) (Saleh et al., 1963; Potesilova et al., 1969). Eight more alkaloids have now been examined and all belong to the new class of substances derived from 1-phenethyl-isoquinoline (II). One of the alkaloids, autumnaline (III), is the first unmodified 1-phenethylisoquinoline to be found in nature. The remaining seven alkaloids and colchicene could in principle be derived biosynthetically from the (+)- and (-)- forms of autumnaline (III) by two alternative modes of phenol coupling.

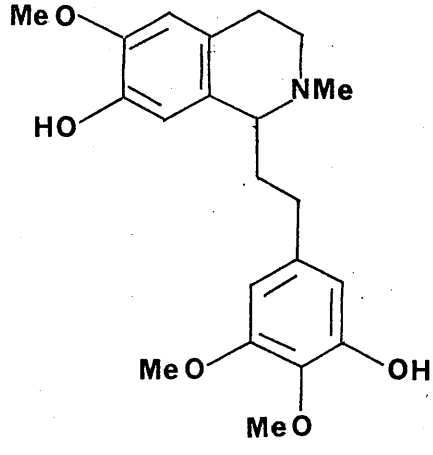
During their investigation, which relied heavily on physical methods with biogenetic argument where necessary because only small quantities of material were available, they were unable to distinguish between two possible structures (IV and V) for one of the alkaloids known as CC-2. The O - acetyl derivative of CC-2 afforded a methiodide suitable for X-ray analysis. This was prepared by Dr. R.Ramage by adding an excess of methyl iodide to a solution of the acetate in ethyl acetate at 20° and the precipitated methiodide was crystallised from ethanol, m.p. 285 - 286°.


MeO
MeO
MeO
NHAc
O
MeO

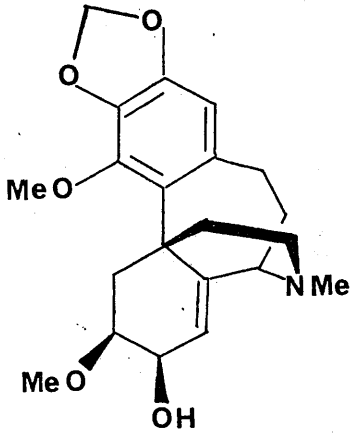
I


N

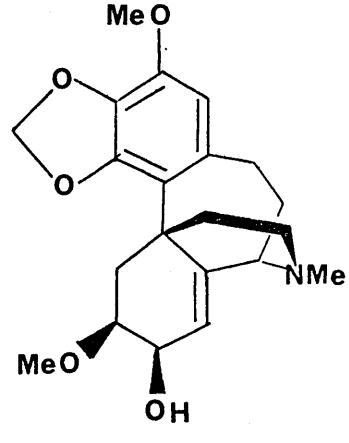
II


MeO
HO
NMe
MeO
OH
MeO

III


O
O
MeO
NMe
MeO
OH

IV


MeO
O
O
NMe
MeO
OH

V

1.2 EXPERIMENTAL.

Crystal Data.

The methiodide derivative of a homomorphinane alkaloid

$C_{24}H_{32}O_6NI$, M = 557.5.

Orthorhombic,

a = 7.75 ± 0.02, b = 14.57 ± 0.02, c = 21.55 ± 0.03 Å.

U = 2433.3 Å^3, D_m = 1.51 (by flotation), Z = 4, D_c = 1.52.

F(000) = 1136. Space group $P2_12_12_1$ (D_2^4, No. 19).

Linear absorption coefficient for X-rays (λ = 1.5418 Å), μ = 108.6 cm^{-1}.

Crystallographic Measurements.

The cell dimensions were measured from oscillation and equatorial-layer Weissenberg photographs taken with Cu-K_α radiation. The space group was determined from the systematic absences (h00, 0k0, and 00ℓ absent when h, k, and ℓ are odd). The three-dimensional intensity data consisting of reciprocal lattice nets 0kℓ - 6kℓ were obtained from an equi-inclination Weissenberg camera using the multiple-film technique (Robertson, 1943) and using Cu-K_α radiation. The 1739 reflexions were measured visually by comparison with a calibrated step-wedge. The data were collected using one needle-shaped crystal mounted along a and the structure amplitudes derived by correcting the intensities for Lorentz,

polarisation and rotation factors. In the early stages of the structure analysis the structure factors were put on an approximately absolute scale by correlation with the calculated structure factors such that $k \Sigma |F_o| = \Sigma |F_c|$ for each layer. Unobserved reflexions were not included in any of the calculations and no absorption corrections were applied.

Structure Determination.

Initial coordinates for the iodine ion were deduced from the three-dimensional Patterson synthesis. The Harker sections at $u = \frac{1}{2}$, $v = \frac{1}{2}$, and $w = \frac{1}{2}$ are shown in Figures 1.1 and 1.2. Structure factors based on the iodine ion position were calculated and the value of R, the average discrepancy between the measured and calculated structure amplitudes, was 0.45. The three-dimensional electron-density distribution derived from Sim-weighted Fourier coefficients was drawn as contoured sections ($1 in. = 1$ Å) on glass sheets and stacked in a frame. From this the coordinates of 17 carbon atoms, 2 oxygen atoms, 1 nitrogen atom and the iodine ion were revealed and when structure factors were calculated using all these atom positions, R fell to 0.34. Three further rounds of structure factor and Fourier calculations revealed all the non-hydrogen atoms and reduced R to 0.22. In all these calculations an overall isotropic temperature factor, $U_{iso} = 0.06$ Å^2, was used.

Structure Refinement.

Refinement was carried out using eight cycles of least-squares calculations minimising the expression,

$$M = \sum w(|F_o| - |F_c|)^2.$$

The progress of the refinement is outlined in Table 1.1. The weighting scheme adopted was of the form,

$$\sqrt{w} = \left\{[1 - \exp(-p_1(\sin\theta/\lambda)^2]/[1 + p_2|F_o| + p_3|F_o|^2]\right\}^{\frac{1}{2}},$$

and the final values of p_1, p_2, and p_3 were 100, 0.001, and 0.0005 respectively.

In the first four cycles positional and isotropic thermal parameters for all non-hydrogen atoms as well as layer scale factors were refined. Before carrying out anisotropic refinement of the iodine ion, the data were placed on a common scale by use of the layer scale factors obtained at the end of the isotropic refinement. In the last refinement cycle no shifts were larger than one-fifth of the estimated standard deviation and the R-factor was 0.134. The agreement between the observed and calculated structure amplitudes at the conclusion of the refinement are shown in Table 1.2. The phase angles are also included. The atomic scattering factors used in the structure factor calculations were taken from "International Tables for X-ray Crystallography", Vol. III.

The final fractional coordinates and thermal parameters with e.s.d.s for all non-hydrogen atoms are listed in Table 1.3. The anisotropic temperature factors are values of U_{ij} in the expression,

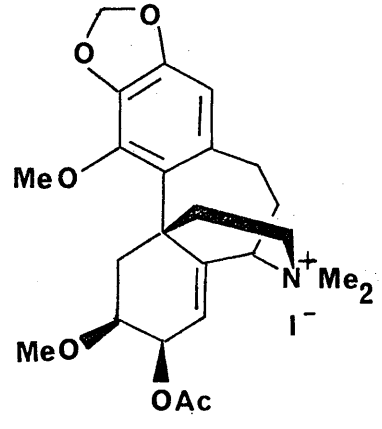
$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)].$$

The final electron density map for the molecule is shown in Figure 1.3 as superimposed contour sections drawn parallel to (100) and the atomic arrangement corresponding to the electron-density distribution is shown in Figure 1.4. The atom numbering scheme is also shown in this Figure. Figures 1.5 and 1.6 give details of the intramolecular bonded distances and valence angles. Average e.s.d.s in bond lengths and angles are in Table 1.4. Some intermolecular contacts <4.0 Å are in Table 1.5, and Table 1.6 contains the displacement of atoms from various planes in the molecule and also the equations of these planes . The packing arrangement of the molecules in the crystal projected down the a-axis is illustrated in Figure 1.7.

Absolute Configuration.

The absolute configuration of the methiodide derivative of the homomorphinane alkaloid, CC-2, was determined by means of Bijvoet's method (1949). Because of the anomalous dispersion of the Cu-K_α radiation by the iodine ion, Friedel's Law breaks down and differences in intensity are expected between reflexions $hk\ell$ and $hk\bar{\ell}$. The reflexions were indexed in a right-handed system (Peerdeman and Bijvoet, 1956) and the intensities of 45 Bijvoet pairs were measured visually. Structure factors were calculated with the inclusion of the

anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$. All 45 Bijvoet pairs showed differences in the same direction as the observed structure factors which indicated that the molecule chosen was the one with the correct absolute configuration (see Figure 1.4). Table 1.7 shows the results of this calculation. Values of $\Delta f'$ and $\Delta f''$ for iodine were taken from "International Tables for X-ray Crystallography", Vol. III.



VI

Table 1.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-4}$	Final R′
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, full-matrix.	1-4	0.186	-	0.048
x,y,z,Uij(i,j=1,2,3) for I atom; x,y,z,Uiso for all other non-hydrogen atoms; one scale factor, block-diagonal.	5-8	0.134	2.95	0.029.

Table 1.2

Observed and calculated structure amplitudes with phase angles.

H	K	L	FO	FC	AL	H	K	L	FO	FC	AL
0	0	6	75.3	92.2	0	0	3	14	16.3	15.4	270
0	0	8	91.8	87.1	180	0	3	15	44.4	39.4	270
0	0	10	141.7	154.6	0	0	3	16	16.3	18.2	90
0	0	12	43.0	47.4	180	0	3	17	13.4	9.1	90
0	0	14	52.0	67.5	180	0	3	19	11.7	7.5	90
0	0	16	27.2	25.5	0	0	3	21	13.5	8.4	270
0	0	18	35.2	29.7	180	0	3	22	13.0	10.1	90
0	0	20	13.9	10.6	0	0	3	23	18.6	15.3	90
0	0	22	11.7	8.4	0	0	4	0	154.0	192.4	0
0	0	24	13.3	13.6	180	0	4	1	45.4	52.1	180
0	1	4	[illegible]	[illegible]	90	0	4	2	97.9	124.3	180
0	1	6	9.6	6.3	90	0	4	3	94.5	125.4	0
0	1	7	57.2	66.6	270	0	4	4	4.3	3.0	180
0	1	8	18.0	29.5	270	0	4	5	38.7	41.2	360
0	1	9	4.6	5.6	270	0	4	6	20.6	14.2	180
0	1	10	22.3	29.1	270	0	4	7	5.6	2.1	150
0	1	11	51.3	56.9	90	0	4	8	135.4	141.2	180
0	1	12	17.5	19.8	270	0	4	9	31.3	27.0	0
0	1	13	75.7	74.7	270	0	4	10	104.7	133.5	0
0	1	15	46.5	44.6	90	0	4	11	5.7	1.2	360
0	1	17	22.3	24.9	270	0	4	12	15.4	12.3	180
0	1	19	29.5	23.4	270	0	4	13	28.0	31.7	0
0	1	21	13.7	9.6	90	0	4	14	37.4	30.0	180
0	1	23	22.3	25.7	270	0	4	15	14.5	14.2	180
0	2	0	57.3	64.6	180	0	4	16	46.7	47.6	0
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

H	K	L	FO	FC	AL
3	2	4	[illegible]	[illegible]	227
3	2	5	37.7	[illegible]	159
3	2	7	24.7	27.2	74
3	2	8	[illegible]	47.6	252
3	2	9	[illegible]	59.0	[illegible]
3	2	10	11.6	13.8	341
3	2	11	[illegible]	53.7	177
3	2	12	[illegible]	50.9	175
3	2	14	[illegible]	24.9	331
3	2	15	[illegible]	37.4	297
3	2	16	[illegible]	37.4	[illegible]
3	3	[illegible]	[illegible]	64.5	[illegible]
3	3	[illegible]	[illegible]	93.7	[illegible]
3	3	[illegible]	[illegible]	54.7	[illegible]
3	3	[illegible]	[illegible]	54.1	[illegible]
3	3	[illegible]	[illegible]	[illegible]	[illegible]
3	3	[illegible]	[illegible]	[illegible]	262
3	3	[illegible]	[illegible]	[illegible]	259
[illegible]	3	[illegible]	[illegible]	[illegible]	[illegible]
3	3	[illegible]	[illegible]	55.7	125
3	3	10	[illegible]	[illegible]	[illegible]
3	3	11	[illegible]	39.2	243
3	3	12	[illegible]	26.4	172
3	3	13	[illegible]	23.0	[illegible]
3	3	14	[illegible]	33.2	[illegible]

[illegible]

Table 1.3

Fractional coordinates and thermal parameters ($Å^2$) with estimated standard deviations.

	x/a	y/b	z/c	Uiso
I(1)	0.20782±28	0.25804±11	0.19354±10	*
O(1)	0.6990 ±32	-0.1634 ±14	0.5289 ±09	0.075±5
O(2)	0.4272 ±26	-0.1602 ±13	0.4841 ±08	0.061±5
O(3)	0.3300 ±23	-0.0374 ±11	0.3869 ±07	0.051±4
O(4)	0.6206 ±30	0.2157 ±14	0.4507 ±09	0.070±5
O(5)	0.6943 ±32	0.3736 ±13	0.3880 ±09	0.074±5
O(6)	0.4571 ±31	0.4543 ±14	0.4018 ±09	0.075±6
N(1)	0.7768 ±31	0.0650 ±13	0.2241 ±09	0.051±5
C(1)	0.5332 ±38	-0.0982 ±17	0.4559 ±12	0.050±6
C(2)	0.7020 ±42	-0.0978 ±17	0.4815 ±12	0.055±6
C(3)	0.8128 ±48	-0.0459 ±21	0.4629 ±14	0.072±8
C(4)	0.7815 ±41	0.0210 ±17	0.4140 ±12	0.057±7
C(5)	0.6229 ±37	0.0241 ±16	0.3873 ±11	0.046±6
C(6)	0.4987 ±34	-0.0365 ±16	0.4094 ±11	0.046±6
C(7)	0.2596 ±45	-0.1232 ±21	0.3600 ±14	0.070±8
C(8)	0.9388 ±42	0.0724 ±19	0.3892 ±13	0.063±7
C(9)	0.9694 ±41	0.0510 ±19	0.3205 ±12	0.058±7
C(10)	0.8558 ±36	0.1148 ±17	0.2792 ±12	0.049±6
C(11)	0.7158 ±34	0.1578 ±14	0.3171 ±10	0.040±5
C(12)	0.5663 ±36	0.0968 ±17	0.3398 ±12	0.050±6
C(13)	0.4233 ±33	0.1616 ±15	0.3663 ±10	0.042±6
C(14)	0.4847 ±40	0.2409 ±21	0.4026 ±13	0.065±7
C(15)	0.5916 ±36	0.3031 ±17	0.3579 ±11	0.050±6
C(16)	0.7145 ±40	0.2507 ±19	0.3246 ±12	0.067±7
C(17)	0.4923 ±35	0.0539 ±16	0.2815 ±11	0.046±6
C(18)	0.6371 ±37	0.0013 ±16	0.2451 ±11	0.048±6

Table 1.3 cont.

	x/a	y/b	z/c	Uiso
C(19)	0.7240 ±55	0.1363 ±25	0.1769 ±16	0.089±11
C(20)	0.9358 ±57	0.0073 ±27	0.1949 ±18	0.096±11
C(21)	0.6047 ±43	0.4471 ±20	0.4088 ±13	0.063±7
C(22)	0.7441 ±46	0.5147 ±20	0.4338 ±14	0.070±8
C(23)	0.5256 ±62	0.1765 ±31	0.5068 ±18	0.104±13
C(24)	0.5457 ±46	-0.2157 ±22	0.5202 ±15	0.073±8

* Anisotropic thermal parameters Uij ($Å^2$) with e.s.d.'s.

	U 11	U 22	U 33	2U 23	2U 31	2U 12
I(1)	0.0641 12	0.0475 7	0.0911 12	0.0260 19	-0.0112 22	-0.0194 19

Table 1.4

Average estimated standard deviations in bond lengths and angles.

C - N	.... ± 0.039 Å	C - C - C	.... ± 2.4°
C - O	.... ± 0.037	C - N - C	.... ± 2.2
C - C	.... ± 0.039	N - C - C	.... ± 2.0
		O - C - C	.... ± 2.5
		C - O - C	.... ± 2.3

Table 1.5

a) Some intramolecular non-bonded distances (Å).

O(1) ...O(2)	2.32	N(1) ...C(5)	3.76
O(2) ...O(3)	2.86	N(1) ...C(8)	3.78
O(2) ...C(7)	3.02	N(1) ...C(9)	2.57
O(3) ...C(1)	2.34	N(1) ...C(11)	2.46
O(3) ...C(5)	2.44	N(1) ...C(12)	3.02
O(3) ...C(12)	2.86	N(1) ...C(16)	3.50
O(3) ...C(13)	3.02	N(1) ...C(17)	2.53
O(3) ...C(17)	2.92	C(1) ...C(7)	2.98
O(3) ...C(18)	3.91	C(2) ...C(8)	3.67
O(4) ...O(5)	2.73	C(3) ...C(8)	2.54
O(4) ...O(6)	3.85	C(3) ...C(9)	3.59
O(4) ...C(4)	3.20	C(4) ...C(10)	3.26
O(4) ...C(5)	3.11	C(4) ...C(11)	2.93
O(4) ...C(6)	3.90	C(4) ...C(13)	3.60
O(4) ...C(8)	3.49	C(4) ...C(14)	3.95
O(4) ...C(11)	3.09	C(4) ...C(16)	3.90
O(4) ...C(12)	2.98	C(4) ...C(17)	3.66
O(4) ...C(16)	2.86	C(4) ...C(18)	3.82
O(5) ...O(6)	2.20	C(4) ...C(23)	3.62
O(5) ...C(11)	3.50	C(5) ...C(7)	3.59
O(5) ...C(13)	3.76	C(5) ...C(13)	2.57
O(5) ...C(23)	3.50	C(5) ...C(14)	3.35
O(6) ...C(14)	3.12	C(5) ...C(16)	3.64
O(6) ...C(15)	2.61	C(5) ...C(17)	2.53
O(6) ...C(16)	3.94	C(5) ...C(18)	3.09
O(6) ...C(22)	2.49		

Table 1.5 cont.

a) cont.

C(5) ...C(23)	3.48	C(11)...C(20)	3.83
C(6) ...C(7)	2.48	C(12)...C(15)	3.04
C(6) ...C(8)	3.79	C(12)...C(18)	2.53
C(6) ...C(11)	3.85	C(12)...C(19)	3.76
C(6) ...C(13)	3.09	C(12)...C(23)	3.80
C(6) ...C(17)	3.05	C(13)...C(17)	2.47
C(6) ...C(18)	3.74	C(13)...C(18)	3.88
C(6) ...C(23)	3.75	C(13)...C(23)	3.14
C(7) ...C(17)	3.57	C(14)...C(17)	3.77
C(8) ...C(16)	3.42	C(14)...C(21)	3.15
C(9) ...C(16)	3.52	C(14)...C(23)	2.45
C(9) ...C(17)	3.79	C(15)...C(22)	3.68
C(9) ...C(18)	3.13	C(15)...C(23)	3.74
C(9) ...C(19)	3.84	C(16)...C(17)	3.47
C(9) ...C(20)	2.79	C(16)...C(19)	3.59
C(10)...C(17)	2.95	C(16)...C(21)	3.49
C(10)...C(18)	2.48	C(17)...C(19)	3.12
C(10)...C(19)	2.45	C(17)...C(20)	3.97
C(10)...C(20)	2.48	C(18)...C(19)	2.55
C(11)...C(17)	2.42	C(18)...C(20)	2.56
C(11)...C(18)	2.82	C(19)...C(20)	2.53
C(11)...C(19)	3.04		

Table 1.5 cont.

b) Some Intermolecular Contacts < 4.0 Å.

I(1) ....C(10)^{I}	3.90	O(6) ....C(20)^{II}	3.77
I(1) ....C(18)^{II}	3.97	O(6) ....C(2)^{VI}	3.82
O(1) ....O(2)^{III}	3.13	C(1) ....C(2)^{VI}	3.49
O(1) ....C(19)^{IV}	3.27	C(2) ....C(24)^{III}	3.81
O(1) ....C(24)^{III}	3.38	C(3) ....C(21)^{V}	3.85
O(1) ....O(6)^{V}	3.94	C(3) ....C(24)^{III}	3.93
O(1) ....C(7)^{III}	3.95	C(6) ....C(22)^{VI}	3.93
O(2) ....C(22)^{VI}	3.11	C(7) ....C(8)^{I}	3.83
O(2) ....C(24)^{VII}	3.47	C(7) ....C(9)^{I}	3.50
O(3) ....C(9)^{I}	3.39	C(7) ....C(19)^{VIII}	3.60
O(3) ....C(8)^{I}	3.43	C(7) ....C(24)^{VII}	3.86
O(3) ....C(22)^{VI}	3.94	C(9) ....C(13)^{IX}	3.99
O(4) ....C(23)^{V}	3.63	C(14)....C(21)^{VIII}	3.89
O(5) ....C(23)^{V}	3.50	C(19)....C(24)^{X}	3.99
O(6) ....C(18)^{II}	3.32	C(20)....C(22)^{XI}	3.72
O(6) ....C(3)^{VI}	3.40	C(22)....C(23)^{V}	3.76
O(6) ....C(19)^{II}	3.45	C(22)....C(24)^{V}	3.88
O(6) ....N(1)^{II}	3.64		

The subscripts refer to the following equivalent positions:

I	x - 1,	y,	z;
II	1 - x,	1/2 + y,	1/2 - z;
III	1/2 + x,	-1/2 - y,	1 - z;
IV	3/2 - x,	-y,	1/2 + z;
V	1/2 + x,	1/2 - y,	1 - z;

Table 1.5 cont.

b) cont.

VI	-1/2 + x,	1/2 - y,	1 - z;
VII	-1/2 + x,	-1/2 - y,	1 - z;
VIII	1 - x,	-1/2 + y,	1/2 - z;
IX	1 + x,	y,	z;
X	3/2 - x,	-y,	-1/2 + z;
XI	2 - x,	-1/2 + y,	1/2 - z;

Table 1.5 cont.

b) cont.

VI	-1/2 + x,	1/2 - y,	1 - z;
VII	-1/2 + x,	-1/2 - y,	1 - z;
VIII	1 - x,	-1/2 + y,	1/2 - z;
IX	1 + x,	y,	z;
X	3/2 - x,	-y,	-1/2 + z;
XI	2 - x,	-1/2 + y,	1/2 - z;

Table 1.6

Distances (Å) of atoms from various planes in the molecule.

Atoms included in calculation of planes.

Plane 1	Plane 2	Plane 3
C(1) 0.002	C(1) 0.001	C(4) ....-0.079
C(2) ....-0.002	C(2) ....-0.004	C(5) 0.058
O(1) 0.001	C(3) 0.006	C(12)....-0.005
O(2) ....-0.001	C(4) ....-0.005	C(11)....-0.020
	C(5) 0.003	C(8) 0.046
	C(6) ....-0.001	

Atoms not included in calculation of planes.

C(24)....-0.320	C(8) 0.204	C(9) 1.362
	C(12)....-0.141	C(10).... 1.201
	O(1) ....-0.060	
	O(2) ....-0.039	
	O(3) ....-0.037	
	C(7) 1.043	

Plane Equations.

Plane 1: $-0.283X + 0.702Y + 0.654Z = -4.247$ Å

Plane 2: $0.287X - 0.675Y - 0.680Z = 4.530$

Plane 3: $0.199X - 0.670Y - 0.716Z = 5.307$

Table 1.6 cont.

Atoms included in calculation of planes.

Plane 4	Plane 5	Plane 6
C(8) ....-0.052	C(11)....-0.003	C(12)....-0.026
C(9) 0.089	C(12).... 0.054	C(10).... 0.025
C(10)....-0.090	C(13)....-0.055	C(17).... 0.026
C(11).... 0.053	C(15).... 0.059	N(1) ....-0.026
	C(16)....-0.055	

Atoms not included in calculation of planes.

	C(14).... 0.683	C(11).... 0.606
		C(18)....-0.702
		C(19).... 1.376
		C(20)....-0.908

Plane Equations.

Plane 4: $-0.609X - 0.793Y - 0.025Z = 5.428$ Å

Plane 5: $0.435X - 0.142Y + 0.889Z = -8.165$

Plane 6: $-0.287X + 0.891Y - 0.353Z = 2.561$

X, Y and Z are coordinates in Å referred to the orthogonal axes a, b and c.

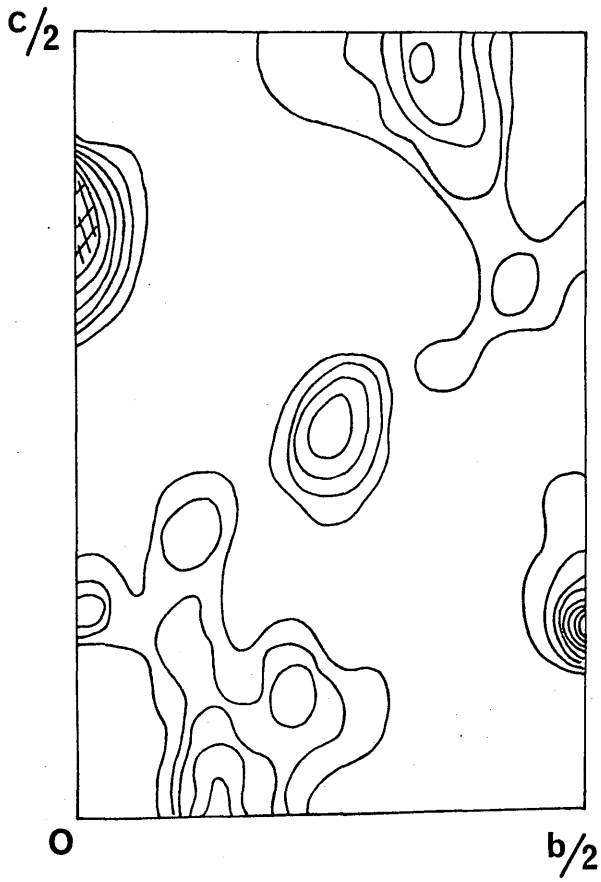
Table 1.7

Bijvoet pairs used in the anomalous-dispersion calculation.

h	k	l	$I_\ell/I_{\bar{\ell}}$	$F_\ell^2/F_{\bar{\ell}}^2$	h	k	l	$I_\ell/I_{\bar{\ell}}$	$F_\ell^2/F_{\bar{\ell}}^2$
1	1	12	2.00	2.28	3	9	1	0.56	0.69
1	1	10	1.33	1.03	3	10	1	0.89	0.86
1	1	16	0.80	0.66	3	11	1	0.63	0.76
1	2	13	1.50	1.26	3	9	2	0.88	0.91
1	1	14	1.60	1.43	3	10	2	0.65	0.79
1	10	1	0.17	0.19	3	12	2	0.67	0.83
1	7	2	2.17	2.51	3	7	2	0.83	0.77
1	6	1	0.64	0.64	4	1	17	1.50	1.07
1	4	1	1.29	1.50	4	1	16	0.63	0.86
1	5	2	1.40	1.25	4	5	1	0.56	0.42
1	8	2	0.80	0.90	4	10	1	0.55	0.47
1	7	3	0.67	0.67	4	12	1	2.50	2.37
2	1	9	1.83	1.42	4	10	2	1.44	1.40
2	1	12	1.63	1.63	5	1	7	0.16	0.21
2	1	15	1.40	1.28	5	1	14	1.50	1.62
2	1	11	1.50	1.66	5	1	12	1.60	1.03
2	2	13	0.67	0.62	5	1	4	1.80	1.20
2	4	1	1.82	1.49	5	7	1	2.40	2.38
2	6	1	0.69	0.74	5	9	2	1.54	1.35
2	7	1	1.78	1.62	5	5	1	0.67	0.85
2	9	1	0.83	0.68	6	8	1	0.33	0.46
2	3	1	1.82	2.36	6	5	3	0.33	0.34
3	1	17	1.33	1.47					

Figure 1.1

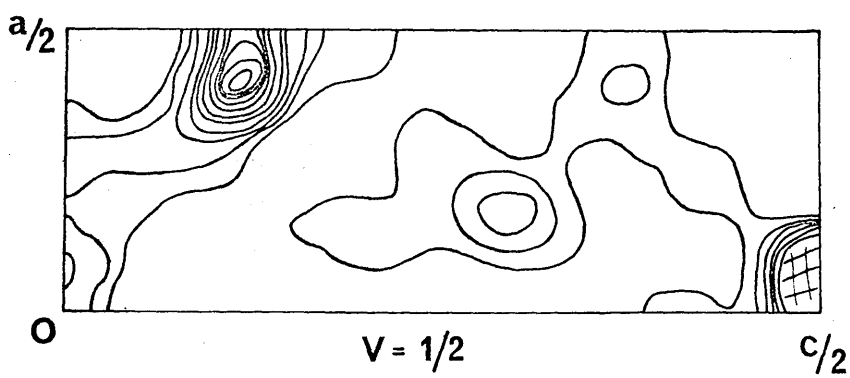
Harker section at u = 1/2 through the three-dimensional Patterson distribution. Contour levels are at equal arbitrary intervals.

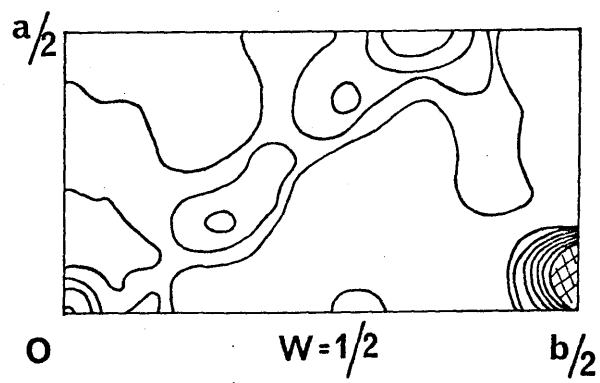


U = 1/2

Figure 1.2

Harker sections at v = 1/2 and w = 1/2 through the three-dimensional Patterson distribution. Contour levels are at equal arbitrary intervals.


a/2
O
V = 1/2
c/2


a/2
O
W=1/2
b/2

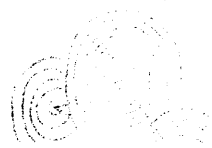
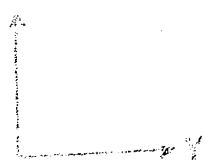


Figure 1.3

Superimposed sections parallel to the (100) plane of the three-dimensional electron-density distribution over one molecule. The contours start at 1e $Å^{-3}$ and are drawn at intervals of 1e $Å^{-3}$ except around the iodine atom, where the intervals are 10e $Å^{-3}$.



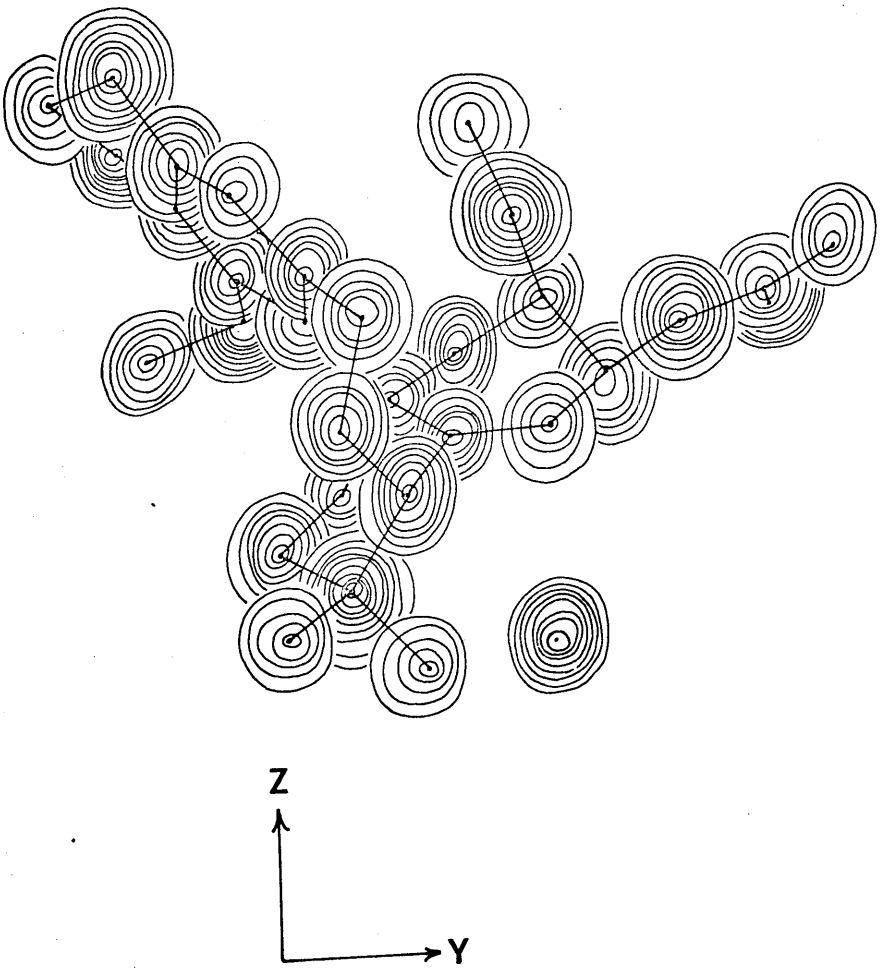

Z
Y

Figure 1.4

The arrangement of the atoms corresponding to the electron-density distribution in Figure 1.3 with an explanation of the numbering scheme adopted in the analysis.

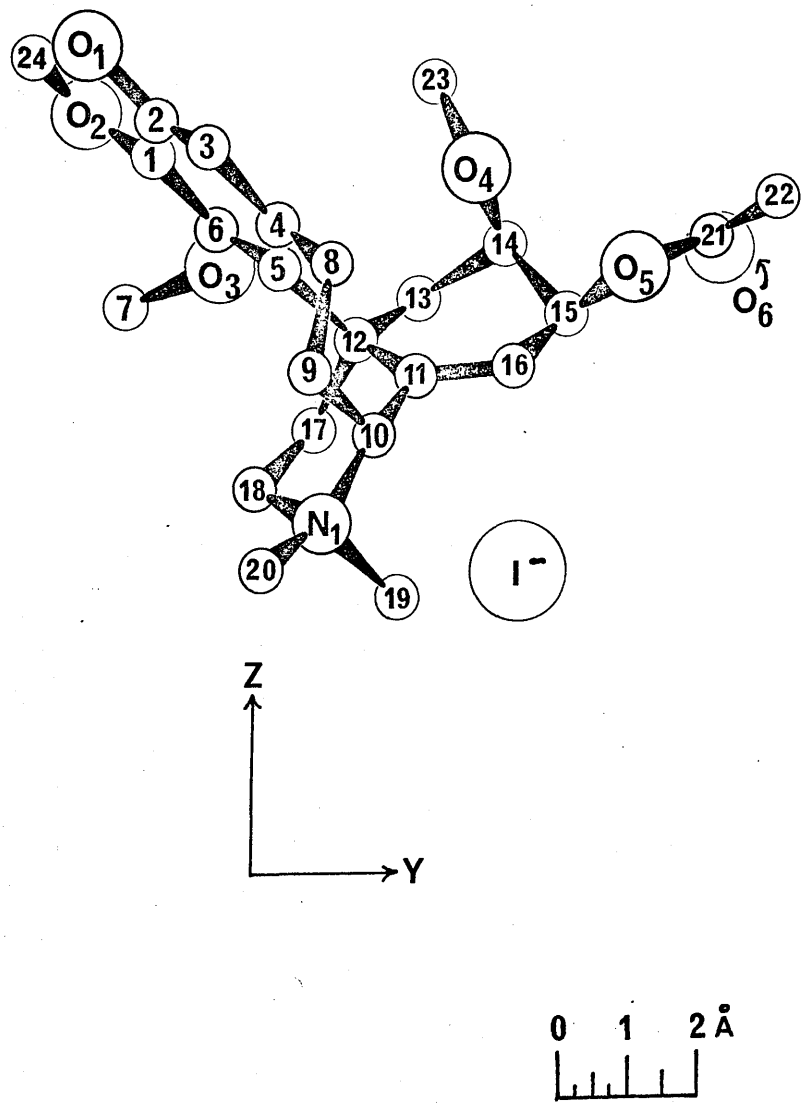

O1
O2
O3
O4
O5
O6
N1
I−
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
Z
Y
0 1 2 Å

Figure 1.5

Bond lengths (Å).

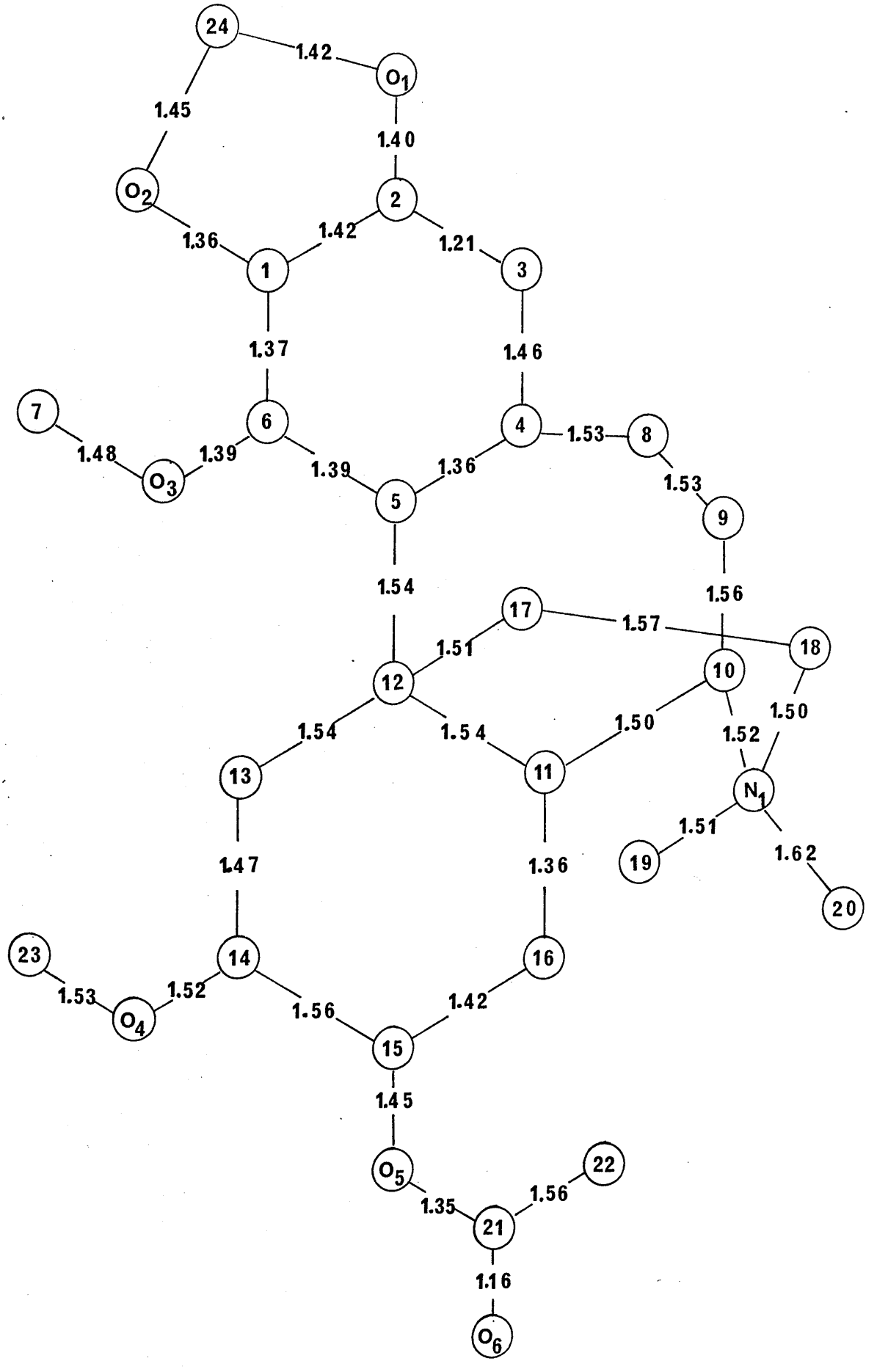

24
1.42
O1
1.45
1.40
O2
2
1.36
1.42
1.21
1
3
1.37
1.46
7
6
4
1.53
8
1.48
1.39
1.39
1.36
1.53
O3
5
9
1.54
1.56
17
1.57
18
1.51
10
12
1.50
1.50
1.54
1.54
1.52
13
11
N1
1.51
1.62
19
20
1.47
1.36
23
14
16
1.53
1.52
1.56
1.42
O4
15
1.45
O5
22
1.35
1.56
21
1.16
O6

Figure 1.6

Bond angles (degrees).

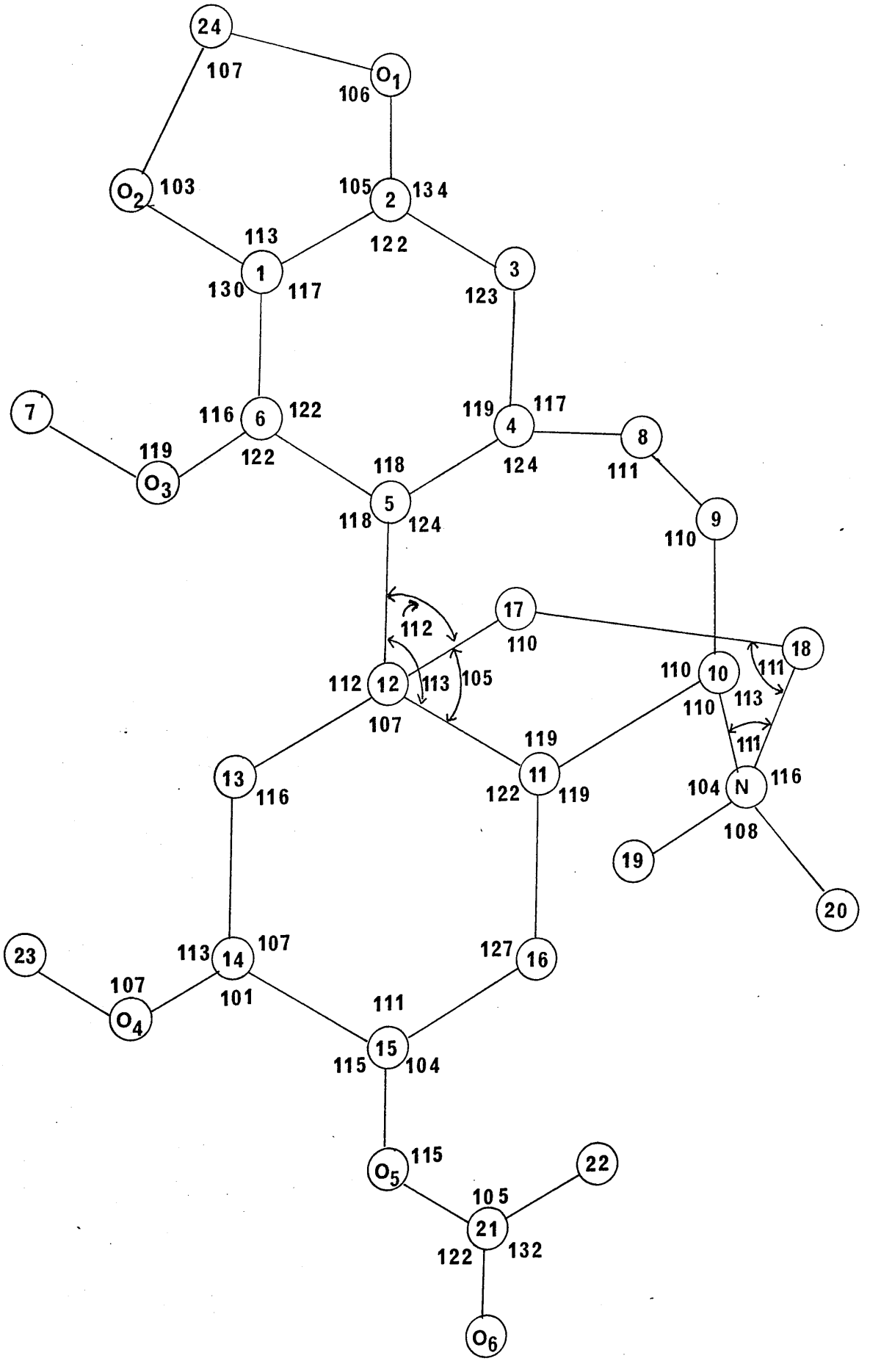

24
107
O1
106
O2
103
105
2
134
113
122
1
3
130
117
123
7
116
6
122
119
4
117
119
O3
122
118
8
111
5
118
124
9
110
17
112
110
18
112
12
113
105
110
10
111
107
110
113
119
111
13
11
104
N
116
116
122
119
108
19
20
23
113
14
107
127
16
107
O4
101
111
15
115
104
O5
115
22
105
21
122
132
O6

Figure 1.7

A molecular-packing diagram viewed along the a axis. The hydrogen-bonding is shown by broken lines.

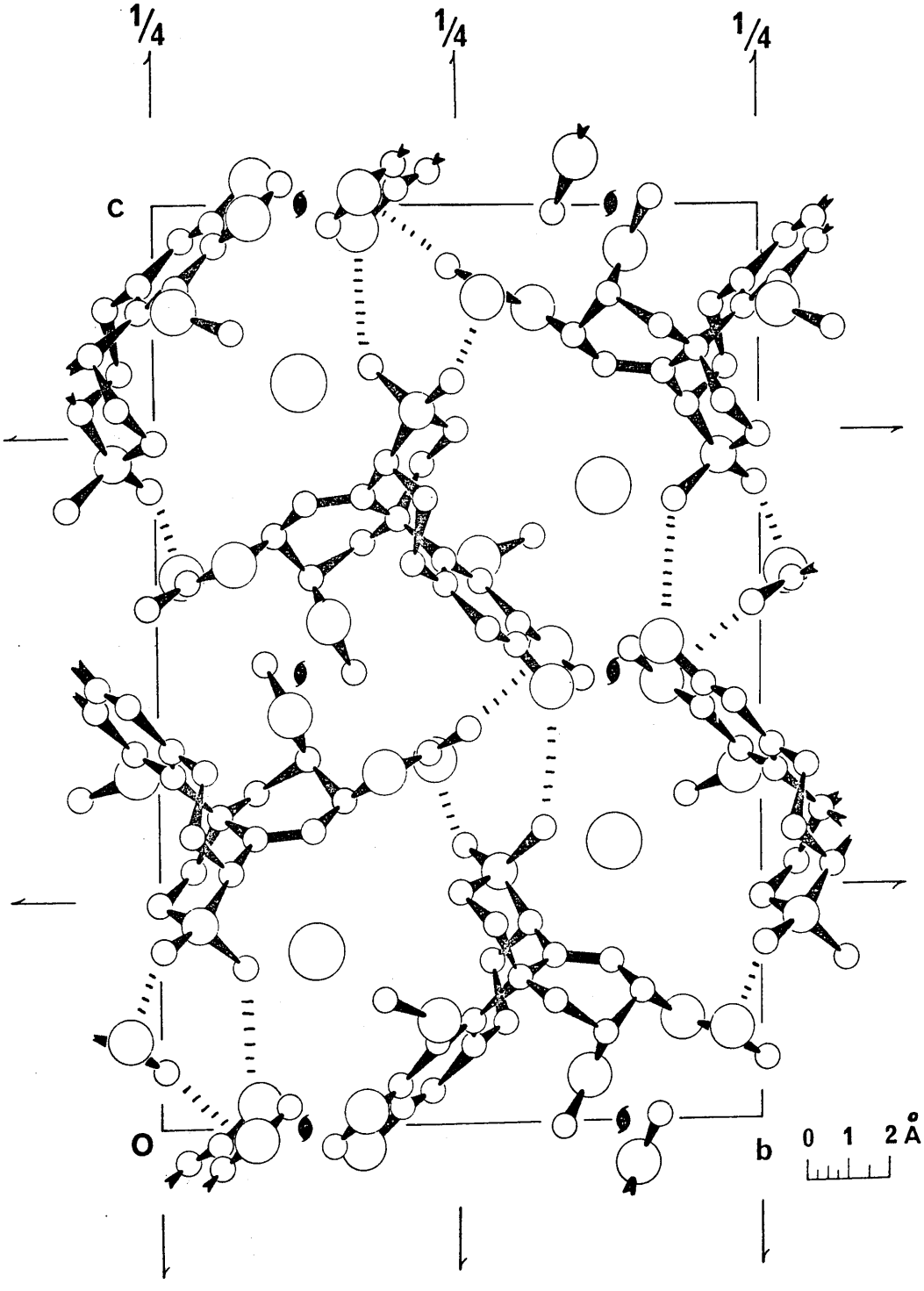
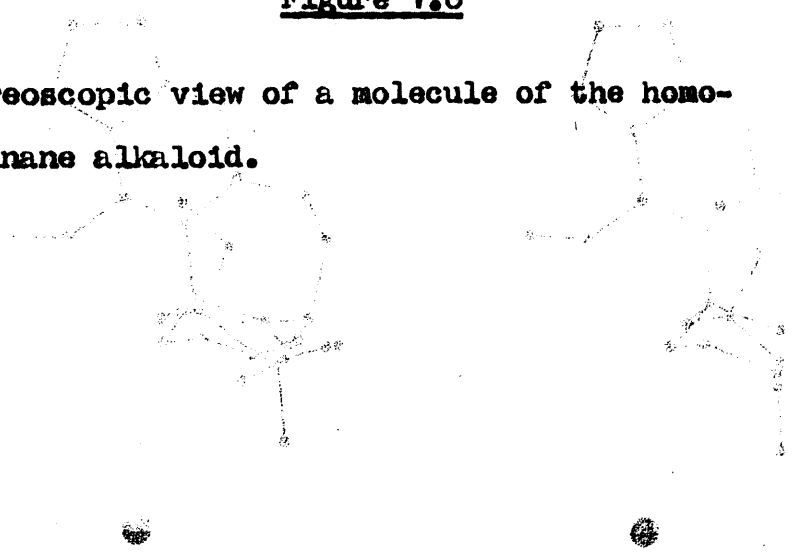
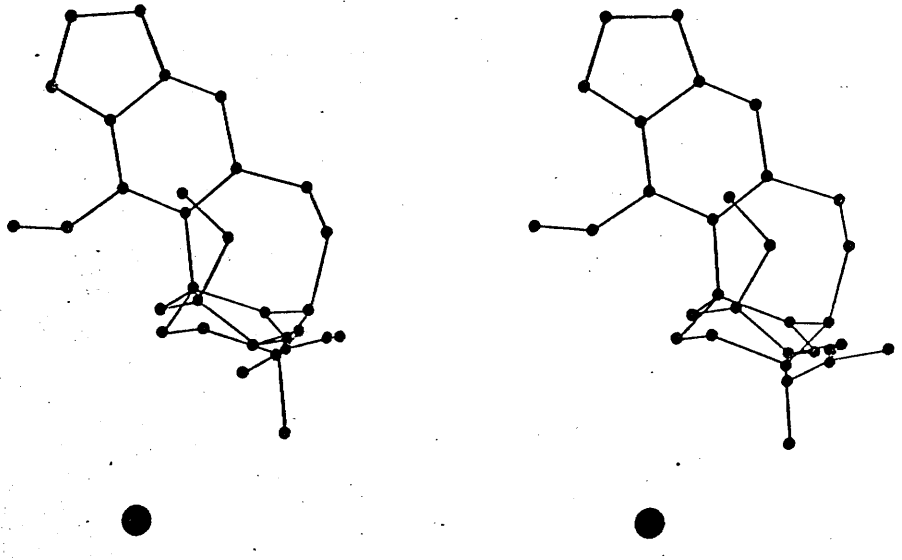

1/4
1/4
1/4
c
O
b
0 1 2 Å

Figure 1.8

A stereoscopic view of a molecule of the homomorphinane alkaloid.





1.3 DISCUSSION.

The X-ray analysis of the methiodide derivative of the homomorphinane alkaloid, CC-2, has establisned that (VI) is a true representation of its structure and absolute stereochemistry. It is inferred that the parent alkaloid, CC-2, has the structure and absolute atereochemistry shown in (IV).

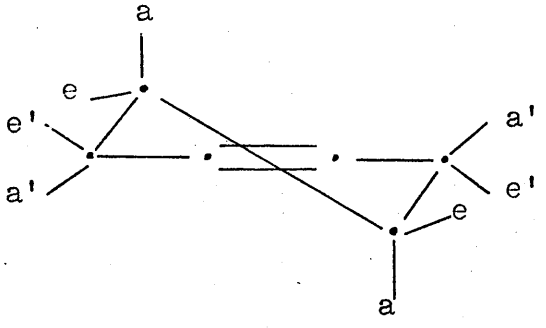
For the most part, the molecular dimensions correspond to literature values for similar bond types, and any slight discrepancies may possibly be attributed to the inaccuracies caused by the presence of the iodine ion and by the relatively poor quality of the diffraction data resulting from the decomposition of the crystals on prolonged exposure to the X-ray beam. For example, the N(1) - C(20) bond length of 1.62 Å is almost 0.1 Å greater than expected, and this may be a result of the poor resolution in the x-direction along which this bond lies.

The benzene ring is planar and the atoms O(1), O(2), O(3), and C(12) do not deviate significantly from this plane but C(8), however, lies 0.20 Å above this plane which is just significant. C(24) is twisted out of the plane containing atoms O(1), C(2), C(1), and O(2) by 0.32 Å which has the effect of reducing the angle strain within the methylene ether system.

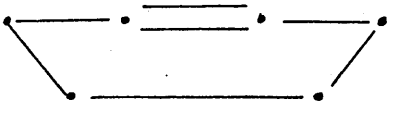
The cycloheptene ring adopts an "envelope-type" conformation. Atoms C(4), C(5), C(12), C(11), and C(8) all lie in one plane which is at an angle of 65° to the plane

containing atoms C(8), C(9), C(10), and C(11). This can be seen clearly in the stereoscopic diagram (Figure 1.8). The torsion angle C(11),C(10) - C(9),C(8) is 16° which is significantly greater than the value of 0° expected if the atoms C(8), C(9), C(10), and C(11) were perfectly planar. As a result the substituents around atoms C(9) and C(10) are not quite fully eclipsed.

The cyclohexene ring system, C(11), C(12), C(13), C(14), C(15), and C(16), does not adopt either of the conformations usually found in cyclohexene rings. Ideally, four of the carbon atoms should lie in one plane and the other two atoms may be displaced above and below or both on the same side of this plane as shown in the diagrams.

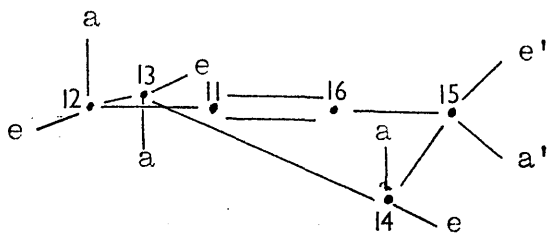


'half-chair'



'half-boat'

However, in the ring system in this homomorphinane alkaloid, five of the carbon atoms (C(13), C(12), C(11), C(15), and C(16)) all lie in one plane and C(14) is displaced 0.68 Å above this plane as shown in the diagram below.



The torsion angles C(15),C(16) - C(11),C(12) (6^{o}) and C(13),C(12) - C(11),C(16) (4^{o}) do not differ significantly from the value of 0^{o} expected for this arrangement. If the ring was in the ideal half-chair conformation, the methyl ester substituent on C(15) would be in a pseudo-equatorial position such that the torsional interaction between it and the methoxy group on C(14) would be increased. The ring conformation has therefore been distorted in order to increase the distance between these two functional groups.

The bridging piperidine ring is in a chair conformation with C(11) and C(18) displaced 0.61 Å and 0.70 Å above and below the plane containing atoms C(12), C(17), C(10), and N(1). The methyl groups, C(19) and C(20), on the quaternary nitrogen atom lie above and below this plane at 1.38 Å and 0.91 Å respectively.

There are six O ... C intermolecular contacts less than the oxygen - carbon van der Waal's distance of 3.4 Å (Pauling, 1960). Three of these short contacts are less than 3.33 Å and since intermolecular hydrogen bonds between C and O have been reported with the C ... O contacts ranging

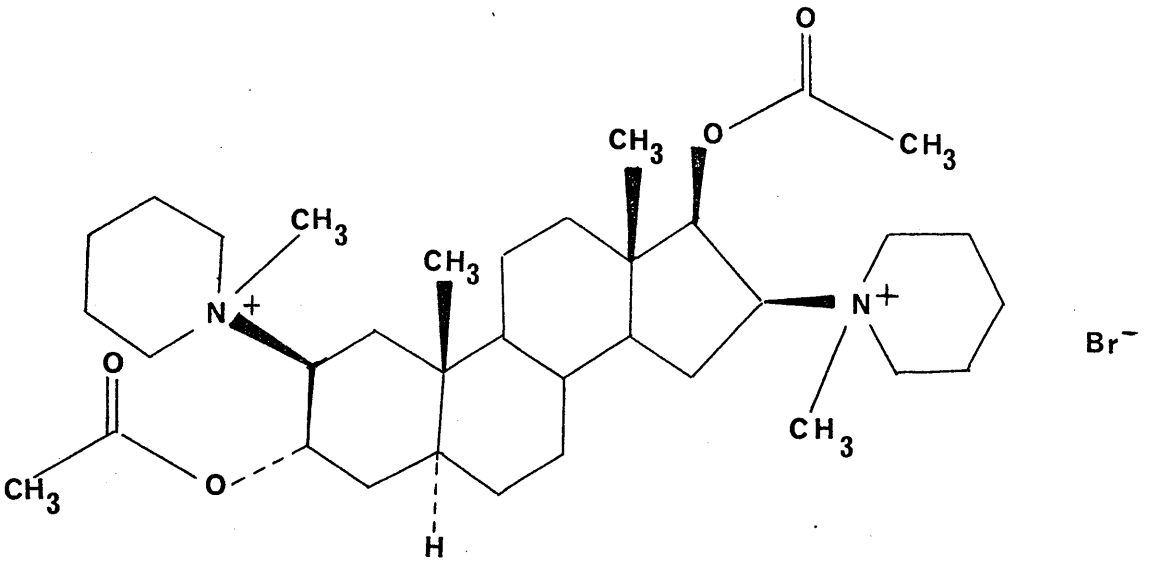
from 2.92 Å to 3.33 Å (Sutor, 1963), it is probable that these three contacts correspond to C-H ... O hydrogen bonds.

THE MOLECULAR STRUCTURE OF PANCURONIUM BROMIDE (3α,17β-DIACETOXY-2β,16β-DIPIPERIDINO-5α-ANDROSTANE DIMETHOBROMIDE), A NEUROMUSCULAR BLOCKING AGENT. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE WATER: METHYLENE CHLORIDE SOLVATE.

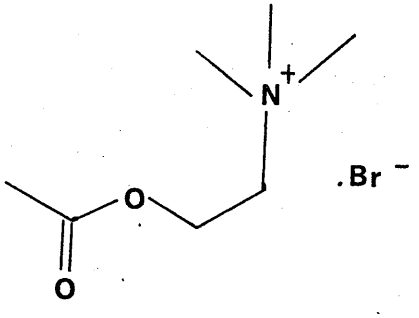
2.1 INTRODUCTION.

An investigation of the biological activities of amino-steroids resulting from the incorporation in 5α-androstane of molecular fragments resembling acetylcholine led to the discovery (Buckett et al., 1967; Buckett et al., 1968) of pancuronium bromide (3α,17β-diacetoxy-2β,16β-dipiperidino-5α-androstane dimethobromide) (I) which has proved clinically useful as a neuromuscular blocking agent of high potency and specificity of action (Baird and Reid, 1967; Baird, 1968). The potency and specificity of action of the agent may be associated with the rigidity of the molecule (deduced form n.m.r. considerations) and in particular with the geometries of the two acetylcholine-like fragments. Our X-ray analysis was undertaken to investigate the geometries of these two fragments in pancuronium bromide in order that a comparison might be made with the geometries of acetylcholine bromide (Canepa et al.,1966) and lactoyl-choline iodide (Chothia and Pauling, 1968) since these molecules can play a significant part in cholinergic trans-mission systems.

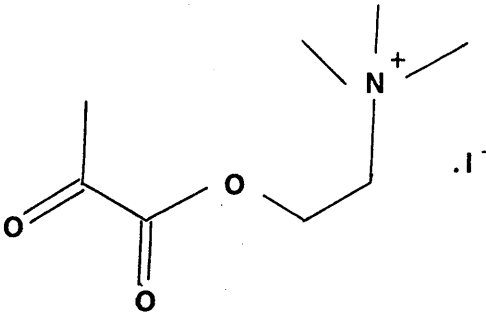
The bis-quaternary pancuronium cation may be



I



II



III

considered to have an almost constant conformation and further, the molecular structure which associates with a receptor to effect neuromuscular blockade will aproximate to the structure determined by our X-ray analysis.

2.2 EXPERIMENTAL.

Crystal Data.

Pancuronium bromide, $[C_{35}H_{60}O_4N_2]^{2+}.\ 2Br^-,\ CH_2Cl_2,\ H_2O$, M (pancuronium bromide) = 732.

Orthorhombic,

$a = 11.10 \pm 0.03$, $b = 13.99 \pm 0.04$, $c = 26.07 \pm 0.06$ Å.

$U = 4048$ Å^3, $D_m = 1.40$ (by flotation in aqueous potassium iodide), $Z = 4$, $D_c = 1.35$ (including the contribution from methylene chloride and water).

$F(000) = 1752$. Space group $P2_12_12_1$ (D_2^4, No. 19).

Linear absorption coefficient for X-rays ($\lambda = 1.5418$ Å), $\mu = 24.1$ cm^{-1}.

Crystallographic Measurements.

The unit cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-K_α ($\lambda = 1.5418$ Å) radiation and from precession photographs taken with Mo-K_α ($\lambda = 0.7107$ Å) radiation. The space group was established uniquely from the systematic absences (h00, 0k0, and 00ℓ absent when h, k, and ℓ are odd).

The crystals proved relatively unstable, decomposing after exposure to X-rays for only two to three days. The diffraction data were tnerefore collected using four small crystals in turn, rotating about a and exposed to Cu-K_α

radiation. Some 2113 independent reflexions from the reciprocal-lattice nets 0 - 8kℓ were recorded on equatorial and equi-inclination Weissenberg photographs using the multiple-film technique (Robertson, 1943). The intensities, estimated by comparison with a calibrated strip, were corrected for the appropriate Lorentz, polarisation and rotation factors and were subsequently placed on an approximate absolute scale by making $k \Sigma|F_o| = \Sigma|F_c|$ for each layer. Absorption effects were not considered.

Structure Determination.

The coordinates of the two bromide ions were determined from the three-dimensional Patterson synthesis and the analysis thereafter proceeded directly on the basis of the phase-determining heavy-atom method (Robertson and Woodward, 1940). The complete steroid skeleton was revealed in the first (heavy-atom-phased) electron-density distribution. Four subsequent electron-density distributions and difference syntheses refined the identified atomic positions and in addition repeatedly showed several peaks which were indicative of other molecular species being present in the structure. Chemical analyses of the crystals suggested the presence of a dichloro-alkane and at least one molecule of water for each pancuronium unit. The additional peaks were then interpreted on the basis of one molecule of methylene chloride and one molecule of water in the asymmetric unit. In the five previous structure factor calculations an overall isotropic temperature factor $U_{iso} = 0.05$ Å^2 was

assumed. The R-factor at the end of these calculations was 0.21.

Structure Refinement.

The refinement of positional, vibrational and scale parameters by block-diagonal least-squares calculations converged after 12 cycles when R was 0.129. Details of the refinement are given in Table 2.1. After cycle 4 the data were converted to an overall absolute scale using the refined values of the layer scale factors, and in all subsequent cycles the overall-scale factor was refined. Anisotropic thermal parameters for the bromine and chlorine atoms only were refined after cycle 9.

A weighting scheme of the form,

$$\sqrt{w} = \left\{[1 - \exp(-p_1(\sin\theta/\lambda)^2]/[1 + p_2|F_o| + p_3|F_o|^2]\right\}^{\frac{1}{2}} .$$

was applied in all cycles. Initially the p-parameters were chosen to give unit weights to all reflexions, but they were varied in later cycles as indicated by an ($|F_o|$ and $\sin\theta/\lambda$) analysis of $w\Delta^2$. The final values were $p_1 = 100$, $p_2 = 0.01$, $p_3 = 0.0001$.

At the conclusion of the refinement, structure factors were calculated and a difference synthesis and electron-density distribution were evaluated. The difference synthesis revealed no errors in the structure, and it was not possible to identify any additional molecules of water which could have been present. No attempt was made to locate hydrogen atoms. Both the structure determination and refinement were therefore considered complete.

In all the structure factor calculations we used the atomic scattering factors given in "International Tables for X-ray Crystallography", Vol. III. Values of the observed and final calculated structure amplitudes are listed in Table 2.2. The final fractional coordinates, U_{iso} and U_{ij} values are in Table 2.3. The U_{ij} values are taken from the expression,

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)\right].$$

Table 2.4 contains bond lengths, valency angles, intra- and intermolecular non-bonded distances. The appropriate estimated standard deviations derived from the inverse of the least-squares normal-equation matrix are included in Tables 2.3 and 2.4. The average e.s.d.s for C-C, C-O, and C-N bonds is 0.03 Å, and for valency angles the average e.s.d. is 2.1°. These are probably best regarded as minimum values.

The atomic numbering scheme is shown in Figure 2.1 and the molecular packing viewed down b is shown in Figure 2.2.

Absolute Configuration.

The absolute configuration of the 5α-androstane used in the preparation of the pancuronium cation is well known (Klyne, 1965), and the initial coordinates of the atoms were derived to conform with this stereochemistry. In addition, at the conclusion of the refinement, 15 pairs of reflexions which showed the effects of anomalous scattering of X-rays (Bijvoet, 1949) were used in a calculation which proved that the derived coordinates did describe a model with

the correct absolute stereochemistry. This is shown in all drawings of the molecule.

Table 2.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final R'
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, unit weights, block-diagonal.	1-4	0.182	0.064
x,y,z,Uiso for all non-hydrogen atoms, overall scale factor, weighting scheme adjusted.	5-8	0.178	0.056
x,y,z,Uiso for C,O,N, x,y,z,Uij(i,j=1,2,3) for Br and Cl, overall scale factor, weighting scheme used.	9-12	0.129	0.025.

Table 2.2

Observed and calculated structure amplitudes.

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
0	0	4	56.42	57.59	-57.59	0.00	-1.17	1
0	0	6	23.86	15.09	-15.09	0.00	8.77	1
0	0	8	87.71	70.77	70.77	-0.00	16.94	1
0	0	10	22.50	17.75	17.75	-0.00	4.74	1
0	0	12	114.26	101.14	101.14	-0.00	13.12	1
0	0	14	167.18	134.20	134.20	-0.00	32.98	1
0	0	16	85.36	79.47	-79.47	0.00	5.89	1
0	0	18	16.24	16.16	-16.16	0.00	0.07	1
0	0	20	65.24	59.16	-59.16	0.00	6.07	1
0	0	22	47.29	43.71	43.71	-0.00	3.58	1
0	0	26	18.19	13.45	13.45	-0.00	4.73	1
0	0	28	35.06	25.93	-25.93	0.00	9.13	1
0	1	5	57.86	61.60	-0.00	-61.60	-3.74	1
0	1	6	103.78	124.50	0.00	124.50	-20.72	1
0	1	7	165.51	187.29	-0.00	-187.29	-21.78	1
0	1	8	177.94	187.03	-0.00	-187.03	-9.09	1
0	1	9	36.52	40.46	0.00	40.46	-3.94	1
0	1	10	79.14	70.62	-0.00	-70.62	8.52	1
0	1	11	36.95	23.90	0.00	-23.90	13.05	1
0	1	12	54.80	48.25	-0.00	-48.25	6.55	1
0	1	13	239.74	217.66	0.00	217.66	22.08	1
0	1	14	39.67	40.20	-0.00	40.20	-0.53	1
0	1	15	88.28	88.49	-0.00	-88.49	-0.21	1
0	1	16	17.29	8.40	0.00	-8.40	8.89	1
0	1	17	12.78	6.62	0.00	6.62	6.16	1
0	1	18	11.52	9.29	0.00	-9.29	2.23	1
0	1	19	20.71	22.79	0.00	-22.79	-2.08	1
0	1	20	47.33	30.18	0.00	-30.18	17.15	1
0	1	21	44.61	40.02	0.00	40.02	4.59	1
0	1	22	41.00	40.54	-0.00	-40.54	0.46	1
0	1	24	18.64	13.71	0.00	13.71	4.92	1
0	1	25	10.68	6.35	0.00	-6.35	4.33	1
0	1	26	12.84	13.07	-0.00	13.07	-0.24	1
0	1	29	22.31	22.80	-0.00	-22.80	-0.49	1
0	2	0	139.75	150.72	-150.72	0.00	-10.97	1
0	2	1	43.28	7.66	7.66	-0.00	35.62	1
0	2	2	52.02	63.96	63.96	-0.00	-11.94	1
0	2	3	59.68	60.83	-60.83	0.00	-1.15	1
0	2	4	55.46	58.58	-58.58	0.00	-3.12	1
0	2	5	152.23	163.43	-163.43	0.00	-11.19	1
0	2	6	100.59	106.17	106.17	-0.00	-5.58	1
0	2	7	210.40	244.97	244.97	-0.00	-34.57	1
0	2	9	90.52	97.74	97.74	-0.00	-7.21	1
0	2	10	21.55	13.68	-13.68	0.00	7.88	1
0	2	11	38.55	38.12	38.12	0.00	0.43	1
0	2	12	107.77	91.60	-91.60	0.00	16.17	1
0	2	13	29.01	29.61	-29.61	-0.00	-0.60	1
0	2	16	29.74	29.38	29.38	-0.00	0.36	1
0	2	19	12.08	8.26	8.26	-0.00	3.82	1
0	2	20	35.96	26.37	26.37	0.00	9.59	1
0	2	21	67.61	60.03	60.03	-0.00	7.58	1
0	2	22	46.32	39.60	-39.60	0.00	6.73	1
0	2	23	28.41	25.82	-25.82	0.00	2.59	1
0	2	24	17.00	14.03	14.03	-0.00	2.97	1
0	2	25	19.93	18.03	18.03	-0.00	1.90	1
0	2	26	20.85	20.54	-20.54	0.00	0.31	1
0	2	27	37.68	37.64	-37.64	0.00	0.04	1
0	2	28	15.17	15.37	15.37	-0.00	-0.21	1
0	3	1	78.84	94.63	0.00	94.63	-15.79	1
0	3	2	162.22	204.14	-0.00	-204.14	-41.92	1
0	3	3	168.22	190.18	0.00	190.18	-21.96	1
0	3	4	18.72	18.67	0.00	-18.67	0.05	1
0	3	5	27.56	23.32	0.00	-23.32	4.25	1
0	3	6	41.24	43.37	-0.00	-43.37	-2.13	1
0	3	7	38.48	44.90	-0.00	-44.90	-6.43	1
0	3	8	47.00	55.73	0.00	55.73	-8.73	1
0	3	9	50.95	39.38	-0.00	-39.38	11.57	1
0	3	10	61.83	54.55	-0.00	-54.55	7.27	1
0	3	11	64.17	60.63	0.00	60.63	3.54	1
0	3	12	60.75	54.00	0.00	54.00	6.75	1
0	3	13	28.37	28.23	0.00	28.23	0.14	1
0	3	14	133.03	139.56	-0.00	-139.56	-6.53	1
0	3	15	40.51	33.94	0.00	33.94	6.57	1
0	3	16	29.07	26.51	-0.00	-26.51	2.56	1
0	3	17	51.13	42.27	-0.00	-42.27	8.86	1
0	3	19	35.37	34.85	-0.00	-34.85	0.52	1
0	3	20	30.86	25.81	0.00	25.81	5.06	1
0	3	22	27.24	21.58	0.00	21.58	5.66	1
0	3	28	14.89	9.62	-0.00	-9.62	5.27	1
0	4	0	80.80	95.58	-95.58	0.00	-14.78	1
0	4	1	119.42	118.70	118.70	-0.00	0.72	1
0	4	2	82.18	68.31	68.31	-0.00	13.87	1
0	4	3	139.23	151.28	-151.28	0.00	-12.05	1
0	4	4	50.42	48.58	48.58	-0.00	1.84	1
0	4	5	80.60	90.82	90.82	-0.00	-10.23	1
0	4	6	110.80	130.77	130.77	-0.00	-19.98	1
0	4	8	56.61	64.29	64.29	-0.00	-7.68	1
0	4	9	36.81	28.78	-28.78	0.00	8.03	1
0	4	10	23.34	23.46	-23.46	0.00	-0.12	1
0	4	12	66.91	61.09	-61.09	0.00	5.82	1
0	4	15	40.77	29.21	29.21	-0.00	11.56	1
0	4	16	35.79	37.19	37.19	-0.00	-1.39	1
0	4	17	32.49	29.31	-29.31	0.00	3.18	1
0	4	19	17.65	13.72	13.72	0.00	3.93	1
0	4	21	15.02	13.83	-13.83	0.00	1.19	1
0	4	23	38.04	35.12	35.12	-0.00	2.91	1
0	5	1	66.48	70.00	-0.00	-70.00	-3.52	1
0	5	2	37.58	30.09	0.00	30.09	7.49	1
0	5	3	18.98	19.41	0.00	19.41	-0.43	1
0	5	4	50.93	43.32	0.00	43.32	7.61	1
0	5	5	70.95	71.73	0.00	71.73	-0.79	1
0	5	6	35.87	47.46	-0.00	47.46	-11.59	1
0	5	7	86.39	97.72	0.00	97.72	-11.33	1
0	5	8	38.39	32.22	-0.00	-32.22	6.17	1
0	5	9	65.51	76.62	-0.00	-76.62	-11.11	1
0	5	10	85.13	95.89	0.00	95.89	-10.76	1
0	5	11	12.61	16.18	0.00	16.18	-3.57	1
0	5	12	32.61	32.54	0.00	-32.54	0.07	1
0	5	13	70.39	75.57	-0.00	-75.57	-5.18	1
0	5	15	15.49	15.03	0.00	15.03	0.46	1
0	5	16	49.70	51.57	-0.00	-51.57	-1.87	1
0	5	18	21.53	12.86	0.00	12.86	8.67	1
0	5	19	49.29	48.75	0.00	48.75	0.54	1
0	5	20	44.91	39.54	0.00	39.54	5.37	1
0	5	21	34.71	28.36	-0.00	-28.36	6.36	1
0	5	23	21.43	9.22	-0.00	-9.22	12.21	1
0	5	29	22.86	25.35	0.00	25.35	-2.50	1
0	6	0	90.50	92.03	92.03	-0.00	-1.53	1
0	6	1	16.45	11.16	-11.16	0.00	5.29	1
0	6	2	63.13	67.46	-67.46	0.00	-4.33	1
0	6	3	59.94	72.86	72.86	-0.00	-12.92	1
0	6	4	96.20	85.44	85.44	-0.00	10.76	1
0	6	5	70.09	65.32	65.32	-0.00	4.77	1
0	6	6	85.94	66.85	-66.85	0.00	19.09	1
0	6	7	68.42	62.46	-62.46	0.00	5.96	1
0	6	8	71.89	66.38	66.38	-0.00	5.53	1
0	6	9	51.51	42.83	-42.83	0.00	8.68	1
0	6	10	43.41	35.90	-35.90	0.00	7.51	1
0	6	11	47.58	41.93	41.93	-0.00	5.64	1
0	6	12	13.85	5.73	-5.73	0.00	8.13	1
0	6	13	57.95	58.02	58.02	-0.00	-0.07	1
0	6	14	30.99	25.12	25.12	-0.00	5.87	1
0	6	15	35.39	35.64	35.64	-0.00	-0.25	1
0	6	16	38.39	30.55	-30.55	0.00	7.84	1
0	6	19	26.98	18.30	-18.30	0.00	8.68	1
0	6	21	39.55	33.34	-33.34	0.00	6.21	1
0	6	22	35.58	31.81	31.81	-0.00	3.77	1
0	6	23	34.34	26.47	-26.47	0.00	7.87	1
0	6	24	25.38	22.55	-22.55	0.00	2.83	1
0	6	26	19.54	17.13	-17.13	0.00	2.40	1
0	7	1	24.69	14.17	0.00	14.17	10.52	1
0	7	2	51.89	50.30	0.00	50.30	1.59	1
0	7	3	16.05	9.41	0.00	9.41	6.64	1
0	7	4	41.29	29.77	-0.00	-29.77	11.52	1
0	7	5	50.52	53.43	0.00	53.43	-2.91	1
0	7	7	17.23	12.86	-0.00	-12.86	4.37	1
0	7	8	51.31	56.90	-0.00	-56.90	-5.58	1
0	7	9	74.70	75.34	0.00	75.34	-0.64	1
0	7	10	17.55	13.84	0.00	13.84	3.71	1
0	7	11	61.16	54.83	-0.00	-54.83	6.33	1
0	7	13	27.78	23.76	0.00	23.76	4.01	1
0	7	14	20.25	12.69	0.00	12.69	7.57	1
0	7	15	49.63	35.47	-0.00	-35.47	14.16	1
0	7	17	46.76	41.98	0.00	41.98	4.78	1
0	7	20	17.02	11.37	-0.00	-11.37	5.65	1
0	7	21	28.37	27.20	0.00	27.20	1.17	1
0	7	22	22.48	19.75	-0.00	-19.75	2.72	1
0	7	26	19.28	12.86	0.00	12.86	6.42	1
0	8	0	26.46	2.95	2.95	-0.00	23.51	1
0	8	1	51.74	58.10	-58.10	0.00	-6.36	1
0	8	2	48.99	52.14	52.14	-0.00	-3.15	1
0	8	3	47.24	48.51	48.51	-0.00	-1.28	1
0	8	4	94.23	92.53	-92.53	0.00	1.70	1
0	8	5	45.34	45.81	-45.81	0.00	-0.48	1
0	8	7	17.57	14.20	-14.20	0.00	3.37	1
0	8	8	44.36	43.93	-43.93	0.00	0.42	1
0	8	11	55.37	53.19	53.19	-0.00	2.18	1
0	8	12	42.07	39.90	39.90	-0.00	2.17	1
0	8	13	17.31	10.43	-10.43	-0.00	6.88	1
0	8	15	22.04	19.69	-19.69	0.00	2.34	1
0	8	17	22.63	26.14	26.14	-0.00	-3.51	1
0	8	18	30.39	28.02	-28.02	0.00	2.37	1
0	8	21	22.40	14.31	14.31	-0.00	8.09	1
0	8	22	16.33	10.78	10.78	-0.00	5.55	1
0	8	24	27.95	25.57	25.57	-0.00	2.38	1
0	8	26	16.93	15.44	-15.44	0.00	1.49	1
0	9	1	30.24	33.78	0.00	33.78	-3.55	1
0	9	2	12.64	7.21	-0.00	-7.21	5.43	1
0	9	3	19.11	15.48	-0.00	15.48	3.63	1
0	9	4	58.18	62.33	0.00	62.33	-4.15	1
0	9	5	49.89	46.85	-0.00	-46.85	3.05	1
0	9	6	13.16	11.45	-0.00	-11.45	1.71	1
0	9	8	20.34	15.58	0.00	15.58	4.76	1
0	9	10	46.50	50.72	-0.00	-50.72	-4.22	1
0	9	11	43.37	42.03	0.00	42.03	1.34	1
0	9	12	48.62	52.81	0.00	52.81	-4.19	1
0	9	13	28.49	21.73	-0.00	-21.73	6.77	1
0	9	16	45.53	43.89	0.00	43.89	1.64	1
0	9	17	15.22	5.68	-0.00	-5.68	9.53	1
0	9	18	22.77	20.71	-0.00	-20.71	2.06	1
0	9	19	18.43	16.73	0.00	-16.73	1.70	1
0	9	20	18.14	18.29	-0.00	-18.29	-0.15	1
0	9	23	13.39	11.37	0.00	11.37	2.02	1
0	9	24	15.52	1.95	-0.00	1.95	13.57	1
0	10	0	13.59	6.22	6.22	-0.00	7.37	1
0	10	1	31.16	24.75	24.75	-0.00	6.41	1
0	10	2	11.81	13.16	13.16	-0.00	-1.36	1
0	10	3	63.55	55.17	-55.17	0.00	8.39	1
0	10	4	39.62	40.00	-40.00	0.00	-0.37	1
0	10	5	35.47	27.14	27.14	-0.00	8.33	1
0	10	6	12.17	13.61	13.61	-0.00	-1.44	1
0	10	9	44.17	42.45	42.45	-0.00	1.72	1
0	10	10	17.99	14.13	-14.13	0.00	3.86	1
0	10	11	14.85	12.85	-12.85	0.00	2.01	1
0	10	13	32.05	29.66	-29.66	0.00	2.39	1
0	10	15	24.05	15.66	-15.66	0.00	8.41	1
0	10	16	16.98	9.04	9.04	-0.00	7.94	1
0	10	18	21.05	18.24	18.24	-0.00	2.81	1
0	10	19	33.42	39.34	39.34	-0.00	-5.92	1
0	10	23	15.14	7.91	7.91	-0.00	7.23	1
0	11	2	16.20	12.43	-0.00	-12.43	3.76	1
0	11	3	19.22	20.65	0.00	20.65	-1.43	1
0	11	4	53.62	49.68	-0.00	-49.68	3.94	1
0	11	5	19.41	16.97	-0.00	-16.97	2.44	1
0	11	6	41.09	35.62	0.00	35.62	5.47	1
0	11	8	41.63	32.80	0.00	32.80	8.83	1
0	11	9	32.79	24.75	-0.00	-24.75	8.04	1
0	11	10	46.63	42.45	0.00	42.45	4.18	1
0	11	11	21.48	26.61	0.00	26.61	-5.13	1
0	11	12	39.53	34.84	-0.00	-34.84	4.69	1
0	11	15	27.10	32.13	0.00	32.13	-5.03	1
0	11	16	21.00	22.47	-0.00	-22.47	-1.47	1
0	11	18	21.34	23.47	0.00	23.47	-2.13	1
0	11	20	14.81	17.41	0.00	17.41	-2.60	1
0	12	0	38.35	44.06	44.06	-0.00	-5.72	1
0	12	1	15.05	5.67	-5.67	0.00	9.38	1
0	12	2	69.83	70.69	-70.69	0.00	-0.86	1
0	12	3	31.99	20.62	20.62	-0.00	11.37	1
0	12	4	26.18	24.05	24.05	-0.00	2.13	1
0	12	5	22.71	21.02	-21.02	0.00	1.69	1
0	12	6	27.43	19.82	19.82	-0.00	7.62	1
0	12	8	27.43	20.47	-20.47	0.00	6.97	1
0	12	10	18.61	17.22	-17.22	0.00	1.39	1
0	12	12	21.26	16.92	-16.92	0.00	4.34	1
0	12	13	16.66	17.26	17.26	-0.00	-0.61	1
0	12	18	14.75	24.21	24.21	-0.00	-9.47	1
0	12	20	14.63	10.87	-10.87	0.00	3.76	1
0	13	1	31.35	25.36	-0.00	-25.36	5.99	1
0	13	2	21.51	20.25	-0.00	-20.25	1.26	1
0	13	4	30.37	25.24	0.00	25.24	5.14	1
0	13	5	33.05	27.71	0.00	27.71	5.34	1
0	13	7	35.36	33.93	-0.00	-33.93	1.43	1
0	14	0	32.29	26.57	-26.57	0.00	5.72	1
0	14	2	32.22	25.95	25.95	-0.00	6.26	1
0	14	4	17.99	11.69	-11.69	0.00	6.30	1
0	14	6	14.61	11.81	-11.81	0.00	2.80	1
1	0	5	87.94	91.19	-0.00	-91.19	-3.26	1
1	0	6	147.08	169.87	169.87	-0.00	-22.79	1
1	0	7	105.71	102.03	-0.00	-102.03	3.68	1
1	0	8	62.23	66.28	66.28	-0.00	-4.06	1
1	0	9	89.64	93.35	0.00	93.35	-3.71	1
1	0	10	47.76	56.70	56.70	-0.00	-5.95	1
1	0	11	58.52	36.98	0.00	36.98	21.54	1
1	0	12	44.72	46.93	-46.93	0.00	-2.21	1
1	0	13	70.28	66.72	-0.00	-66.72	3.56	1
1	0	14	35.96	26.48	-26.48	0.00	9.48	1
1	0	15	37.77	34.30	0.00	34.30	3.47	1
1	0	16	48.49	47.34	-47.34	0.00	1.15	1
1	0	17	31.11	31.54	-0.00	-31.54	-0.43	1
1	0	18	64.52	58.85	58.85	-0.00	5.67	1
1	0	19	48.94	41.32	0.00	41.32	7.62	1
1	0	20	30.49	26.20	26.20	-0.00	4.30	1
1	0	21	39.02	37.06	-0.00	-37.06	1.96	1
1	0	22	14.31	8.27	8.27	-0.00	6.04	1
1	0	25	16.13	15.67	-0.00	-15.67	0.46	1
1	0	26	25.53	21.98	-21.98	0.00	3.55	1
1	0	27	16.77	12.93	0.00	12.93	3.85	1
1	0	28	16.01	12.70	-12.70	0.00	3.31	1
1	1	3	64.47	62.32	-27.18	-56.08	2.15	1
1	1	4	92.91	104.44	77.47	-70.04	-11.53	1
1	1	5	98.18	107.70	107.09	11.41	-9.52	1
1	1	6	72.93	67.33	-64.64	-18.82	5.60	1
1	1	7	91.12	91.20	-72.06	-37.41	-0.08	1
1	1	8	63.20	75.24	45.67	-57.38	-12.04	1
1	1	9	69.58	67.16	38.84	57.20	2.42	1
1	1	10	80.93	76.89	-74.12	20.47	4.04	1
1	1	11	80.89	52.40	-32.56	-41.06	28.49	1
1	1	12	54.57	54.41	7.04	53.95	0.16	1
1	1	13	74.49	72.31	33.97	-63.83	2.19	1
1	1	14	30.17	21.57	12.97	17.24	8.60	1
1	1	15	57.11	49.11	-39.56	-29.10	8.00	1
1	1	16	37.11	31.27	25.71	-17.74	5.87	1
1	1	17	51.64	39.24	3.10	-39.12	12.39	1
1	1	18	76.58	72.06	-29.07	-65.94	4.52	1
1	1	19	55.79	49.07	-3.10	45.97	6.72	1
1	1	20	16.75	13.29	10.19	8.53	3.47	1
1	1	21	31.40	26.02	-18.55	17.94	5.38	1
1	1	22	32.03	27.03	-19.53	18.68	5.00	1
1	1	23	36.24	33.34	-3.12	33.20	2.90	1
1	1	24	22.98	15.76	-5.09	14.91	7.22	1
1	1	25	33.70	30.29	-1.13	-30.36	3.41	1
1	1	26	14.13	10.61	10.85	-8.27	3.52	1
1	2	0	49.24	56.01	0.00	56.01	-6.76	1
1	2	1	93.96	120.43	-103.43	66.45	-26.47	1
1	2	2	125.36	132.81	-112.56	-70.57	-7.46	1
1	2	3	20.12	13.85	-13.85	0.13	6.27	1
1	2	4	51.63	59.74	42.61	43.44	2.89	1
1	2	5	173.48	210.00	173.43	-118.42	-36.51	1
1	2	6	74.81	81.45	-61.39	-53.54	-6.64	1
1	2	7	69.66	62.92	46.13	-42.80	6.74	1
1	2	8	79.02	72.38	64.52	32.83	6.64	1
1	2	9	27.19	13.52	13.42	-1.61	13.67	1
1	2	10	49.75	46.79	-44.56	-14.48	2.96	1
1	2	11	117.02	130.47	-130.41	-3.48	-13.45	1
1	2	12	44.87	30.49	-7.62	-29.52	14.38	1
1	2	13	44.81	42.22	39.54	-14.78	2.59	1
1	2	14	17.18	12.63	-4.97	11.61	4.54	1
1	2	15	20.53	18.78	10.80	-15.39	1.75	1
1	2	16	23.04	19.50	-4.24	-19.04	3.54	1
1	2	17	61.75	55.15	53.38	13.86	6.60	1
1	2	18	39.24	36.07	-12.71	33.75	3.17	1
1	2	19	24.09	18.47	9.29	-15.96	5.62	1
1	2	20	30.02	24.53	-1.78	-24.47	5.49	1
1	2	21	38.03	32.76	31.21	9.96	5.27	1
1	2	22	32.94	27.33	12.65	25.16	5.61	1
1	2	23	37.71	36.99	-36.90	2.55	0.72	1
1	2	24	33.26	31.05	3.19	-30.88	2.22	1
1	2	25	31.30	28.03	-21.41	18.08	3.28	1
1	2	26	14.04	12.64	1.99	12.49	1.40	1
1	2	27	19.16	19.98	18.86	-6.61	-0.82	1
1	3	0	116.24	125.76	0.00	125.76	-9.52	1
1	3	1	73.48	72.32	-50.29	51.97	1.15	1
1	3	2	115.65	133.86	89.99	-99.09	-18.21	1
1	3	3	115.77	130.68	130.10	12.30	-14.91	1
1	3	4	139.38	161.05	-33.21	157.59	-21.67	1
1	3	5	69.12	67.31	-22.19	-63.54	1.81	1
1	3	6	39.25	38.87	-6.93	38.25	0.38	1
1	3	7	67.47	58.99	50.30	30.81	8.48	1
1	3	8	76.63	80.98	31.73	74.50	-4.35	1
1	3	9	68.37	73.17	-11.74	72.22	-4.80	1
1	3	10	43.37	36.73	33.41	-15.27	6.63	1
1	3	11	81.85	89.72	84.13	31.18	-7.87	1
1	3	12	74.03	77.24	-34.27	-69.22	-3.20	1
1	3	13	77.59	75.24	-64.85	-38.14	2.35	1
1	3	14	17.69	13.96	-8.87	-10.78	3.72	1
1	3	15	81.02	75.97	41.41	-63.79	5.05	1
1	3	16	17.22	19.91	16.68	-10.85	-2.69	1
1	3	17	41.51	32.69	-31.17	9.87	8.82	1
1	3	18	59.43	65.14	-15.91	63.19	-5.72	1
1	3	19	38.34	35.31	26.13	23.75	3.03	1
1	3	20	47.77	40.48	26.02	-31.01	7.29	1
1	3	21	26.63	26.59	-24.60	10.09	0.04	1
1	3	22	21.67	14.63	4.79	-13.82	7.05	1
1	3	24	32.38	27.71	-8.57	-26.35	4.68	1
1	3	25	26.71	23.61	0.85	-23.59	3.10	1
1	3	27	14.94	11.69	-8.15	-8.38	3.26	1
1	3	28	10.96	3.68	3.55	0.97	7.28	1
1	4	0	77.13	64.67	0.00	64.67	12.46	1
1	4	1	47.44	34.93	5.08	34.56	12.51	1
1	4	2	133.95	170.64	141.75	95.01	-36.70	1
1	4	3	89.24	90.31	51.29	74.34	-1.07	1
1	4	4	157.03	170.64	140.34	-97.08	-13.61	1
1	4	5	61.71	51.01	-1.67	-50.98	10.70	1
1	4	6	126.97	139.68	-90.17	106.66	-12.71	1
1	4	7	19.69	13.97	2.81	-13.69	5.73	1
1	4	8	43.25	38.90	-35.11	-16.75	4.34	1
1	4	9	30.71	29.89	-29.34	-5.57	0.82	1
1	4	10	32.08	37.71	-36.43	-9.74	-5.63	1
1	4	11	71.36	73.08	61.23	-39.89	-1.72	1
1	4	12	50.08	51.10	47.67	18.42	-1.02	1
1	4	13	59.69	55.06	-42.39	-35.14	4.63	1
1	4	14	48.18	42.26	34.55	-24.34	5.91	1
1	4	15	24.14	27.97	24.79	12.96	-3.83	1
1	4	16	62.37	62.18	57.23	24.32	0.19	1
1	4	17	72.04	69.38	-58.65	37.08	2.66	1
1	4	18	47.44	41.80	-7.50	-41.12	5.64	1
1	4	19	37.80	35.70	12.00	-33.62	2.10	1
1	4	20	60.35	61.91	-54.56	28.79	-1.57	1
1	4	21	22.72	22.40	-22.36	1.40	0.32	1
1	4	22	38.39	37.78	-9.77	-36.59	0.61	1
1	4	23	22.97	17.83	9.27	-15.23	5.14	1
1	4	24	16.10	13.54	4.44	12.79	2.56	1
1	4	25	23.68	22.02	19.80	-9.63	1.66	1
1	4	27	16.00	14.40	-9.68	-10.65	1.60	1
1	4	28	19.45	20.22	16.11	12.22	-0.77	1
1	5	0	111.38	126.47	-0.00	-126.47	-15.09	1
1	5	1	14.68	18.04	-14.49	10.75	-3.36	1
1	5	2	59.75	54.30	32.38	-43.59	5.45	1
1	5	3	82.70	86.46	7.01	86.18	-3.77	1
1	5	4	66.50	51.13	-35.54	-36.75	15.37	1
1	5	5	36.99	26.27	-2.29	26.17	10.72	1
1	5	6	99.72	101.06	82.96	57.71	-1.33	1
1	5	7	86.46	86.38	-83.91	-20.51	0.09	1
1	5	8	57.09	49.22	-41.17	26.97	7.86	1
1	5	9	115.05	128.23	84.53	-96.43	-13.18	1
1	5	10	80.07	77.63	74.23	22.72	2.44	1
1	5	11	20.96	10.97	-0.70	10.95	9.99	1
1	5	12	62.61	63.96	-15.99	-61.93	-1.35	1
1	5	13	49.17	47.16	-12.49	45.45	2.01	1
1	5	14	49.55	40.96	30.92	-26.90	8.59	1
1	5	15	45.35	42.70	-36.36	22.40	2.65	1
1	5	16	39.45	36.72	-25.07	26.97	2.73	1
1	5	17	34.10	34.82	30.73	16.38	-0.72	1
1	5	18	21.73	22.29	21.25	6.73	-0.56	1
1	5	19	69.63	62.72	-54.44	-31.11	6.92	1
1	5	20	26.80	17.57	-3.16	17.29	9.23	1
1	5	22	26.20	24.98	-14.04	-20.66	1.22	1
1	5	23	27.04	30.74	10.44	-28.91	-3.70	1
1	5	25	27.72	29.70	2.00	29.63	-1.98	1
1	5	26	14.97	12.90	-4.00	-12.26	2.07	1
1	5	28	15.63	17.59	3.11	17.31	-1.96	1
1	6	0	30.74	34.46	-0.00	-34.46	-3.72	1
1	6	1	127.48	131.19	107.59	74.65	-3.71	1
1	6	2	52.62	42.94	34.47	-25.61	9.67	1
1	6	3	68.57	66.48	-35.83	-56.13	2.09	1
1	6	4	77.61	73.58	-55.61	48.19	4.03	1
1	6	5	27.34	32.21	-32.11	-2.53	-4.87	1
1	6	6	35.01	30.64	30.64	-0.00	4.37	1
1	6	7	56.68	59.92	-59.63	5.87	-3.24	1
1	6	8	33.10	26.43	-14.37	22.18	6.67	1
1	6	9	39.28	40.28	15.77	37.08	-1.00	1
1	6	10	77.78	83.93	83.71	6.16	-6.15	1
1	6	11	53.04	56.33	56.26	2.92	-3.30	1
1	6	12	30.31	24.22	-24.19	1.36	6.09	1
1	6	13	55.94	54.42	53.64	-9.21	1.51	1
1	6	15	33.30	25.30	7.26	24.23	8.00	1
1	6	16	37.40	33.23	-28.56	-16.99	4.17	1
1	6	17	22.85	22.59	-12.42	-18.88	0.26	1
1	6	18	17.24	11.72	11.72	-0.00	5.52	1
1	6	19	50.12	46.88	-1.99	46.84	3.24	1
1	6	20	27.08	23.10	21.27	-9.00	3.98	1
1	6	21	29.07	31.56	10.57	-29.74	-2.49	1
1	6	22	12.54	8.67	8.38	2.21	3.87	1
1	6	23	29.45	28.41	18.46	21.59	1.04	1
1	6	25	13.47	10.49	5.30	-9.01	2.98	1
1	7	0	101.33	107.79	0.00	107.79	-6.46	1
1	7	1	46.61	44.43	-14.79	41.89	2.18	1
1	7	2	77.13	79.87	-7.73	79.50	-2.74	1
1	7	3	40.77	38.40	-25.44	-28.75	2.37	1
1	7	4	76.68	74.93	58.52	-46.98	1.74	1
1	7	5	43.96	45.17	-16.90	41.88	-1.21	1
1	7	6	75.37	[illegible]	-52.20	-56.05	[illegible]	1
1	7	7	28.13	18.10	12.75	-12.85	10.03	1
1	7	8	39.53	46.54	46.47	2.25	[illegible]	1
1	7	9	28.39	26.58	8.72	-25.11	1.81	1
1	7	10	30.93	27.24	-16.57	21.43	3.69	1
1	7	11	40.58	33.99	-6.89	-33.29	6.59	1
1	7	12	55.17	58.86	32.30	49.20	-3.69	1
1	7	13	19.38	18.16	5.28	-17.37	1.22	1
1	7	14	46.41	42.83	-32.99	27.31	3.58	1
1	7	15	34.65	34.65	3.70	34.45	-0.00	1
1	7	16	40.50	38.05	20.75	-23.72	2.44	1
1	7	17	21.22	19.34	14.62	-12.66	1.88	1
1	7	18	37.17	36.01	-19.46	-30.35	[illegible]	1
1	7	21	35.45	32.56	13.71	-29.53	2.89	1
1	7	23	17.12	16.87	-5.27	16.02	0.25	1
1	7	24	19.12	16.45	5.31	15.60	2.67	1
1	8	0	18.39	17.92	-0.00	17.92	0.47	1
1	8	1	29.35	25.85	3.53	-25.61	3.50	1
1	8	2	55.53	51.81	-49.67	-14.65	3.72	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
1	8	3	43.21	37.54	13.34	35.41	5.37	1
1	8	4	49.24	51.20	-50.89	5.59	-1.95	1
1	8	5	32.09	33.61	20.62	-26.54	-1.52	1
1	8	6	29.85	30.78	-7.16	-29.93	-0.92	1
1	8	7	13.33	11.87	-3.84	11.23	1.46	1
1	8	8	57.60	47.54	47.44	3.67	9.84	1
1	8	9	31.05	23.50	23.24	3.48	7.55	1
1	8	10	19.04	10.07	6.54	-7.67	8.96	1
1	8	11	49.82	42.74	-41.30	10.98	7.08	1
1	8	12	19.89	16.91	12.79	11.06	2.98	1
1	8	13	11.73	4.39	0.96	4.29	7.34	1
1	8	14	50.30	57.07	-53.47	19.93	-6.76	1
1	8	15	19.89	21.75	-20.43	7.46	-1.86	1
1	8	16	41.62	39.77	-7.64	-39.03	1.85	1
1	8	17	45.64	41.54	36.82	19.23	4.10	1
1	8	19	39.11	34.98	-7.50	-34.17	4.13	1
1	8	20	16.14	13.61	12.06	-6.31	2.53	1
1	8	21	24.65	25.42	-8.06	24.11	-0.77	1
1	8	22	19.67	17.24	10.19	13.90	2.44	1
1	8	23	20.19	17.41	-10.81	-14.90	1.78	1
1	9	0	61.61	58.40	0.00	58.40	3.21	1
1	9	1	53.09	49.64	-21.31	-44.83	3.45	1
1	9	2	34.88	30.40	-2.23	-30.32	4.48	1
1	9	3	60.81	50.51	26.61	-42.92	10.30	1
1	9	4	42.26	31.23	-15.33	27.21	11.03	1
1	9	5	28.55	27.57	-22.30	-16.22	0.98	1
1	9	6	30.91	28.08	12.71	-25.03	2.84	1
1	9	7	36.77	29.83	9.36	28.32	6.94	1
1	9	9	57.97	58.81	-42.32	40.64	-0.84	1
1	9	10	22.28	15.08	5.38	-14.09	7.20	1
1	9	11	25.56	20.32	19.56	5.49	5.25	1
1	9	12	27.77	22.47	-22.28	2.91	5.30	1
1	9	13	28.17	25.94	-21.00	-15.23	2.23	1
1	9	14	31.91	28.77	-3.18	28.59	3.15	1
1	9	15	38.81	32.98	26.84	-19.17	5.83	1
1	9	16	20.51	14.23	-14.22	0.13	6.28	1
1	9	18	16.20	12.88	5.91	11.45	3.31	1
1	9	19	12.42	10.31	10.15	1.77	2.12	1
1	9	20	28.22	27.71	-14.46	-23.63	0.51	1
1	9	21	22.82	22.91	-19.74	11.63	-0.09	1
1	9	22	11.51	8.24	-4.60	6.84	3.27	1
1	10	0	57.15	50.23	-0.00	-50.23	6.93	1
1	10	1	36.88	30.25	-26.36	14.83	6.63	1
1	10	2	21.68	14.69	10.00	10.76	7.00	1
1	10	3	13.14	10.48	10.20	-2.42	2.66	1
1	10	4	37.41	33.05	26.20	-20.14	4.36	1
1	10	6	39.81	37.71	7.79	36.90	2.10	1
1	10	7	69.35	76.52	76.43	-3.85	-7.17	1
1	10	8	22.80	18.35	8.22	-16.40	4.45	1
1	10	9	23.06	15.68	-3.27	15.34	7.38	1
1	10	10	26.31	24.74	-18.88	-15.98	1.57	1
1	10	12	12.42	8.30	6.88	4.64	4.13	1
1	10	13	52.10	48.67	-48.58	2.96	3.43	1
1	10	14	25.14	20.28	16.28	-12.09	4.87	1
1	10	15	16.25	14.91	13.39	-6.57	1.34	1
1	10	16	27.11	26.95	5.90	25.43	0.16	1
1	10	19	13.89	13.20	13.14	1.30	0.69	1
1	10	20	13.50	10.14	-2.00	9.94	3.36	1
1	11	0	63.02	67.27	-0.00	-67.27	-4.25	1
1	11	1	11.99	5.82	-0.31	-5.82	6.17	1
1	11	2	16.99	14.97	14.61	3.26	2.02	1
1	11	3	19.68	15.13	-14.79	3.20	4.55	1
1	11	4	26.15	22.13	15.64	15.66	4.02	1
1	11	5	28.10	23.60	16.09	-17.27	4.50	1
1	11	6	38.70	35.23	7.51	34.42	3.48	1
1	11	7	20.12	12.52	-9.75	8.29	7.29	1
1	11	8	26.77	17.91	-15.64	-8.74	8.85	1
1	11	9	22.75	21.46	20.96	4.60	1.29	1
1	11	12	12.59	9.21	-8.37	-3.85	3.38	1
1	11	13	29.04	20.11	19.83	-3.34	8.93	1
1	11	15	18.96	20.41	-16.90	-11.45	-1.45	1
1	11	17	13.88	10.97	7.83	-7.65	2.91	1
1	11	20	14.07	11.90	-2.19	11.69	2.17	1
1	11	21	16.92	15.70	5.41	14.73	1.23	1
1	11	22	12.58	8.58	5.93	-6.23	4.00	1
1	12	2	20.37	14.96	12.31	-8.51	5.41	1
1	12	3	17.67	15.31	14.77	4.02	2.36	1
1	12	4	14.45	12.68	10.36	7.31	1.78	1
1	12	5	12.54	6.75	-3.32	5.87	5.80	1
1	12	6	29.89	25.92	7.91	-24.69	3.97	1
1	12	7	16.24	17.60	-12.03	-12.84	-1.36	1
1	12	8	27.20	22.30	-21.25	-6.78	4.90	1
1	12	9	14.53	7.19	-1.12	7.10	7.34	1
1	12	10	17.76	14.74	-10.90	9.92	3.02	1
1	12	12	16.03	13.38	-11.39	7.03	2.65	1
1	12	13	23.53	20.51	19.96	-4.73	3.03	1
1	12	14	22.12	18.60	18.08	-4.37	3.53	1
1	12	17	13.01	11.37	-7.15	-6.74	1.64	1
1	12	18	10.86	9.05	8.35	-3.48	1.81	1
1	12	19	11.97	9.90	1.71	9.75	2.08	1
1	12	20	12.66	13.99	-11.76	-7.58	-1.33	1
1	12	21	12.95	13.22	9.35	-9.35	-0.27	1
1	13	1	25.15	20.19	3.39	19.90	4.96	1
1	13	2	12.57	12.20	9.84	-7.22	0.37	1
1	13	3	21.75	22.25	-14.63	16.81	-0.52	1
1	13	5	20.46	18.56	6.41	17.42	1.90	1
1	13	6	28.86	29.36	-24.00	16.91	-0.49	1
1	13	7	21.58	18.07	-2.03	-17.95	3.51	1
1	13	8	25.61	23.17	25.42	6.25	2.44	1
1	13	9	15.87	11.18	-4.35	-10.30	4.69	1
1	13	10	22.24	18.25	-15.91	8.94	3.99	1
1	13	13	14.99	11.33	11.33	-0.14	3.66	1
1	13	14	11.34	12.28	-8.21	-9.14	-0.95	1
1	13	15	14.20	12.95	-4.98	11.95	1.25	1
1	14	0	14.12	8.49	-0.00	8.49	5.63	1
1	14	1	15.77	14.95	14.56	-3.39	0.83	1
1	14	2	22.27	23.21	-16.66	-15.96	-0.94	1
1	14	6	16.92	14.54	-14.04	-3.79	2.38	1
1	14	7	23.71	22.40	-19.38	11.23	1.31	1
1	14	8	15.13	13.77	11.06	8.20	1.36	1
1	15	0	16.05	16.83	0.00	16.83	-0.78	1
1	15	1	11.34	9.28	-9.18	1.31	2.06	1
1	15	2	13.05	8.91	4.53	-7.67	4.14	1
1	15	3	15.91	12.70	12.68	0.57	3.21	1
1	15	4	12.90	4.61	-1.70	4.29	8.29	1
1	15	6	20.94	21.32	-3.26	-21.07	-0.38	1
1	16	0	12.87	15.14	-0.00	-15.14	-2.26	1
1	16	3	11.36	10.80	5.20	-9.47	0.55	1
1	16	4	12.56	14.31	0.41	-14.30	-1.74	1
1	16	5	9.59	5.38	4.71	2.59	4.22	1
1	16	6	15.39	14.62	-6.49	13.10	0.77	1
1	16	7	9.21	6.71	1.51	-6.54	2.50	1
2	0	4	60.86	58.46	58.46	-0.00	2.39	1
2	0	5	14.03	19.09	0.00	-19.09	-5.06	1
2	0	6	174.78	174.65	174.65	-0.00	0.13	1
2	0	7	138.62	119.91	0.00	119.91	18.71	1
2	0	8	99.29	94.92	94.92	-0.00	4.37	1
2	0	9	132.66	128.11	-0.00	-128.11	4.56	1
2	0	10	141.49	122.13	-122.13	0.00	19.35	1
2	0	11	109.33	87.82	0.00	87.82	21.51	1
2	0	12	45.38	12.89	12.89	-0.00	32.50	1
2	0	13	88.82	82.43	-0.00	-82.43	6.39	1
2	0	14	10.91	14.41	-14.41	0.00	-3.49	1
2	0	15	83.19	73.95	0.00	73.95	9.25	1
2	0	16	9.80	8.96	-8.96	0.00	0.84	1
2	0	17	7.24	5.23	0.00	-5.23	2.01	1
2	0	18	65.24	52.05	52.05	-0.00	13.18	1
2	0	19	75.29	64.50	0.00	64.50	10.79	1
2	0	20	13.95	10.19	10.19	-0.00	3.76	1
2	0	21	8.26	5.26	-0.00	-5.26	3.00	1
2	0	22	8.42	2.23	2.23	-0.00	6.18	1
2	0	23	12.01	13.96	-0.00	-13.96	-1.94	1
2	0	24	14.72	19.22	-19.22	0.00	-4.50	1
2	0	25	11.88	18.03	-0.00	-18.03	-6.15	1
2	1	3	113.27	93.28	26.57	-89.71	19.99	1
2	1	4	121.91	111.46	88.44	-67.83	10.45	1
2	1	5	119.42	120.54	60.19	104.44	-1.13	1
2	1	6	124.66	108.31	-102.94	-33.37	16.34	1
2	1	7	113.50	100.88	-36.70	93.94	12.65	1
2	1	8	51.89	52.84	49.07	19.58	-0.95	1
2	1	9	51.62	45.14	-2.43	45.07	6.48	1
2	1	10	30.10	28.24	4.70	27.84	1.94	1
2	1	11	97.06	101.32	20.45	-99.23	-4.26	1
2	1	12	36.62	27.92	-27.90	0.90	8.70	1
2	1	13	84.64	75.15	51.89	-54.36	9.48	1
2	1	14	45.30	42.32	-2.49	-42.24	2.98	1
2	1	15	13.32	12.82	-5.01	-11.80	0.49	1
2	1	16	83.00	86.39	-23.67	-83.08	-3.39	1
2	1	17	14.54	16.48	8.61	14.05	-1.94	1
2	1	18	26.19	24.98	21.67	12.41	1.21	1
2	1	19	33.23	31.26	30.49	6.89	1.96	1
2	1	20	41.17	43.85	-31.03	30.98	-2.68	1
2	1	21	14.32	17.38	-17.32	-1.45	-3.06	1
2	1	22	35.72	38.23	38.14	-2.67	-2.51	1
2	1	23	20.81	21.11	1.09	-21.08	-0.30	1
2	1	24	24.02	26.60	-26.42	-3.12	-2.58	1
2	1	25	23.75	24.56	-12.57	-21.10	-0.81	1
2	1	26	18.33	20.94	20.74	-2.85	-2.61	1
2	1	27	15.81	16.38	16.34	1.18	-0.57	1
2	2	0	49.79	41.90	41.90	0.00	7.89	1
2	2	1	100.59	85.27	60.37	60.22	15.32	1
2	2	2	84.48	72.76	72.75	0.59	11.72	1
2	2	3	231.42	225.75	216.90	62.55	5.67	1
2	2	4	55.76	43.56	-36.36	-23.99	12.20	1
2	2	5	69.03	57.53	23.40	52.55	11.50	1
2	2	6	83.64	85.49	44.99	73.85	-2.85	1
2	2	7	93.16	100.44	-40.69	-91.83	-7.28	1
2	2	8	63.10	55.34	35.24	-41.96	6.76	1
2	2	9	86.71	107.83	-83.97	67.78	-21.12	1
2	2	10	18.20	16.51	-11.81	11.54	1.70	1
2	2	11	77.93	66.44	-52.44	-40.79	11.49	1
2	2	12	95.62	89.04	-45.68	-76.42	6.58	1
2	2	13	73.33	69.14	62.94	28.62	4.18	1
2	2	14	76.95	75.75	9.16	75.19	1.21	1
2	2	15	80.58	88.08	63.25	-61.30	-7.50	1
2	2	16	22.34	25.36	17.02	-18.80	-3.02	1
2	2	17	45.36	47.51	7.70	46.88	-2.14	1
2	2	18	25.59	25.56	-19.33	21.29	0.03	1
2	2	19	22.35	23.42	-2.82	-23.25	-1.07	1
2	2	20	19.91	19.87	-0.05	-19.87	0.04	1
2	2	21	31.12	36.02	-27.09	-23.74	-4.90	1
2	2	23	8.50	12.39	-5.68	11.01	-3.88	1
2	2	24	18.96	20.24	3.14	19.99	-1.28	1
2	2	25	14.49	14.97	13.51	5.78	-0.48	1
2	2	26	14.12	11.37	-6.46	-9.36	2.75	1
2	2	27	15.69	17.96	17.50	4.04	-2.28	1
2	3	0	122.46	105.28	105.28	-0.00	17.18	1
2	3	1	169.62	168.90	-167.81	-19.14	0.73	1
2	3	2	98.41	89.09	24.59	85.63	9.33	1
2	3	3	117.43	103.36	41.65	94.59	14.07	1
2	3	4	122.79	125.91	-71.57	103.38	-3.12	1
2	3	5	116.55	100.77	-88.66	47.90	15.77	1
2	3	6	24.17	18.68	13.28	13.13	5.45	1
2	3	7	77.10	78.65	50.72	60.11	-1.55	1
2	3	8	81.23	78.15	46.35	-62.92	3.08	1
2	3	9	41.87	39.01	-0.23	39.01	2.85	1
2	3	10	41.91	44.11	27.03	-34.85	-2.20	1
2	3	11	14.16	16.36	-6.06	-15.20	-2.20	1
2	3	12	26.43	27.80	12.35	24.91	-1.38	1
2	3	13	40.67	46.51	16.68	-43.42	-5.84	1
2	3	14	26.57	24.18	7.96	22.83	2.40	1
2	3	15	39.23	41.56	-19.55	36.68	-2.33	1
2	3	16	57.78	55.32	-26.52	48.55	2.46	1
2	3	17	21.22	24.98	21.75	12.28	-3.76	1
2	3	18	13.45	13.60	-8.60	-10.36	-0.14	1
2	3	19	45.31	42.56	-32.97	26.97	2.75	1
2	3	20	8.21	19.30	3.16	-19.04	-11.09	1
2	3	21	39.29	42.41	41.82	7.04	-3.12	1
2	3	23	24.05	27.33	-12.50	-24.30	-3.28	1
2	3	24	16.87	20.58	16.29	9.43	-3.69	1
2	3	25	8.31	10.26	9.95	-2.51	-1.95	1
2	3	26	13.96	15.61	3.35	16.33	-2.65	1
2	3	27	15.43	16.67	-14.57	8.10	-1.24	1
2	4	0	143.65	153.80	153.80	-0.00	-10.15	1
2	4	1	41.07	38.52	24.69	-29.57	2.55	1
2	4	2	46.56	49.37	48.60	-8.68	-2.81	1
2	4	3	42.68	34.96	-34.75	3.85	7.72	1
2	4	4	103.51	92.59	-74.52	54.96	10.91	1
2	4	5	77.20	66.45	34.40	56.85	10.75	1
2	4	6	91.35	87.53	-86.67	-12.24	3.82	1
2	4	7	44.32	46.03	3.41	-45.90	-1.71	1
2	4	8	72.03	69.88	-2.88	69.83	2.15	1
2	4	9	82.69	73.33	58.85	43.76	9.35	1
2	4	10	94.95	101.00	46.29	-89.77	-6.05	1
2	4	11	43.41	43.32	39.78	-17.15	0.09	1
2	4	12	68.33	74.54	35.94	65.30	-6.21	1
2	4	13	33.72	32.01	6.96	31.25	1.71	1
2	4	14	38.97	41.46	31.52	-26.57	-2.49	1
2	4	15	22.65	22.81	-1.32	-22.77	-0.16	1
2	4	16	34.85	30.22	-24.98	17.01	4.63	1
2	4	17	10.88	12.96	-4.09	-12.30	-2.08	1
2	4	18	29.68	25.97	-25.89	-2.08	3.71	1
2	4	19	25.75	26.04	25.16	6.73	-0.29	1
2	4	21	14.62	18.63	8.53	16.40	-4.01	1
2	4	22	26.89	24.86	-23.28	-8.72	2.03	1
2	4	23	12.00	16.92	-15.62	6.50	-4.91	1
2	4	24	23.72	23.87	23.41	-4.65	-0.15	1
2	5	0	78.95	76.20	-76.20	0.00	2.75	1
2	5	1	53.11	59.77	29.65	51.90	-6.66	1
2	5	2	66.09	47.74	46.39	11.27	18.35	1
2	5	3	81.37	85.45	-85.34	-4.27	-4.08	1
2	5	4	75.50	68.31	-59.31	33.89	7.19	1
2	5	5	18.11	25.33	16.62	-19.11	-7.22	1
2	5	6	72.65	60.17	59.50	8.94	12.49	1
2	5	7	37.74	40.45	16.62	-36.88	-2.71	1
2	5	8	65.70	54.66	-27.10	-47.47	11.03	1
2	5	9	34.31	26.90	21.70	-15.90	7.41	1
2	5	10	35.61	38.30	17.94	-33.84	-2.70	1
2	5	11	59.33	63.22	5.34	62.99	-3.89	1
2	5	12	23.14	24.24	-18.49	-15.68	-1.10	1
2	5	13	29.40	30.55	30.43	2.61	-1.14	1
2	5	14	12.44	16.99	-6.01	15.89	-4.54	1
2	5	15	37.90	35.46	20.08	-29.22	2.44	1
2	5	16	32.57	36.21	20.42	29.90	-3.64	1
2	5	18	14.05	6.31	5.55	2.37	7.74	1
2	5	19	31.01	32.43	18.22	-26.83	-1.42	1
2	5	20	33.67	34.40	11.59	-32.35	-0.73	1
2	5	21	26.56	28.65	-26.91	10.37	-1.99	1
2	5	22	31.80	32.16	-32.01	-3.19	-0.36	1
2	5	23	15.86	14.91	4.24	14.30	1.95	1
2	5	24	11.70	11.92	11.77	1.91	-0.22	1
2	5	25	13.91	15.92	-14.57	6.47	-2.01	1
2	5	26	17.22	20.65	-20.00	5.16	-3.44	1
2	5	27	12.61	13.39	5.78	-10.11	-0.78	1
2	6	0	24.27	15.12	15.12	-0.00	9.12	1
2	6	1	27.69	31.54	-30.16	9.23	-3.85	1
2	6	2	81.17	73.07	-28.27	-67.38	8.10	1
2	6	3	90.53	86.22	-59.44	62.46	4.32	1
2	6	4	83.57	74.65	-50.23	-55.23	8.91	1
2	6	5	8.75	9.10	-5.71	2.15	-0.35	1
2	6	6	30.03	19.43	-9.53	-16.93	10.60	1
2	6	7	38.73	43.95	35.01	26.58	-5.22	1
2	6	8	29.20	27.42	22.47	-15.98	-0.22	1
2	6	9	74.26	72.05	43.84	-57.18	2.21	1
2	6	10	57.32	53.29	-19.61	49.55	4.03	1
2	6	11	63.00	62.72	27.40	56.42	0.28	1
2	6	12	26.40	26.23	-24.62	-9.07	0.16	1
2	6	13	41.19	44.56	-38.16	-23.00	-3.37	1
2	6	14	18.39	11.95	-3.57	-11.40	6.44	1
2	6	15	61.84	64.29	-30.22	56.75	-2.45	1
2	6	16	33.69	36.30	33.70	-13.48	-2.61	1
2	6	17	58.06	67.16	10.65	-66.31	-9.09	1
2	6	18	26.22	28.33	-23.06	-16.46	-2.11	1
2	6	19	35.70	39.23	22.04	32.44	-3.53	1
2	6	21	14.73	14.57	13.79	4.69	0.16	1
2	7	0	28.15	29.52	29.52	-0.00	-1.37	1
2	7	1	52.09	41.88	15.82	38.78	10.21	1
2	7	2	108.56	116.51	-91.04	-72.71	-7.95	1
2	7	3	67.48	66.46	-33.06	57.65	1.02	1
2	7	4	101.16	99.31	96.02	-15.95	1.85	1
2	7	5	42.69	31.87	31.82	1.68	10.82	1
2	7	6	61.88	53.34	-47.01	25.20	8.54	1
2	7	7	33.43	25.27	-8.34	-23.86	8.16	1
2	7	8	58.15	61.96	15.45	59.15	-3.81	1
2	7	9	11.92	16.71	-13.21	10.23	-4.79	1
2	7	10	22.35	25.62	-17.37	18.83	-3.27	1
2	7	11	37.01	39.61	-14.10	37.02	-2.61	1
2	7	12	16.67	14.22	-13.80	3.42	2.45	1
2	7	13	35.88	38.33	11.25	36.64	-2.45	1
2	7	14	29.35	40.13	30.07	-26.59	-10.79	1
2	7	15	27.81	32.71	27.71	-17.39	-4.91	1
2	7	16	30.65	35.16	-16.96	-30.80	-4.51	1
2	7	17	31.18	29.95	-8.98	-28.60	1.23	1
2	7	18	24.69	24.07	11.76	23.26	0.61	1
2	7	20	26.88	27.02	-14.38	22.87	-0.14	1
2	7	21	8.44	9.03	7.53	-4.99	-0.60	1
2	7	22	8.31	17.48	13.77	10.76	-9.17	1
2	7	23	8.10	12.12	10.29	6.41	-4.02	1
2	7	24	19.15	24.67	-20.44	-13.81	-5.53	1
2	8	0	52.71	41.90	-41.90	0.00	10.82	1
2	8	1	42.26	31.82	-31.32	-5.64	10.44	1
2	8	2	37.52	33.04	-0.98	33.03	4.48	1
2	8	3	34.05	30.36	24.68	-17.69	3.71	1
2	8	4	21.37	15.21	15.09	-1.96	6.16	1
2	8	5	43.84	48.51	8.91	47.69	-4.68	1
2	8	6	60.22	62.44	60.11	16.90	-2.22	1
2	8	7	22.38	21.14	-1.31	-21.10	1.23	1
2	8	8	57.70	56.30	10.52	-55.31	1.40	1
2	8	9	20.82	24.58	-8.06	21.09	-1.76	1
2	8	10	72.51	69.28	-34.29	60.19	3.23	1
2	8	11	36.03	39.28	13.34	-36.94	-3.25	1
2	8	12	33.28	27.47	-24.42	-14.62	4.82	1
2	8	13	17.89	18.47	15.95	9.40	-0.58	1
2	8	14	25.78	30.95	-14.35	27.43	-5.17	1
2	8	15	31.00	37.62	17.99	-33.04	-6.62	1
2	8	16	26.54	36.81	35.86	8.31	-10.27	1
2	8	17	33.88	38.63	0.16	38.63	-4.74	1
2	8	18	34.02	32.35	32.30	-1.83	1.67	1
2	8	19	16.94	15.46	-15.01	-3.70	1.52	1
2	8	22	13.96	16.57	-16.55	0.79	-2.61	1
2	8	23	7.78	12.70	10.90	-6.51	-4.92	1
2	9	0	16.03	9.73	-9.73	-0.00	6.30	1
2	9	1	40.60	41.97	-25.89	-31.75	-0.36	1
2	9	2	26.96	27.25	21.57	16.65	-0.29	1
2	9	3	69.91	65.46	65.30	4.53	4.45	1
2	9	4	20.68	21.58	-19.68	8.81	-0.89	1
2	9	5	53.27	55.53	-10.91	54.45	-2.26	1
2	9	6	7.40	4.33	2.45	-3.57	3.14	1
2	9	7	26.26	23.93	16.64	17.21	2.33	1
2	9	8	21.77	25.26	-16.59	19.05	-3.49	1
2	9	9	36.66	35.93	-24.48	-26.30	0.73	1
2	9	11	25.50	24.85	-5.13	-24.31	0.65	1
2	9	12	32.74	40.64	25.09	31.97	-7.89	1
2	9	13	16.60	14.25	-12.19	-7.39	2.35	1
2	9	14	8.40	11.25	-3.25	-10.76	-2.86	1
2	9	15	8.47	14.73	9.48	11.27	-6.26	1
2	9	17	24.04	31.60	20.23	24.25	-7.56	1
2	9	18	8.46	14.02	-13.93	3.28	-5.56	1
2	9	19	11.82	21.14	-15.91	13.91	-9.32	1
2	9	21	15.93	23.40	21.61	-8.97	-7.47	1
2	9	23	20.72	22.83	-20.99	-8.99	-2.11	1
2	10	0	15.41	13.57	-13.57	0.00	1.84	1
2	10	1	39.35	41.28	36.68	18.86	-1.93	1
2	10	2	17.30	18.35	-9.51	15.69	-1.04	1
2	10	3	19.04	14.97	7.94	-12.69	4.07	1
2	10	4	28.21	33.61	-31.53	11.66	-5.41	1
2	10	5	17.63	13.41	13.41	-0.10	4.22	1
2	10	6	33.74	41.25	-22.64	-34.50	-7.52	1
2	10	7	13.91	15.19	-13.41	-7.13	-1.28	1
2	10	8	30.36	39.10	-19.97	33.61	-8.73	1
2	10	9	11.60	14.37	-14.06	-2.96	-2.77	1
2	10	10	38.85	41.63	2.39	-41.56	-2.77	1
2	10	11	8.36	6.12	-0.10	6.12	2.24	1
2	10	12	16.86	18.95	9.67	16.30	-2.09	1
2	10	13	18.96	25.01	20.76	13.94	-6.05	1
2	10	14	24.05	25.04	1.98	-24.96	-0.99	1
2	10	15	19.00	16.41	9.65	-13.27	2.59	1
2	10	16	11.96	17.35	-13.34	11.45	-5.39	1
2	10	17	20.51	25.56	15.79	20.10	-5.06	1
2	10	20	11.04	15.87	5.50	14.89	-4.83	1
2	10	21	13.00	15.57	-15.56	0.51	-2.57	1
2	11	0	52.26	55.96	-55.96	0.00	-3.70	1
2	11	1	23.10	14.25	11.12	-8.91	8.86	1
2	11	2	39.24	34.17	25.88	21.69	5.12	1
2	11	3	25.95	31.96	-27.39	16.46	-6.01	1
2	11	4	28.53	26.00	-25.55	4.87	2.53	1
2	11	6	20.38	20.38	19.37	-6.32	0.00	1
2	11	7	26.45	30.10	-29.37	-6.59	-3.64	1
2	11	8	14.57	13.67	-10.14	-9.16	0.90	1
2	11	14	33.71	35.54	-19.57	29.67	-1.83	1
2	12	0	26.72	20.57	20.57	-0.00	6.15	1
2	12	1	29.28	24.30	-24.36	-1.11	5.19	1
2	12	5	26.85	26.77	-7.98	-25.51	0.12	1
2	12	6	17.00	18.97	-7.92	17.24	-1.97	1
2	12	8	12.02	14.18	-0.20	-14.18	-2.16	1
2	12	11	18.81	19.03	-1.46	18.97	-0.22	1
2	12	12	20.44	22.89	22.50	-4.19	-2.45	1
2	12	13	23.33	28.88	0.57	-28.87	-5.55	1
2	12	14	8.12	12.07	-0.18	12.07	-3.95	1
2	12	15	25.15	30.59	-19.41	23.64	-5.43	1
2	12	17	16.76	20.83	-2.70	-20.65	-4.06	1
2	13	0	47.99	43.79	43.79	-0.00	4.20	1
2	13	1	18.96	12.56	-3.77	11.98	6.40	1
2	13	2	26.82	28.78	-28.78	0.50	-1.97	1
2	13	3	8.48	2.36	-0.77	-2.23	6.11	1
2	13	4	23.92	25.88	21.22	14.81	-1.96	1
2	13	5	8.44	14.37	-7.69	-12.21	-5.94	1
2	13	6	8.42	13.39	-12.90	-3.60	-4.98	1
2	13	7	20.52	23.90	6.35	-23.04	-3.38	1
2	13	8	16.65	18.35	14.35	-0.22	[illegible]	1
2	13	9	11.67	15.84	7.63	13.89	-4.17	1
2	14	0	11.59	14.49	-14.49	0.00	-2.90	1
2	14	2	8.17	12.23	7.20	-9.89	-4.06	1
2	14	5	13.97	19.26	-17.88	7.14	-5.29	1
2	15	1	13.08	16.92	-16.60	-3.15	-3.84	1
2	15	2	10.65	15.56	2.23	-15.40	-4.91	1
3	1	3	31.50	23.43	6.99	22.34	[illegible]	1
3	1	4	101.21	115.13	-113.47	-19.49	-13.92	1
3	1	5	123.12	110.40	-82.27	73.62	12.72	1
3	1	6	39.17	44.86	31.53	31.91	-5.69	1
3	1	7	96.04	86.59	21.17	-84.27	9.45	1
3	1	8	43.18	21.91	-21.68	3.16	21.27	1
3	1	9	44.13	32.46	-19.12	-26.23	11.67	1
3	1	10	34.22	38.11	4.54	-37.84	-3.89	1
3	1	11	49.76	50.27	49.81	12.03	-0.51	1
3	1	12	63.35	66.05	-24.19	-61.46	-2.67	1
3	1	13	15.48	14.24	-14.19	-1.26	[illegible]	1
3	1	14	41.80	38.74	37.36	-10.98	[illegible]	1
3	1	15	67.35	63.36	11.64	62.29	3.99	1
3	1	16	42.17	45.65	-26.58	37.11	-3.48	1
3	1	17	33.21	29.41	-4.83	-28.40	[illegible]	1
3	1	18	8.61	4.98	-4.41	2.31	3.63	1
3	1	19	12.59	5.88	-4.37	-3.94	6.71	1
3	1	20	20.45	22.71	-21.28	7.92	-2.26	1
3	1	21	29.53	36.52	-2.34	-36.46	[illegible]	1
3	1	22	32.78	34.19	2.98	-34.06	[illegible]	1
3	1	23	23.29	24.48	4.75	24.02	[illegible]	1
3	2	0	43.14	21.15	-0.00	-21.15	[illegible]	1
3	2	1	152.23	127.79	97.27	82.89	24.44	1
3	2	2	153.51	143.41	12.27	142.89	[illegible]	1
3	2	3	62.81	39.02	-32.72	21.27	23.79	1
3	2	4	40.50	37.10	-2.88	-37.99	2.41	1
3	2	5	36.96	23.00	22.53	-4.66	13.45	1
3	2	6	45.66	46.30	-42.57	18.18	[illegible]	1
3	2	7	78.18	76.55	-75.56	-12.25	[illegible]	1
3	2	8	96.91	95.16	92.80	-25.19	[illegible]	1
3	2	9	102.85	125.95	121.38	33.64	[illegible]	1
3	2	10	30.83	28.09	20.48	19.23	2.74	1
3	2	11	27.05	19.82	-7.00	-18.54	[illegible]	1
3	2	12	28.52	26.67	10.60	24.47	1.85	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
3	2	13	99.15	96.02	95.31	11.65	3.12	1
3	2	14	71.42	75.59	-68.00	33.01	-4.17	1
3	2	15	55.31	55.65	-52.65	18.05	-0.34	1
3	2	16	18.07	11.39	11.20	-2.11	6.67	1
3	2	17	42.83	43.29	-42.78	-6.62	-0.46	1
3	2	18	49.22	51.50	5.79	-50.74	-2.28	1
3	2	19	15.54	18.19	-15.34	9.79	-2.65	1
3	2	20	13.01	12.43	0.36	12.42	0.58	1
3	2	21	32.48	31.74	21.31	-23.52	0.74	1
3	3	0	185.25	159.79	0.00	159.79	25.46	1
3	3	1	24.84	14.15	-13.63	3.81	10.69	1
3	3	2	117.85	101.82	-73.84	-70.11	16.03	1
3	3	3	67.64	62.47	-6.40	62.14	5.16	1
3	3	4	55.37	38.95	-10.07	-37.63	16.42	1
3	3	5	80.03	79.32	42.07	67.24	0.71	1
3	3	6	92.95	90.46	4.87	-90.33	2.50	1
3	3	7	20.32	21.26	-4.08	-20.87	-0.94	1
3	3	8	93.47	91.97	84.61	36.07	1.50	1
3	3	9	71.73	68.94	37.40	-57.91	2.79	1
3	3	10	50.62	40.88	40.87	0.82	9.74	1
3	3	11	79.15	78.47	-63.58	-46.00	0.67	1
3	3	12	47.23	51.25	9.76	50.31	-4.02	1
3	3	13	10.30	13.88	-4.67	13.07	-3.58	1
3	3	14	30.45	32.26	2.55	32.16	-1.81	1
3	3	15	37.22	41.17	-31.96	25.95	-3.94	1
3	3	16	66.01	69.54	7.01	-69.18	-3.53	1
3	3	17	36.29	41.03	39.41	-11.43	-4.74	1
3	3	19	25.69	24.99	-24.26	-6.02	0.70	1
3	3	20	37.13	47.50	2.04	-47.46	-10.37	1
3	3	21	16.32	20.57	0.76	-20.56	-4.25	1
3	3	22	44.56	52.73	15.88	50.29	-8.17	1
3	3	23	21.21	22.66	-7.97	-20.35	-1.45	1
3	4	0	58.16	41.07	-0.00	-41.07	17.10	1
3	4	1	42.48	33.42	-32.57	-7.46	9.07	1
3	4	2	136.44	101.25	-90.67	-45.06	35.19	1
3	4	3	60.72	48.11	41.50	-24.33	12.61	1
3	4	4	120.43	98.17	-7.69	97.87	22.25	1
3	4	5	57.81	58.74	-45.54	-37.10	-0.93	1
3	4	6	65.43	49.95	-5.73	-49.62	15.48	1
3	4	7	70.15	62.49	44.98	-43.39	7.66	1
3	4	8	53.18	67.54	66.44	12.14	-14.35	1
3	4	9	76.38	79.65	-50.05	61.96	-3.27	1
3	4	10	53.52	51.95	49.49	-15.80	1.57	1
3	4	11	60.44	62.67	41.52	46.67	-2.22	1
3	4	12	17.83	15.50	1.92	15.38	2.33	1
3	4	13	35.56	50.24	-39.03	-31.67	-14.68	1
3	4	14	44.60	51.45	-50.58	9.40	-6.85	1
3	4	15	41.74	52.32	43.23	-29.48	-10.58	1
3	4	16	14.68	19.35	-0.24	-19.35	-4.67	1
3	4	17	8.75	13.14	-9.69	8.87	-4.39	1
3	4	18	22.05	22.39	-21.70	-5.53	-0.35	1
3	4	19	26.06	31.41	30.41	-7.90	-5.35	1
3	4	20	26.53	30.17	28.83	-8.89	-3.63	1
3	4	21	16.42	23.78	-20.89	11.36	-7.36	1
3	4	22	13.44	15.36	9.19	12.31	-1.92	1
3	4	23	18.88	21.64	13.83	16.64	-2.76	1
3	5	0	54.20	42.80	-0.00	-42.80	11.40	1
3	5	1	104.11	97.72	-50.41	-83.71	6.40	1
3	5	2	67.18	61.00	38.91	46.98	6.19	1
3	5	3	53.45	54.51	34.94	-41.84	-1.06	1
3	5	4	46.85	49.22	24.57	-42.65	-2.37	1
3	5	5	66.68	62.34	15.38	-60.41	4.34	1
3	5	6	34.49	28.40	-4.06	28.11	6.09	1
3	5	7	74.05	61.71	-3.10	61.64	12.34	1
3	5	8	26.48	20.93	20.08	-5.91	5.55	1
3	5	9	59.42	65.35	-43.03	49.19	-5.93	1
3	5	10	50.81	47.36	-32.09	34.82	3.46	1
3	5	11	27.52	31.18	3.65	30.97	-1.66	1
3	5	12	28.64	28.28	27.50	6.59	0.36	1
3	5	13	7.93	10.00	-5.17	-8.56	-2.07	1
3	5	15	77.72	84.02	31.10	-78.06	-6.31	1
3	5	16	15.14	21.76	15.24	15.53	-6.62	1
3	5	17	12.70	11.84	-1.01	11.80	0.86	1
3	5	18	44.05	52.20	14.33	-50.20	-8.15	1
3	5	19	20.91	26.82	26.47	4.35	-5.92	1
3	5	20	9.46	15.40	-3.63	14.96	-5.94	1
3	5	21	26.59	29.58	5.41	29.39	-2.99	1
3	5	22	9.47	5.50	-3.17	-4.49	3.98	1
3	6	0	60.07	51.11	0.00	51.11	8.96	1
3	6	1	69.25	52.07	-27.12	-44.45	17.18	1
3	6	2	98.29	85.54	75.91	39.43	12.75	1
3	6	3	37.68	55.98	-18.10	52.97	-18.29	1
3	6	4	69.14	58.36	-52.20	26.09	10.79	1
3	6	5	78.77	79.44	78.98	-8.52	-0.65	1
3	6	6	58.60	54.87	19.80	51.17	3.73	1
3	6	7	60.15	52.55	52.55	0.26	7.60	1
3	6	8	51.02	57.21	-55.21	15.00	-6.19	1
3	6	9	7.36	10.88	1.30	10.80	-3.52	1
3	6	10	44.88	33.13	31.16	-11.25	11.76	1
3	6	11	62.59	68.95	-63.28	27.45	-6.36	1
3	6	12	55.32	57.09	-57.07	1.58	-1.78	1
3	6	13	5.88	4.84	0.51	4.79	1.03	1
3	6	14	43.65	46.33	42.18	-19.17	-2.68	1
3	6	15	24.88	22.96	-2.27	-22.85	1.92	1
3	6	16	22.07	27.82	-20.48	18.83	-5.75	1
3	6	17	36.80	39.42	37.19	13.06	-2.62	1
3	6	18	18.70	26.05	2.48	25.93	-7.35	1
3	6	19	26.76	28.16	27.22	7.20	-1.40	1
3	7	0	15.41	11.07	0.00	-11.07	4.34	1
3	7	1	59.52	47.36	-6.44	47.22	12.16	1
3	7	2	48.61	47.29	27.90	-38.42	1.32	1
3	7	3	58.69	47.15	-4.12	-46.97	11.54	1
3	7	4	42.04	28.05	19.94	-19.73	13.99	1
3	7	5	38.89	37.54	-31.57	20.32	1.35	1
3	7	6	58.88	47.98	7.40	47.41	10.90	1
3	7	7	23.77	18.54	3.10	-18.28	5.23	1
3	7	8	54.93	49.26	-47.87	11.61	5.67	1
3	7	9	56.27	50.58	-28.51	41.78	5.69	1
3	7	10	32.32	41.24	34.78	-25.01	-8.91	1
3	7	11	16.58	22.64	20.13	10.35	-6.06	1
3	7	12	31.80	28.69	-3.97	-28.41	3.11	1
3	7	13	24.63	18.67	-10.76	-15.26	5.96	1
3	7	14	8.91	13.92	13.66	2.69	-5.01	1
3	7	15	22.28	24.39	-0.37	24.38	-2.11	1
3	7	16	32.08	23.47	18.25	14.76	8.61	1
3	7	17	44.04	47.74	-27.14	-39.28	-3.70	1
3	7	20	13.39	18.26	-2.50	18.09	-4.86	1
3	7	21	9.37	22.06	6.72	-18.83	-12.70	1
3	7	23	12.59	20.27	5.63	19.47	-7.68	1
3	8	1	51.56	42.46	42.11	5.45	9.10	1
3	8	2	52.11	47.27	36.11	30.50	4.84	1
3	8	3	52.50	40.69	5.28	40.35	11.81	1
3	8	4	92.21	98.90	73.05	-66.67	-6.70	1
3	8	5	17.53	10.72	10.72	0.25	6.81	1
3	8	6	40.57	32.71	-19.44	27.02	7.86	1
3	8	7	46.49	51.58	-48.26	-18.19	-5.09	1
3	8	8	18.43	8.62	-2.05	-8.37	9.81	1
3	8	9	29.11	27.82	24.58	13.03	1.29	1
3	8	10	42.85	42.06	-42.04	-1.46	0.79	1
3	8	13	28.70	29.15	19.06	23.63	-0.45	1
3	8	16	32.72	37.43	37.14	-4.69	-4.71	1
3	8	17	9.49	15.93	9.63	12.72	-6.44	1
3	8	18	9.49	8.64	-8.63	0.08	0.86	1
3	8	19	23.13	27.14	-27.13	-0.29	-4.00	1
3	8	20	9.32	11.55	0.93	11.52	-2.24	1
3	8	21	9.13	18.71	9.47	-16.14	-9.58	1
3	8	22	12.52	16.34	-11.41	-11.70	-3.82	1
3	9	0	14.19	14.12	-0.00	-14.12	0.07	1
3	9	1	11.60	10.03	-4.27	9.08	1.57	1
3	9	2	55.83	48.12	34.71	-33.34	7.70	1
3	9	3	59.13	54.95	-23.90	49.48	4.18	1
3	9	4	44.95	43.42	-7.57	42.76	1.53	1
3	9	5	14.60	13.80	-13.36	3.48	0.80	1
3	9	6	14.78	15.83	-15.65	2.38	-1.05	1
3	9	7	8.63	4.04	1.53	-3.74	4.59	1
3	9	8	27.70	31.68	16.97	26.75	-3.99	1
3	9	9	41.67	48.35	21.16	-43.47	-6.68	1
3	9	10	20.15	23.07	21.13	-9.26	-2.92	1
3	9	11	18.27	21.42	-16.95	-13.10	-3.15	1
3	9	13	22.93	24.88	24.85	-1.26	-1.95	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
3	9	15	26.85	30.77	-30.77	0.60	-3.93	1
3	9	17	16.40	27.98	25.03	12.50	-11.57	1
3	9	18	37.54	46.37	21.23	41.22	-8.83	1
3	9	19	13.06	23.18	-12.89	-19.27	-10.11	1
3	10	0	49.63	51.50	0.00	51.50	-1.88	1
3	10	1	27.77	21.46	9.05	19.46	6.31	1
3	10	2	44.89	44.91	8.65	-44.07	-0.01	1
3	10	3	33.08	29.83	29.56	-3.95	3.25	1
3	10	4	41.70	41.27	-11.60	39.61	0.43	1
3	10	5	50.65	46.81	-46.74	2.52	3.83	1
3	10	6	18.05	10.95	1.65	-10.83	7.10	1
3	10	7	18.21	18.63	0.84	18.61	-0.42	1
3	10	9	22.70	26.56	-22.66	13.86	-3.86	1
3	10	11	54.09	65.31	54.80	-35.54	-11.22	1
3	10	13	13.43	14.85	-9.25	11.62	-1.42	1
3	10	15	9.46	11.38	6.92	9.04	-1.92	1
3	10	16	13.28	16.90	0.85	-16.88	-3.63	1
3	10	17	9.26	14.26	-14.26	0.03	-5.00	1
3	11	0	22.61	23.61	-0.00	23.61	-1.00	1
3	11	1	13.07	5.75	5.27	2.29	7.33	1
3	11	2	39.25	50.75	-19.11	47.02	-11.50	1
3	11	3	22.72	19.17	6.46	18.05	3.55	1
3	11	4	32.24	35.47	3.60	-35.28	-3.23	1
3	11	5	9.34	16.92	-15.11	7.61	-7.58	1
3	11	6	32.50	32.53	-28.56	-15.56	-0.03	1
3	11	7	13.33	15.36	1.57	15.28	-2.04	1
3	11	8	26.75	30.56	26.60	-15.03	-3.81	1
3	11	9	18.97	20.08	-13.84	-14.55	-1.11	1
3	11	10	23.28	25.99	-2.54	25.87	-2.71	1
3	11	11	19.01	22.54	15.89	-15.98	-3.53	1
3	11	12	18.97	23.76	6.26	22.92	-4.79	1
3	11	13	16.33	21.98	-19.87	9.40	-5.65	1
3	11	14	13.22	11.43	-11.31	-1.63	1.79	1
3	11	15	9.22	15.29	15.18	-1.87	-6.07	1
3	12	0	13.41	12.11	-0.00	-12.11	1.31	1
3	12	1	16.43	20.85	-0.32	-20.84	-4.41	1
3	12	2	26.84	27.04	-24.73	10.94	-0.20	1
3	12	4	26.88	32.62	-31.58	8.17	-5.75	1
3	12	6	19.01	19.25	13.90	-13.31	-0.24	1
3	12	7	16.45	20.15	2.78	19.96	-3.70	1
3	12	10	21.02	26.04	24.00	10.11	-5.03	1
3	12	11	16.16	23.62	-20.14	12.34	-7.46	1
3	13	0	13.34	12.29	-0.00	-12.29	1.05	1
3	14	0	15.63	22.19	-0.00	-22.19	-6.56	1
3	0	4	65.01	75.45	75.45	-0.00	-10.44	1
3	0	5	36.57	13.36	-0.00	-13.36	23.21	1
3	0	6	20.74	16.15	16.15	-0.00	4.60	1
3	0	7	94.56	78.82	0.00	78.82	15.74	1
3	0	8	139.29	143.54	-143.54	0.00	-4.25	1
3	0	9	98.05	89.35	-0.00	-89.35	8.70	1
3	0	10	84.35	60.64	-60.64	0.00	23.71	1
3	0	11	59.77	63.24	-0.00	-63.24	-3.47	1
3	0	12	37.46	36.17	-36.17	0.00	1.28	1
3	0	13	23.82	19.16	-0.00	-19.16	4.66	1
3	0	14	69.75	69.45	69.45	-0.00	0.30	1
3	0	16	27.48	19.76	-19.76	0.00	7.72	1
3	0	17	38.78	36.91	0.00	36.91	1.87	1
3	0	20	79.04	80.49	-80.49	0.00	-1.45	1
3	0	21	13.19	17.37	0.00	17.37	-4.19	1
3	0	22	18.91	20.39	-20.39	0.00	-1.48	1
4	1	2	102.70	112.65	-70.03	88.24	-9.95	1
4	1	3	77.45	68.59	-66.55	16.62	8.86	1
4	1	4	116.09	108.58	100.15	41.93	7.51	1
4	1	5	137.25	134.60	60.90	-120.03	2.65	1
4	1	6	49.68	40.13	24.15	-32.04	9.55	1
4	1	7	25.56	21.04	16.11	-13.53	4.52	1
4	1	8	30.94	22.18	19.49	-10.60	8.76	1
4	1	9	61.69	57.89	-2.47	-57.84	3.80	1
4	1	10	72.88	70.29	-39.99	-57.80	2.59	1
4	1	11	116.76	115.66	-13.72	114.84	1.10	1
4	1	12	60.39	50.13	-46.02	19.89	10.25	1
4	1	13	34.50	31.01	-2.65	-30.89	3.49	1
4	1	14	15.10	13.35	-12.93	3.31	1.75	1
4	1	15	17.65	12.90	-10.31	7.75	4.75	1
4	1	16	56.42	51.25	25.40	44.51	5.17	1
4	1	17	54.71	54.50	-2.65	-54.43	0.22	1
4	1	18	44.19	43.78	42.99	-8.32	0.40	1
4	1	19	15.75	14.89	9.46	-11.50	0.86	1
4	1	20	16.10	11.30	-11.13	1.92	4.80	1
4	1	21	13.35	8.99	4.54	-7.76	4.36	1
4	1	22	21.26	14.85	-9.62	-11.31	6.42	1
4	1	23	26.84	26.41	3.46	26.18	0.42	1
4	1	24	20.95	18.92	-17.21	-7.86	2.03	1
4	1	25	15.84	11.76	-6.75	9.63	4.09	1
4	1	26	15.27	14.97	-0.07	14.97	0.29	1
4	1	27	8.58	10.33	-9.50	-4.06	-1.75	1
4	2	0	13.59	16.03	16.03	-0.00	-2.44	1
4	2	1	29.04	23.77	1.36	-23.73	5.27	1
4	2	2	50.43	45.66	-39.38	23.12	4.77	1
4	2	3	121.20	133.21	-127.97	37.00	-12.01	1
4	2	4	28.17	29.51	24.30	-16.73	-1.34	1
4	2	5	83.17	76.40	-7.38	76.04	6.76	1
4	2	6	47.91	38.14	-29.29	24.43	9.78	1
4	2	7	75.28	65.67	1.96	-65.64	9.60	1
4	2	8	32.26	26.08	24.71	8.34	6.18	1
4	2	9	88.35	94.22	94.07	-5.32	-5.87	1
4	2	10	84.75	76.07	-13.64	74.84	8.68	1
4	2	11	58.67	50.67	49.51	10.75	8.00	1
4	2	12	12.11	8.88	-7.98	-3.89	3.23	1
4	2	13	36.66	35.90	-33.59	12.68	0.76	1
4	2	14	21.71	23.46	8.58	-21.83	-1.75	1
4	2	15	16.02	13.20	-11.65	-6.20	2.82	1
4	2	16	32.27	27.13	-8.63	-25.72	5.15	1
4	2	17	48.09	44.06	-28.96	33.21	4.03	1
4	2	18	28.19	23.54	2.87	23.37	4.65	1
4	2	19	31.72	26.88	26.35	5.29	4.84	1
4	2	20	29.54	32.47	-16.79	27.79	-2.92	1
4	2	22	13.45	9.59	4.87	8.27	3.86	1
4	2	23	29.95	30.12	29.20	7.38	-0.16	1
4	2	24	13.20	13.66	-13.61	-1.10	-0.46	1
4	2	25	25.70	28.47	-28.46	0.96	-2.77	1
4	2	26	17.48	23.43	20.18	-11.90	-5.95	1
4	2	27	11.72	11.31	9.05	6.79	0.41	1
4	3	0	28.84	7.44	7.44	-0.00	21.39	1
4	3	1	55.98	45.28	-44.52	15.68	10.70	1
4	3	2	60.42	41.24	-40.67	6.86	19.18	1
4	3	3	55.30	52.95	39.71	35.03	2.35	1
4	3	4	110.46	108.14	-10.08	-107.67	2.32	1
4	3	5	49.57	49.75	-25.91	-42.47	-0.19	1
4	3	6	37.66	39.04	38.70	5.15	-1.38	1
4	3	7	16.02	9.45	-9.35	1.38	6.57	1
4	3	8	57.82	49.47	-49.35	-3.33	8.35	1
4	3	9	60.81	55.94	-36.40	42.48	4.86	1
4	3	10	97.70	89.85	0.16	89.85	7.84	1
4	3	11	39.69	37.01	16.20	33.28	2.67	1
4	3	12	63.86	64.35	23.45	-59.93	-0.49	1
4	3	13	26.17	24.17	20.15	13.36	2.00	1
4	3	14	19.30	21.09	15.65	14.14	-1.79	1
4	3	16	43.34	40.91	-6.39	-40.04	2.42	1
4	3	17	17.57	17.13	-11.84	-12.37	0.44	1
4	3	18	25.55	24.79	-9.51	22.90	0.76	1
4	3	19	24.46	23.15	-11.29	-20.21	1.30	1
4	3	20	16.29	17.05	17.02	1.12	-0.76	1
4	3	21	18.99	16.80	-8.52	14.43	2.19	1
4	3	23	23.09	21.38	-19.67	8.39	1.71	1
4	3	26	17.20	17.21	-2.89	-16.97	-0.02	1
4	4	1	75.94	68.45	-42.69	-53.51	7.49	1
4	4	2	84.78	85.38	-80.77	27.58	-0.60	1
4	4	3	78.87	78.26	76.85	14.81	0.61	1
4	4	4	69.29	56.05	52.77	-18.89	13.24	1
4	4	5	60.83	54.95	-47.52	-27.60	5.88	1
4	4	6	40.39	43.56	42.97	-7.16	-3.17	1
4	4	7	26.03	27.39	9.66	25.63	-1.35	1
4	4	8	30.00	27.48	24.12	-13.16	2.53	1
4	4	9	16.33	18.59	-3.12	-18.33	-2.26	1
4	4	10	35.46	36.57	-24.52	-27.13	-1.11	1
4	4	11	20.50	27.92	6.91	-27.05	-7.42	1
4	4	12	48.33	49.02	-43.46	22.69	-0.69	1
4	4	13	33.30	36.73	19.22	-31.29	-3.42	1
4	4	14	28.22	21.93	-17.12	-13.71	6.29	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
4	4	15	32.68	35.14	-30.31	-17.79	-2.47	1
4	4	16	40.86	43.41	40.43	15.79	-2.55	1
4	4	17	35.85	31.55	26.06	14.42	4.30	1
4	4	18	47.70	59.13	56.13	-18.59	-11.43	1
4	4	19	32.39	35.27	-25.44	24.43	-2.88	1
4	4	20	26.78	28.31	-28.30	0.63	-1.53	1
4	4	21	13.45	12.03	11.93	-1.57	1.42	1
4	4	22	16.42	13.62	-2.56	-13.37	2.80	1
4	4	23	20.91	25.79	-21.80	-13.79	-4.88	1
4	4	24	20.41	20.17	-19.86	-3.51	0.24	1
4	4	25	15.26	18.06	17.90	-2.43	-2.80	1
4	5	0	20.09	16.75	-16.75	-0.00	3.34	1
4	5	1	94.91	90.25	50.45	-40.90	4.67	1
4	5	2	108.40	99.60	-2.64	-99.57	8.79	1
4	5	3	49.99	32.87	-12.79	30.28	17.12	1
4	5	4	8.63	13.76	-9.98	-9.47	-5.13	1
4	5	5	84.27	83.46	21.04	80.76	0.82	1
4	5	6	33.52	29.61	-5.21	-29.15	3.91	1
4	5	7	31.23	31.51	-16.38	-26.92	-0.28	1
4	5	8	49.18	55.67	-14.50	53.66	-6.49	1
4	5	9	57.03	52.38	-42.75	30.27	4.65	1
4	5	10	10.44	11.35	8.57	7.45	-0.91	1
4	5	11	67.55	69.35	-10.52	-68.55	-1.80	1
4	5	12	44.80	49.93	15.24	47.54	-5.13	1
4	5	13	23.16	20.54	5.79	19.70	2.62	1
4	5	14	35.88	37.32	12.45	-35.19	-1.44	1
4	5	15	40.87	44.45	19.39	-40.00	-3.58	1
4	5	16	25.31	24.08	-23.71	4.23	1.23	1
4	5	17	51.81	58.00	-13.10	56.50	-6.18	1
4	5	19	16.37	15.12	12.53	-8.47	1.25	1
4	5	21	16.44	16.43	-3.97	-15.94	0.01	1
4	5	22	13.30	10.66	-0.94	10.62	2.64	1
4	5	23	22.56	23.31	-10.80	-20.66	-0.74	1
4	6	0	62.88	66.81	-66.81	0.00	-3.93	1
4	6	1	36.78	36.51	29.56	21.44	0.27	1
4	6	2	88.13	79.85	76.76	13.12	8.29	1
4	6	3	37.51	44.74	42.20	14.86	-7.23	1
4	6	4	65.33	70.10	-68.29	15.82	-4.76	1
4	6	5	60.71	61.42	54.78	-27.79	-0.71	1
4	6	6	12.18	14.53	-3.65	14.06	-2.35	1
4	6	7	46.20	36.68	-11.71	34.76	9.52	1
4	6	8	29.66	25.99	-24.59	-8.41	3.67	1
4	6	9	48.84	50.59	-50.54	-2.29	-1.75	1
4	6	10	31.41	28.07	27.24	6.77	3.34	1
4	6	11	25.57	28.15	-11.65	25.61	-2.58	1
4	6	13	29.65	34.30	31.89	-12.63	-4.65	1
4	6	14	15.23	16.29	-13.64	8.91	-1.06	1
4	6	15	22.05	20.80	20.69	-2.10	1.25	1
4	6	16	9.19	8.57	-0.33	8.56	0.62	1
4	6	17	13.21	10.54	2.71	10.19	2.67	1
4	6	18	35.37	38.31	-35.96	13.20	-2.94	1
4	6	20	23.27	27.37	24.66	-11.88	-4.10	1
4	6	21	21.05	17.21	-13.44	10.74	3.84	1
4	6	22	20.68	21.70	-21.33	-3.98	-1.01	1
4	6	23	12.72	14.49	6.77	-12.81	-1.77	1
4	6	24	19.34	23.18	23.15	-1.23	-3.84	1
4	6	25	11.62	14.89	11.43	9.55	-3.27	1
4	6	26	13.34	17.49	-17.36	-2.17	-4.16	1
4	7	0	36.52	35.13	35.13	-0.00	1.38	1
4	7	1	22.69	25.97	24.58	-8.37	-3.28	1
4	7	2	33.85	33.65	19.83	27.18	0.21	1
4	7	3	34.17	34.59	-34.58	0.85	-0.43	1
4	7	4	59.01	64.07	-0.68	64.07	-5.06	1
4	7	5	35.14	29.72	-18.91	-22.92	5.42	1
4	7	6	54.49	59.68	-56.82	-18.27	-5.20	1
4	7	7	65.76	61.08	6.93	60.67	4.68	1
4	7	8	27.78	24.12	10.03	-21.94	3.65	1
4	7	9	55.82	54.58	12.43	-53.15	1.24	1
4	7	10	33.34	35.96	20.56	-29.50	-2.61	1
4	7	11	40.02	38.59	24.53	30.18	1.13	1
4	7	12	24.70	27.63	5.82	27.01	-2.93	1
4	7	13	30.91	34.51	3.55	-34.33	-3.60	1
4	7	14	20.36	19.87	1.17	19.83	0.50	1
4	7	15	37.04	41.71	-10.28	40.42	-4.67	1
4	7	16	26.55	32.08	23.13	22.23	-5.53	1
4	7	17	26.80	23.99	-9.89	-21.86	2.81	1
4	7	19	23.25	28.27	0.85	28.26	-5.02	1
4	7	20	26.58	23.98	10.00	-21.80	2.60	1
4	7	21	13.06	12.06	1.54	-5.96	1.00	1
4	7	22	12.72	13.51	5.13	-12.49	-0.79	1
4	8	0	90.54	82.20	82.20	-0.00	8.34	1
4	8	1	39.95	34.92	31.46	15.16	5.03	1
4	8	2	44.51	48.99	-48.30	-8.14	-4.47	1
4	8	3	29.65	25.12	-21.76	12.56	4.53	1
4	8	4	37.54	37.52	-15.12	32.85	0.02	1
4	8	5	26.06	28.29	22.89	-16.62	-2.23	1
4	8	6	25.98	33.64	-33.62	-1.34	-7.66	1
4	8	7	39.14	37.21	11.34	-35.43	1.93	1
4	8	8	24.01	27.25	26.60	-5.90	-3.24	1
4	8	9	21.16	20.19	16.27	-11.96	0.97	1
4	8	12	22.39	21.89	17.84	-12.52	0.50	1
4	8	13	36.96	39.32	-23.71	31.37	-2.36	1
4	8	14	29.59	39.49	19.93	34.27	-9.90	1
4	8	17	13.23	15.93	15.93	0.00	-2.71	1
4	8	20	18.36	21.07	-16.39	-13.23	-2.71	1
4	8	22	19.25	23.95	23.76	2.95	-4.69	1
4	9	0	54.06	54.01	-54.01	0.00	0.05	1
4	9	1	60.37	58.09	-52.33	25.24	2.27	1
4	9	2	33.92	38.65	-21.70	31.99	-4.73	1
4	9	3	26.96	22.91	-7.72	-21.57	4.05	1
4	9	4	21.04	23.52	-20.76	-11.05	-2.49	1
4	9	5	30.02	19.80	-17.12	9.96	10.22	1
4	9	7	28.01	27.29	5.49	-26.73	0.72	1
4	9	9	15.73	17.12	16.97	2.21	-1.39	1
4	9	10	12.99	15.11	-6.75	13.51	-2.12	1
4	9	11	15.10	19.73	5.64	18.90	-4.63	1
4	9	12	39.52	43.10	-11.53	-41.53	-3.58	1
4	9	13	40.12	43.64	-19.14	39.21	-3.51	1
4	9	14	26.89	35.38	-19.19	30.33	-8.49	1
4	9	15	23.30	[illegible]	-1.11	-25.01	-4.73	1
4	9	17	23.07	23.90	0.48	-23.90	-0.83	1
4	10	0	38.10	41.16	-41.16	0.00	-3.05	1
4	10	1	31.13	32.68	-31.59	-8.39	-1.55	1
4	10	2	31.20	30.34	-10.05	-28.63	0.86	1
4	10	3	18.08	11.98	-8.23	-8.70	6.10	1
4	10	4	51.37	50.16	21.02	-46.01	1.21	1
4	10	6	38.77	38.53	-38.47	2.12	0.24	1
4	10	7	20.71	18.91	18.73	2.60	1.80	1
4	10	8	43.77	49.36	8.39	48.64	-5.59	1
4	10	9	32.54	31.16	25.15	-18.40	1.38	1
4	10	10	9.46	6.22	-6.05	1.47	3.23	1
4	10	12	19.02	23.84	-16.42	17.27	-4.82	1
4	10	14	13.39	19.37	-0.20	-19.37	-5.98	1
4	10	15	7.40	17.46	-15.63	-7.82	-10.06	1
4	11	0	20.94	18.18	-18.18	-0.00	2.76	1
4	11	1	32.46	28.93	23.07	-17.51	3.53	1
4	11	3	29.72	22.12	-21.70	4.28	7.60	1
4	11	4	18.84	15.83	8.38	-13.43	3.01	1
4	11	5	40.05	38.71	34.16	18.21	1.34	1
4	11	6	24.79	24.95	24.37	-5.40	-0.17	1
4	11	7	30.01	28.97	-8.51	-27.69	1.04	1
4	11	8	35.57	36.89	3.15	36.75	-1.33	1
4	11	9	40.37	42.73	-31.40	28.97	-2.36	1
4	11	14	21.56	17.45	-3.06	-17.20	4.11	1
4	12	0	35.60	30.72	-30.72	0.00	4.88	1
4	12	1	26.91	27.45	13.34	-23.99	-0.55	1
4	12	2	26.91	27.54	24.91	11.75	-0.64	1
4	12	3	23.30	24.19	16.44	17.75	-0.89	1
4	12	4	13.44	15.10	-6.71	13.52	-1.65	1
4	12	6	18.97	17.76	17.63	-2.16	1.21	1
4	12	7	13.37	16.41	-9.30	13.52	-3.04	1
4	12	8	23.07	23.49	-13.24	-19.39	-0.42	1
4	12	13	15.40	10.93	2.16	-10.72	4.47	1
4	12	14	15.05	17.67	-11.81	13.14	-2.62	1
4	12	15	14.63	14.17	13.68	3.70	0.46	1
4	13	0	14.21	9.72	9.72	-0.00	4.49	1
4	13	1	16.18	16.00	4.54	-15.34	0.18	1
4	13	7	15.77	18.23	-0.00	18.23	-2.46	1
4	13	8	9.01	6.94	-4.68	-5.12	2.07	1
4	13	9	15.41	15.37	-5.34	-14.42	0.04	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
4	13	10	8.76	10.64	-10.51	-1.62	-1.88	1
4	13	11	14.89	15.53	-1.63	16.75	-1.94	1
4	13	12	14.54	19.07	15.81	10.66	-4.53	1
4	13	13	18.25	21.08	3.35	-20.81	-2.82	1
4	14	0	19.69	15.60	15.60	-0.00	4.09	1
4	14	4	15.04	11.00	4.26	10.15	4.04	1
4	14	5	14.92	14.79	13.62	5.75	0.14	1
4	14	6	14.76	20.66	-13.65	-15.51	-5.91	1
4	15	0	13.70	17.41	-17.41	0.00	-3.71	1
4	15	1	7.90	7.69	-7.36	2.24	0.20	1
4	15	2	11.13	15.08	7.08	13.32	-3.95	1
4	0	4	110.27	117.27	-117.27	0.00	-7.01	1
4	0	5	39.70	31.09	-0.00	-31.09	8.61	1
4	0	6	23.04	16.05	-16.05	0.00	6.99	1
4	0	7	41.14	28.14	-0.00	-28.14	13.00	1
4	0	8	15.00	20.43	-20.43	0.00	-5.43	1
4	0	9	39.36	39.38	-0.00	-39.38	-0.02	1
4	0	10	98.71	70.43	70.43	-0.00	28.29	1
4	0	11	76.50	57.05	0.00	57.05	19.45	1
4	0	12	78.53	54.63	54.63	-0.00	23.90	1
4	0	13	20.21	8.54	-0.00	-8.54	11.67	1
4	0	15	29.38	23.59	-0.00	-23.59	5.79	1
4	0	17	64.84	62.82	-0.00	-62.82	2.02	1
4	0	18	84.97	82.25	-82.25	0.00	2.72	1
4	0	20	16.08	14.20	14.20	-0.00	1.88	1
4	0	24	37.53	39.12	39.12	-0.00	-1.59	1
4	0	25	9.16	12.07	0.00	12.07	-2.91	1
4	0	26	19.77	18.85	-18.85	0.00	0.92	1
5	0	4	10.40	18.63	-18.63	0.00	-8.23	1
5	0	5	65.88	70.85	-0.00	-70.85	-4.97	1
5	0	6	75.81	68.57	-68.57	0.00	7.23	1
5	0	7	32.62	29.50	0.00	29.50	3.12	1
5	0	8	46.74	37.06	37.06	-0.00	9.67	1
5	0	9	23.28	15.35	0.00	15.35	7.93	1
5	0	10	19.61	27.01	27.01	-0.00	-7.40	1
5	0	11	47.38	40.97	0.00	40.97	6.39	1
5	0	14	63.91	64.19	-64.19	0.00	-0.28	1
5	0	15	66.70	69.75	-0.00	-69.75	-3.04	1
5	0	19	22.14	12.61	-0.00	-12.61	9.54	1
5	0	21	37.08	40.60	0.00	40.60	-3.52	1
5	1	2	54.81	65.39	46.46	-46.01	-10.58	1
5	1	3	25.62	34.36	12.60	-31.97	-8.74	1
5	1	4	43.27	48.82	-14.97	-46.47	-5.55	1
5	1	5	42.77	47.58	30.39	-36.61	-4.81	1
5	1	6	63.87	69.24	29.17	-62.79	-5.37	1
5	1	7	94.63	107.72	103.38	30.28	-13.09	1
5	1	8	36.60	44.23	-42.74	11.41	-7.64	1
5	1	9	25.00	19.32	-14.96	12.23	5.68	1
5	1	10	50.89	50.37	48.82	12.41	0.52	1
5	1	11	32.47	29.34	-5.72	28.78	3.13	1
5	1	12	36.97	33.82	-33.07	-7.07	3.15	1
5	1	13	42.79	39.52	-30.85	-24.70	3.27	1
5	1	14	50.95	47.05	46.43	7.65	3.90	1
5	1	15	27.76	21.02	5.72	-19.13	6.74	1
5	1	16	20.38	31.01	-25.53	-17.60	-10.63	1
5	1	18	37.57	39.62	33.16	-21.67	-2.05	1
5	1	21	26.23	19.96	3.69	19.61	6.27	1
5	2	0	74.25	98.06	-0.00	-98.06	-23.81	1
5	2	1	90.12	85.89	-16.43	84.30	4.23	1
5	2	3	61.11	46.28	-33.53	-31.91	14.83	1
5	2	4	35.59	44.86	-8.55	-44.04	-9.28	1
5	2	5	54.57	48.74	41.27	25.92	5.84	1
5	2	6	75.38	87.53	0.36	87.53	-12.16	1
5	2	7	80.54	78.87	78.86	0.99	1.67	1
5	2	8	39.87	30.05	-11.20	27.89	9.82	1
5	2	9	29.89	28.78	-28.69	2.22	1.12	1
5	2	10	37.60	36.63	33.56	14.68	0.97	1
5	2	11	27.18	29.48	-26.01	-13.87	-2.30	1
5	2	12	33.48	38.37	-17.85	-33.96	-4.89	1
5	2	13	50.69	54.91	-51.74	-18.37	-4.21	1
5	2	14	27.03	29.13	-9.68	-27.48	-2.10	1
5	2	15	32.48	32.86	32.60	-4.10	-0.38	1
5	2	17	34.74	35.97	26.01	-24.85	-1.23	1
5	2	19	36.41	38.63	29.75	24.64	-2.22	1
5	2	20	43.27	37.92	2.93	37.80	5.35	1
5	2	21	32.14	30.26	-23.03	-19.63	1.87	1
5	3	0	174.96	102.26	-0.00	-102.26	72.70	1
5	3	1	69.60	70.02	69.50	5.49	-0.43	1
5	3	2	86.55	56.09	53.48	16.90	30.46	1
5	3	3	76.47	66.50	-19.83	-63.47	9.98	1
5	3	4	64.18	57.76	51.43	-26.29	6.42	1
5	3	5	39.87	24.51	21.87	-11.06	15.36	1
5	3	6	90.57	83.14	-24.93	79.31	7.43	1
5	3	7	101.55	88.85	-83.20	31.15	12.70	1
5	3	8	45.72	39.71	-37.01	-14.40	6.00	1
5	3	9	40.61	45.50	43.14	14.47	-4.89	1
5	3	10	46.69	50.15	-32.41	-38.28	-3.47	1
5	3	11	46.81	40.57	-40.30	4.68	6.25	1
5	3	12	43.01	47.37	29.78	-36.84	-4.36	1
5	3	13	54.38	65.20	56.92	-31.81	-10.82	1
5	3	16	34.25	32.01	30.29	10.36	2.24	1
5	3	17	27.86	30.58	30.19	-4.82	-2.72	1
5	3	20	22.67	20.26	-19.60	5.12	2.42	1
5	4	0	59.01	8.21	0.00	8.21	50.80	1
5	4	1	58.39	45.74	45.16	-7.22	12.65	1
5	4	2	85.48	87.39	84.53	-22.16	-1.91	1
5	4	3	29.83	25.49	-14.26	21.13	4.34	1
5	4	4	102.27	97.42	27.60	93.43	4.85	1
5	4	5	63.66	59.41	-1.46	59.39	4.25	1
5	4	6	41.83	49.31	-12.74	-47.64	-7.48	1
5	4	7	74.35	62.22	-19.52	-59.08	12.13	1
5	4	8	79.10	67.46	-45.29	49.99	11.64	1
5	4	9	21.58	27.42	16.18	-22.14	-5.85	1
5	4	10	30.15	29.61	-28.16	9.15	0.54	1
5	4	12	28.74	35.93	-19.37	-29.93	-7.19	1
5	4	13	43.65	43.76	43.52	-4.53	-0.11	1
5	4	14	30.85	25.84	24.69	-7.60	5.02	1
5	4	15	34.03	31.45	-11.47	29.28	2.58	1
5	4	16	35.00	34.11	28.84	18.22	0.89	1
5	4	18	34.12	33.08	-4.44	31.99	1.03	1
5	4	20	22.72	29.69	-21.01	-20.97	-6.96	1
5	4	22	25.85	25.72	-16.78	20.79	-0.87	1
5	5	0	36.62	22.84	-0.00	-22.84	13.78	1
5	5	1	74.46	65.42	61.72	29.53	6.04	1
5	5	2	48.93	47.74	-47.72	-1.99	1.17	1
5	5	3	17.31	15.22	-6.36	13.82	2.10	1
5	5	4	25.01	27.20	-13.04	23.88	-2.19	1
5	5	5	95.55	96.48	-70.12	66.27	-0.93	1
5	5	6	46.68	44.28	-44.12	3.84	2.39	1
5	5	8	57.16	60.30	58.64	14.05	-3.14	1
5	5	9	48.26	42.20	-19.14	-37.62	6.05	1
5	5	10	23.80	26.62	-6.29	-25.87	-2.82	1
5	5	11	24.49	23.63	23.40	-3.29	0.98	1
5	5	13	26.20	31.40	-9.57	29.91	-5.20	1
5	5	14	36.17	35.14	-34.04	-8.74	1.03	1
5	5	15	30.31	35.55	24.33	25.92	-5.24	1
5	5	16	35.78	31.22	-8.87	29.94	4.56	1
5	5	17	28.79	31.84	-31.84	0.10	-3.06	1
5	5	20	26.20	27.02	27.00	-1.11	-0.82	1
5	6	0	72.09	56.96	0.00	56.96	15.13	1
5	6	1	75.86	63.30	23.10	-58.93	12.56	1
5	6	2	26.81	26.26	-0.00	26.26	0.55	1
5	6	3	35.88	30.97	-15.96	26.54	4.91	1
5	6	4	49.68	51.57	-38.77	-34.00	-1.89	1
5	6	5	45.52	38.12	-37.22	-8.22	7.40	1
5	6	6	20.32	25.01	4.81	-24.54	-4.69	1
5	6	7	29.43	36.97	-22.44	29.38	-7.54	1
5	6	8	53.41	62.86	44.14	-44.75	-9.45	1
5	6	9	39.56	32.58	19.08	-26.40	6.99	1
5	6	12	41.19	43.40	-6.74	42.87	-2.21	1
5	6	15	28.41	31.14	-7.86	-30.14	-2.73	1
5	6	17	34.52	35.69	-20.72	29.04	-1.16	1
5	7	0	40.02	39.90	0.00	39.90	0.13	1
5	7	3	31.51	32.69	1.88	32.63	-1.18	1
5	7	6	69.42	66.23	33.68	-57.03	3.19	1
5	7	7	31.64	26.94	17.92	-18.14	4.70	1
5	7	8	34.24	29.90	-28.26	-9.74	4.35	1
5	7	9	30.53	23.97	-1.76	-23.91	6.56	1
5	7	10	46.11	47.29	47.27	-1.08	-1.18	1
5	7	11	21.06	22.30	-22.29	-0.53	-1.24	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
5	7	12	56.81	53.77	-24.96	47.63	3.04	1
5	7	16	22.66	24.00	-6.46	-23.11	-1.34	1
5	7	18	29.27	35.14	27.33	-22.08	-5.87	1
5	8	1	53.95	46.73	-41.00	22.42	7.22	1
5	8	2	52.98	37.12	-35.02	12.31	15.86	1
5	8	3	54.53	50.33	30.78	-39.82	4.19	1
5	8	4	28.10	27.13	-25.06	-10.40	0.97	1
5	8	5	34.80	40.20	14.51	37.49	-5.40	1
5	8	6	48.45	50.90	-8.57	50.18	-2.45	1
5	8	8	35.26	29.98	5.86	-29.64	5.28	1
5	8	13	25.92	36.08	-21.78	-28.77	-10.17	1
5	8	14	36.94	35.22	-34.86	5.07	1.72	1
5	8	15	22.72	31.42	29.81	-9.94	-8.70	1
5	9	0	36.12	30.37	-0.00	-30.37	5.75	1
5	9	1	51.14	36.08	-1.82	-36.03	15.06	1
5	9	2	34.26	37.89	12.26	35.86	-3.62	1
5	9	3	60.72	59.87	-57.83	-15.48	0.85	1
5	9	4	45.74	33.11	-16.62	-28.64	12.63	1
5	9	5	61.59	61.38	59.43	-15.34	0.21	1
5	9	6	39.30	43.70	-18.04	39.81	-4.40	.
5	9	7	37.63	32.19	-20.37	24.92	5.45	1
5	9	9	28.60	28.77	13.80	25.24	-0.17	1
5	9	11	36.78	36.22	-35.00	9.31	0.56	1
5	9	16	25.88	18.53	16.63	8.18	7.34	1
5	10	1	35.90	37.27	-2.71	37.17	-1.37	1
5	10	4	38.40	35.07	7.04	34.36	3.33	1
5	10	5	38.56	28.35	22.32	-17.49	10.21	1
5	10	6	38.75	27.41	11.42	-24.92	11.34	1
5	10	8	47.01	44.15	-36.63	24.65	2.86	1
5	10	10	26.24	27.11	10.05	-25.18	-0.87	1
5	11	3	29.27	24.40	22.36	-9.76	4.87	1
5	11	5	26.23	29.48	-29.29	-3.39	-3.26	1
5	12	0	32.02	36.41	-0.00	-36.41	-4.39	1
5	12	1	29.23	23.41	4.40	-22.99	5.82	1
5	12	3	22.60	28.94	-14.93	24.79	-6.33	1
6	0	4	38.78	35.06	35.06	0.00	3.72	1
6	0	5	56.23	63.49	0.00	63.49	-7.26	1
6	0	6	30.87	36.06	36.06	-0.00	-5.19	1
6	0	7	48.56	42.75	-0.00	-42.75	5.80	1
6	0	8	27.88	22.19	22.19	-0.00	5.68	1
6	0	9	57.39	48.01	0.00	48.01	9.38	1
6	0	10	17.38	13.93	13.93	-0.00	3.45	1
6	0	11	73.79	67.55	-0.00	-67.55	6.24	1
6	0	12	59.84	55.01	-55.01	0.00	4.83	1
6	0	14	25.45	24.47	-24.47	0.00	0.97	1
6	0	15	46.38	38.69	-0.00	-38.69	7.69	1
6	0	16	59.23	45.12	45.12	-0.00	14.11	1
6	0	17	32.16	21.84	0.00	21.84	10.32	1
6	0	18	51.67	41.12	41.12	-0.00	10.55	1
6	0	23	36.21	16.02	-0.00	-16.02	20.19	1
6	0	24	13.26	8.74	8.74	-0.00	4.52	1
6	0	25	12.68	5.42	-0.00	-5.42	7.26	1
6	1	0	5.49	11.07	-11.07	-0.00	-5.58	1
6	1	3	31.18	35.83	33.14	13.61	-4.65	1
6	1	4	50.03	63.29	-52.73	-35.00	-13.26	1
6	1	5	31.85	31.83	1.80	31.79	0.02	1
6	1	6	9.92	10.47	-3.64	-9.74	-0.56	1
6	1	7	32.97	31.87	-7.16	31.05	1.10	1
6	1	8	62.36	62.31	-46.18	41.83	0.56	1
6	1	9	59.39	55.02	-31.63	-45.02	4.37	1
6	1	10	19.40	22.03	10.16	19.55	-2.63	1
6	1	11	17.48	14.38	11.48	8.66	3.10	1
6	1	12	31.83	27.74	24.52	-12.40	4.09	1
6	1	13	36.00	30.83	25.28	-17.65	5.17	1
6	1	14	41.96	36.79	-19.86	-30.97	5.17	1
6	1	15	32.93	23.08	1.99	22.99	9.85	1
6	1	17	31.28	28.25	14.77	24.08	3.02	1
6	1	18	23.97	23.23	-23.01	-3.19	0.74	1
6	1	19	41.34	36.06	-35.21	-7.79	5.28	1
6	1	20	24.49	19.48	2.53	19.31	5.01	1
6	1	24	27.51	26.18	24.21	-9.99	1.33	1
6	2	0	26.91	27.92	27.92	-0.00	-1.01	1
6	2	1	41.50	53.64	50.56	-17.91	-12.14	1
6	2	2	14.17	17.58	-11.34	13.44	-3.41	1
6	2	3	21.17	17.47	3.74	17.46	3.70	1
6	2	4	26.58	37.49	-8.37	36.61	-10.91	1
6	2	5	26.88	26.59	25.77	-6.56	0.28	1
6	2	6	54.26	52.65	-32.57	-41.36	1.61	1
6	2	7	54.54	47.02	-44.75	14.59	7.52	1
6	2	8	13.20	12.26	10.74	-5.92	0.94	1
6	2	9	38.69	41.98	-41.10	-8.56	-3.29	1
6	2	10	40.83	44.10	18.21	-40.17	-3.27	1
6	2	11	26.85	21.47	-9.77	19.12	5.37	1
6	2	12	28.13	29.87	6.57	29.08	-1.74	1
6	2	14	20.35	16.06	5.22	15.19	4.29	1
6	2	15	37.26	34.53	34.19	4.84	2.73	1
6	2	16	42.06	42.32	-19.35	37.64	-0.26	1
6	2	17	22.27	17.66	-12.88	-12.08	4.61	1
6	2	18	40.94	37.80	-11.47	-36.02	3.14	1
6	2	19	33.51	25.70	-22.80	13.90	6.81	1
6	2	20	27.08	20.84	-15.09	-14.37	6.24	1
6	2	21	24.40	24.76	-19.22	-15.62	-0.37	1
6	2	22	24.07	20.28	5.06	-19.64	3.79	1
6	2	26	20.33	19.59	0.17	19.59	0.74	1
6	2	27	17.69	14.82	14.44	3.31	2.87	1
6	2	28	9.74	9.78	-9.20	3.31	-0.04	1
6	3	0	11.75	10.64	10.64	0.00	1.11	1
6	3	1	53.33	54.92	5.73	-54.05	-1.59	1
6	3	2	76.02	88.45	46.77	75.08	-12.43	1
6	3	3	61.00	62.65	-60.92	-14.63	-1.64	1
6	3	5	48.56	48.30	33.15	35.13	0.26	1
6	3	6	38.63	37.61	-27.84	-25.26	1.03	1
6	3	7	24.30	14.60	11.37	9.16	9.70	1
6	3	8	34.26	37.24	5.39	-36.85	-2.98	1
6	3	11	18.56	23.15	0.12	-23.15	-4.59	1
6	3	12	48.81	45.19	33.97	-29.83	3.62	1
6	3	13	34.79	34.18	-32.73	-9.84	0.62	1
6	3	14	64.95	64.99	10.87	64.09	-0.04	1
6	3	15	21.46	17.89	-17.13	-5.18	3.57	1
6	3	17	38.16	36.80	-36.77	1.47	1.37	1
6	3	19	40.76	37.99	37.56	5.75	2.77	1
6	3	20	36.49	35.67	2.58	-35.58	0.82	1
6	3	21	14.03	11.38	-4.12	10.60	2.65	1
6	3	25	18.70	20.16	-14.35	-11.80	-1.46	1
6	4	0	20.73	22.16	22.16	-0.00	-1.43	1
6	4	1	46.27	43.77	-41.82	13.63	2.50	1
6	4	2	14.96	20.14	13.26	15.16	-5.18	1
6	4	3	32.27	19.31	13.69	13.61	12.97	1
6	4	4	37.16	35.20	16.16	-31.27	1.97	1
6	4	5	32.18	36.34	-2.25	-36.27	-4.16	1
6	4	6	35.70	32.19	-17.88	26.77	3.51	1
6	4	7	51.84	53.00	41.92	-32.43	-1.16	1
6	4	8	29.91	25.53	-19.93	-15.96	4.38	1
6	4	9	30.45	32.85	-2.22	-32.79	-2.40	1
6	4	10	54.43	56.05	32.21	45.87	-1.63	1
6	4	11	54.37	53.10	-18.92	49.67	1.27	1
6	4	12	56.31	54.04	32.83	-42.93	2.27	1
6	4	13	16.39	14.29	5.28	-13.27	2.11	1
6	4	14	21.36	20.78	-7.69	19.30	0.58	1
6	4	15	18.98	18.99	-11.97	14.75	-0.01	1
6	4	16	13.71	15.93	-4.47	-15.29	-2.22	1
6	4	17	25.46	30.40	11.46	-28.15	-4.94	1
6	4	19	16.32	13.41	4.59	-10.30	2.91	1
6	4	20	14.08	16.31	-16.27	-1.12	-2.23	1
6	4	21	13.91	12.10	11.56	-3.56	1.81	1
6	4	22	15.71	13.34	12.81	3.71	2.37	1
6	4	23	13.16	11.07	-9.17	6.21	2.09	1
6	4	25	11.49	9.74	9.49	2.22	2.14	1
6	4	26	11.03	10.06	-3.58	-9.40	0.97	1
6	5	0	35.15	26.77	26.77	-0.00	8.38	1
6	5	1	44.27	42.53	-37.01	20.95	1.74	1
6	5	2	54.89	55.00	-45.50	30.90	-0.11	1
6	5	3	12.79	14.19	12.95	-5.73	-1.40	1
6	5	4	44.59	48.02	48.01	-1.02	-3.43	1
6	5	5	30.53	26.69	-17.86	-19.81	3.85	1
6	5	6	45.23	40.10	2.24	-40.04	5.13	1
6	5	7	53.80	57.76	26.23	-51.46	-3.96	1
6	5	8	25.33	22.59	22.24	3.92	2.73	1
6	5	9	28.64	31.97	17.23	26.94	-3.33	1
6	5	10	19.69	14.99	-14.01	5.34	4.71	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
6	5	11	32.09	25.67	-14.77	21.00	6.42	1
6	5	12	30.44	22.09	-15.13	16.10	8.35	1
6	5	13	29.36	26.99	7.88	25.82	2.37	1
6	5	14	44.59	38.88	-2.64	-38.79	5.71	1
6	5	15	26.27	24.36	-22.60	-9.09	1.91	1
6	5	16	26.68	21.70	-15.50	15.19	4.98	1
6	5	17	22.99	17.81	8.64	-15.57	5.18	1
6	5	18	25.82	26.92	25.62	8.24	-1.10	1
6	5	20	13.95	18.44	-18.34	1.85	-4.48	1
6	5	21	17.69	20.39	19.61	-5.34	-2.70	1
6	5	22	18.82	22.19	20.06	-9.49	-3.37	1
6	5	23	16.52	16.70	-2.53	16.46	-0.18	1
6	5	24	22.19	25.04	-24.76	3.76	-2.85	1
6	6	0	36.60	34.44	-34.44	0.00	2.16	1
6	6	1	12.39	8.12	2.57	7.67	4.27	1
6	6	2	27.23	19.58	9.15	-16.17	7.65	1
6	6	3	37.37	32.28	-30.11	-11.63	5.09	1
6	6	4	19.23	16.68	-1.65	-16.61	2.55	1
6	6	5	39.72	37.00	-17.17	32.77	2.72	1
6	6	7	45.75	46.75	-4.52	-46.53	-1.00	1
6	6	8	24.20	20.68	1.78	20.59	3.52	1
6	6	9	45.84	51.04	36.09	36.10	-5.21	1
6	6	10	22.01	18.65	-1.87	18.56	3.36	1
6	6	11	18.39	16.40	9.12	-13.64	1.99	1
6	6	12	26.59	23.33	-22.48	-6.23	3.26	1
6	6	13	42.62	43.90	-16.96	40.50	-1.28	1
6	6	14	34.70	32.17	17.73	-26.84	2.54	1
6	6	15	38.69	39.72	-27.13	-29.02	-1.03	1
6	6	16	18.20	19.01	11.72	-14.97	-0.81	1
6	6	17	28.29	30.57	-20.64	22.55	-2.28	1
6	6	18	18.21	11.64	-9.10	-7.25	6.59	1
6	6	19	16.13	17.57	13.06	-11.81	-1.44	1
6	6	20	13.72	15.02	7.20	13.18	-1.30	1
6	6	23	12.28	10.79	10.55	2.25	1.49	1
6	7	0	80.46	92.54	-92.54	0.00	-12.08	1
6	7	2	11.82	14.74	13.14	-6.69	-2.92	1
6	7	3	47.15	38.95	36.99	12.20	8.21	1
6	7	4	29.50	27.26	5.40	-26.72	2.24	1
6	7	5	15.76	15.95	10.19	-12.27	-0.19	1
6	7	6	45.28	46.56	43.68	16.13	-1.28	1
6	7	7	12.67	9.35	-8.50	-3.89	3.27	1
6	7	9	26.15	20.84	-6.17	-19.92	5.31	1
6	7	8	12.85	9.87	-0.39	-9.86	2.98	1
6	7	10	31.68	26.44	14.79	21.90	5.24	1
6	7	11	34.94	31.57	-16.44	26.95	3.37	1
6	7	12	27.47	21.75	-21.72	1.15	5.73	1
6	7	14	24.33	19.87	-12.16	-15.71	4.46	1
6	7	15	23.07	13.01	11.72	5.65	10.07	1
6	7	16	18.25	20.37	20.36	-0.54	-2.11	1
6	7	20	23.06	28.42	25.93	11.64	-5.35	1
6	7	22	22.42	19.71	-19.33	-3.87	2.71	1
6	7	24	17.50	15.47	15.38	-0.95	2.13	1
6	8	1	53.78	55.74	34.31	-43.93	-1.96	1
6	8	2	53.47	47.27	-45.99	10.94	6.20	1
6	8	3	25.59	22.81	18.09	13.90	2.78	1
6	8	4	37.97	34.75	34.12	6.63	3.21	1
6	8	6	25.21	25.76	24.99	-6.27	-0.55	1
6	8	7	65.70	67.18	-19.17	64.38	-1.48	1
6	8	9	23.63	22.14	-14.44	-16.78	1.49	1
6	8	10	23.91	24.06	-4.59	-23.06	-0.16	1
6	8	12	18.14	20.33	-8.93	18.23	-2.19	1
6	8	13	34.59	43.66	-9.45	-42.62	-9.07	1
6	8	15	14.11	12.31	7.93	9.41	1.80	1
6	8	16	18.08	19.39	-18.10	6.95	-1.31	1
6	8	19	13.18	14.50	-11.25	9.14	-1.32	1
6	8	23	10.68	13.70	1.34	-13.63	-3.02	1
6	8	24	12.56	9.97	-9.07	4.13	2.59	1
6	9	0	40.29	40.58	40.58	-0.00	-0.29	1
6	9	1	30.06	28.22	21.65	-18.11	1.84	1
6	9	3	37.41	40.18	-11.31	-38.56	-2.74	1
6	9	4	34.20	24.45	4.55	-24.03	9.75	1
6	9	5	15.78	19.21	19.08	2.28	-3.43	1
6	9	6	40.51	32.74	-32.70	1.56	7.77	1
6	9	7	37.50	29.85	-14.40	26.09	7.65	
6	9	8	24.15	21.11	-20.93	2.79	3.04	1
6	9	9	24.30	23.81	-23.23	-5.22	0.49	1
6	9	10	24.42	23.61	7.95	22.23	0.81	1
6	9	11	33.65	33.89	7.74	-32.99	-0.24	1
6	9	12	23.06	27.22	13.85	-23.44	-4.16	1
6	9	15	17.87	17.19	11.62	-12.67	0.68	1
6	9	17	17.19	10.92	-3.54	10.33	6.27	1
6	9	19	12.44	13.21	12.57	4.04	-0.76	1
6	9	20	11.88	8.55	-6.76	5.23	3.33	1
6	9	21	14.45	12.94	-12.72	-2.40	1.51	1
6	9	23	9.46	11.09	5.56	-9.60	-1.63	1
6	10	2	24.21	24.69	19.03	15.72	-0.48	1
6	10	3	31.31	26.63	26.51	2.48	4.69	1
6	10	4	26.58	22.08	-1.51	22.03	4.52	1
6	10	5	21.49	13.74	-9.97	-9.45	7.75	1
6	10	8	14.14	9.29	4.33	-9.22	4.85	1
6	10	10	21.55	23.31	23.25	1.66	-1.77	1
6	10	12	13.94	15.65	-0.67	-15.64	-1.71	1
6	10	14	22.15	18.35	-3.47	18.03	3.80	1
6	10	20	10.75	12.42	-3.97	-11.79	-1.67	1
6	11	0	30.55	28.71	28.71	-0.00	1.84	1
6	11	1	20.09	17.30	-14.49	-9.72	2.84	1
6	11	2	19.99	19.70	5.88	18.80	0.29	1
6	11	3	18.24	14.23	-2.56	14.00	4.02	1
6	11	4	14.13	16.46	0.18	16.46	-2.33	1
6	11	6	23.19	21.46	-14.63	-10.66	1.53	1
6	11	9	19.64	14.45	14.36	1.57	5.19	1
6	11	10	29.72	27.34	-5.20	-26.84	2.38	1
6	11	17	16.16	1.92	-0.77	-1.76	14.24	1
6	12	0	16.04	14.26	14.26	-0.00	1.78	1
6	12	1	25.34	19.55	11.44	15.85	5.79	1
6	12	3	21.12	21.67	-19.05	-10.32	-0.54	1
6	12	6	15.74	16.64	-15.07	-4.19	-0.09	1
6	12	7	32.19	35.19	0.64	-35.09	-2.91	1
6	12	9	18.67	16.39	8.60	13.95	2.28	1
6	12	14	19.01	1.62	-0.11	1.61	17.39	1
6	13	0	15.17	15.55	-15.55	0.00	-0.39	1
6	13	6	20.75	17.71	17.71	0.41	3.04	1
6	13	9	12.08	14.77	4.23	-14.15	-2.69	1
6	13	10	11.79	9.14	-1.58	9.00	2.62	1
6	13	11	16.19	22.54	-3.86	22.21	-6.36	1
6	13	12	11.05	8.41	-3.06	-7.57	2.64	1
6	14	2	11.82	12.77	-10.99	-6.51	-0.95	1
6	14	4	11.63	14.64	14.42	2.57	-3.01	1
7	1	2	32.49	45.07	-10.71	-43.79	-12.58	1
7	1	4	54.55	68.66	-56.97	38.33	-14.11	1
7	1	5	28.64	33.82	-21.49	-26.19	-5.18	1
7	1	6	27.66	24.41	2.69	24.27	3.25	1
7	1	7	21.19	18.22	-9.17	15.74	2.97	1
7	1	8	46.88	42.69	41.68	9.23	4.20	1
7	1	9	38.93	38.67	0.49	-38.66	0.26	1
7	1	10	41.20	37.25	21.91	-30.12	3.95	1
7	1	11	13.47	9.53	4.91	-8.17	3.94	1
7	1	13	60.72	51.95	36.79	35.97	8.77	1
7	1	14	42.25	31.04	-30.72	-3.70	11.24	1
7	1	15	20.33	15.24	9.17	12.23	5.09	1
7	1	16	37.31	24.74	-17.10	-17.87	12.57	1
7	1	17	25.89	17.86	-7.36	16.27	8.03	1
7	1	18	23.56	20.77	9.74	18.34	2.80	1
7	1	19	7.33	20.07	-12.45	-21.76	2.26	1
7	1	20	13.61	11.44	9.41	-4.54	2.17	1
7	1	21	9.49	9.34	3.30	8.63	0.14	1
7	1	22	13.13	11.73	10.72	4.76	1.40	1
7	1	23	15.54	12.20	3.65	-11.64	3.34	1
7	2	1	23.61	29.01	27.44	-9.43	-5.40	1
7	2	2	10.03	9.62	5.82	8.58	0.41	1
7	2	3	45.03	45.09	43.52	11.78	-0.06	1
7	2	4	26.57	27.74	-27.74	-0.00	-1.17	1
7	2	5	31.80	37.67	-36.03	10.98	-5.87	1
7	2	6	53.26	63.52	4.89	-62.77	-10.26	1
7	2	8	19.39	19.47	2.96	-19.45	-0.08	1
7	2	9	60.43	55.67	-55.10	-7.91	4.77	1
7	2	10	38.01	35.68	32.94	13.69	2.33	1
7	2	11	66.63	71.34	70.19	-13.03	-4.71	1
7	2	12	53.19	44.69	-19.41	40.26	8.50	1
7	2	13	21.13	12.15	4.03	11.46	8.98	1

H	K	L	F OBS	F CALC	A PART	B PART	DELTA	BATCH
7	2	14	37.85	35.64	26.45	23.89	2.21	1
7	2	15	9.17	4.44	2.65	-3.60	4.73	1
7	2	16	16.26	17.76	-10.82	-14.09	-1.50	1
7	2	18	27.27	22.62	17.45	-14.39	4.65	1
7	2	19	16.73	12.49	-4.95	11.47	4.24	1
7	2	20	16.64	15.74	-10.25	-13.24	-0.11	1
7	2	21	13.36	9.95	-6.74	-7.32	3.41	1
7	2	23	15.39	14.46	11.06	-9.32	0.93	1
7	3	0	14.94	11.94	-0.00	11.94	3.00	1
7	3	1	34.13	34.77	-21.21	27.55	-0.65	1
7	3	3	28.38	19.12	4.49	-18.59	9.26	1
7	3	4	42.41	47.40	-15.05	-44.95	-4.99	1
7	3	5	26.45	26.39	23.55	-11.89	0.07	1
7	3	6	14.66	9.33	-8.62	-3.57	5.33	1
7	3	7	38.37	36.52	34.53	-11.92	1.85	1
7	3	8	36.15	33.41	15.21	-29.75	2.74	1
7	3	9	18.55	16.95	-5.93	-15.88	1.60	1
7	3	10	31.62	32.34	10.21	30.68	-0.72	1
7	3	11	8.22	3.84	1.37	-3.58	4.38	1
7	3	12	20.91	17.56	5.57	-16.65	3.35	1
7	3	13	37.44	39.91	-33.69	21.39	-2.47	1
7	3	14	28.72	25.28	-15.08	20.29	3.44	1
7	3	15	22.79	21.84	21.83	0.65	0.95	1
7	3	16	16.41	13.73	-5.76	12.47	2.68	1
7	3	17	33.26	27.05	11.05	-24.69	6.21	1
7	3	18	15.32	13.94	-2.14	-13.77	1.38	1
7	3	19	9.64	7.61	5.12	5.63	2.03	1
7	3	20	27.00	21.67	11.98	18.08	5.33	1
7	3	21	13.25	11.79	-5.34	-10.51	1.46	1
7	3	22	9.10	13.89	9.77	-9.74	-4.79	1
7	3	24	14.36	15.31	2.38	15.12	-0.94	1
7	4	0	44.39	38.15	-0.00	-38.15	6.24	1
7	4	1	35.33	34.59	-7.65	-33.73	0.74	1
7	4	2	30.39	25.87	-23.05	11.76	4.52	1
7	4	3	54.25	50.93	-39.41	-32.27	3.32	1
7	4	4	21.10	22.07	-21.83	3.27	-0.97	1
7	4	5	34.50	29.34	28.30	-7.74	5.16	1
7	4	6	7.15	8.91	-0.55	-8.89	-1.76	1
7	4	7	23.48	26.15	-11.17	23.65	-2.67	1
7	4	8	30.81	28.39	28.39	-0.27	2.42	1
7	4	9	39.14	43.02	32.70	27.96	-3.88	1
7	4	10	23.41	14.26	2.67	14.01	9.15	1
7	4	11	49.14	50.62	-41.34	29.21	-1.48	1
7	4	12	24.94	20.93	2.50	-20.78	4.01	1
7	4	13	33.90	27.46	22.92	-15.13	6.44	1
7	4	14	16.07	15.88	-10.88	11.56	0.19	1
7	4	15	35.35	33.96	-16.80	-29.52	1.39	1
7	4	16	30.27	28.96	-27.99	7.44	1.32	1
7	4	18	33.45	28.64	25.02	13.95	4.81	1
7	4	20	18.91	14.95	14.12	-4.90	3.96	1
7	4	21	13.05	16.11	2.05	15.98	-3.06	1
7	4	24	16.06	14.49	-5.77	11.53	1.57	1
7	5	0	58.95	54.38	0.00	54.38	4.57	1
7	5	1	22.36	21.43	-13.10	16.96	0.92	1
7	5	2	24.72	19.11	17.47	-7.74	5.61	1
7	5	3	45.22	55.00	-13.65	-53.27	-9.77	1
7	5	4	23.36	20.27	1.21	20.24	3.09	1
7	5	5	18.53	16.52	3.53	16.14	2.01	1
7	5	6	37.22	39.49	6.03	-39.03	-2.27	1
7	5	7	47.21	44.26	42.24	-13.20	2.95	1
7	5	8	23.21	22.08	-20.76	7.52	1.13	1
7	5	9	34.80	37.25	14.62	34.26	-2.45	1
7	5	10	17.35	12.75	-12.35	3.18	4.60	1
7	5	11	50.35	45.93	-44.23	12.38	4.43	1
7	5	12	9.11	9.42	9.42	-0.24	-0.31	1
7	5	13	38.35	36.70	-9.38	-35.49	1.65	1
7	5	14	9.46	12.58	10.10	7.51	-3.12	1
7	5	16	16.71	17.27	-5.25	-16.44	-0.56	1
7	5	19	23.23	17.44	12.24	12.43	5.79	1
7	5	20	9.29	8.71	-7.24	-4.85	0.57	1
7	5	21	9.00	11.85	8.56	7.87	-2.84	1
7	5	22	12.27	16.49	-12.62	10.60	-4.27	1
7	6	0	37.41	27.93	-0.00	-27.93	9.48	1
7	6	1	15.63	15.11	-10.77	10.39	0.52	1
7	6	2	37.73	32.59	29.92	-12.91	5.15	1
7	6	3	22.48	19.12	12.68	-14.31	3.36	1
7	6	4	41.09	37.76	37.22	6.32	3.34	1
7	6	5	32.78	27.78	26.40	8.63	5.01	1
7	6	6	42.58	41.69	-35.69	21.55	0.89	1
7	6	7	26.74	25.01	22.15	-11.62	1.93	1
7	6	8	8.70	6.42	6.42	-0.02	2.28	1
7	6	9	17.77	17.91	10.42	-14.56	-0.13	1
7	6	10	22.20	22.78	-22.39	-4.19	-0.57	1
7	6	11	13.06	9.98	-9.97	0.41	3.08	1
7	6	12	22.99	25.50	24.59	-6.77	-2.51	1
7	6	13	13.45	13.77	-8.44	-10.71	-0.32	1
7	6	15	13.66	17.85	17.74	-2.00	-4.19	1
7	6	16	9.65	17.93	17.02	5.66	-8.27	1
7	6	18	13.41	11.48	1.57	11.37	1.94	1
7	7	0	26.79	14.51	-0.00	-14.51	12.27	1
7	7	1	44.90	49.17	30.11	-38.87	-4.26	1
7	7	2	12.06	11.72	2.66	-11.41	0.34	1
7	7	3	24.28	18.13	-6.07	17.08	6.15	1
7	7	4	34.68	31.89	21.90	24.01	2.79	1
7	7	5	19.61	11.66	-11.54	1.65	7.95	1
7	7	6	21.77	18.35	-12.53	13.41	3.42	1
7	7	7	28.49	25.09	-5.25	24.53	3.40	1
7	7	8	38.78	41.55	-34.39	23.31	-2.77	1
7	7	9	39.33	33.70	16.13	-29.59	5.63	1
7	7	10	13.29	15.04	2.06	-14.82	-1.75	1
7	7	11	9.49	6.85	-6.39	-2.47	2.64	1
7	7	12	13.55	13.16	0.77	-13.14	0.39	1
7	7	13	23.61	24.42	24.36	1.74	-0.81	1
7	7	14	27.06	27.56	13.44	20.47	-0.50	1
7	7	17	13.34	10.39	-8.92	5.54	2.94	1
7	7	18	16.40	19.95	1.22	19.91	-3.55	1
7	7	19	12.70	14.67	-13.21	-6.40	-1.97	1
7	7	20	14.97	14.95	-13.61	-6.13	0.02	1
7	7	21	11.66	7.99	4.64	6.51	3.67	1
7	8	0	9.04	2.56	0.53	2.50	6.48	1
7	8	1	6.49	1.19	-0.35	-1.09	5.30	1
7	8	2	18.16	11.05	0.24	-11.05	7.11	1
7	8	4	31.77	27.49	-7.13	26.54	4.29	1
7	8	5	45.27	44.74	-34.67	28.35	2.52	1
7	8	6	6.50	6.81	4.49	5.14	-0.22	1
7	8	7	23.32	24.87	17.82	-17.35	-1.55	1
7	8	8	26.80	25.11	-21.29	13.33	1.69	1
7	8	9	21.35	19.13	-4.60	-18.57	2.22	1
7	8	10	9.61	16.16	14.21	-7.69	-6.55	1
7	8	13	13.64	15.95	-10.57	11.95	-2.31	1
7	8	14	23.50	22.19	21.35	-6.06	1.30	1
7	8	15	10.97	11.91	0.18	11.91	-0.94	1
7	8	17	12.90	16.80	-16.64	-2.31	-3.90	1
7	8	20	11.50	14.83	-14.76	1.44	-3.33	1
7	8	21	7.65	14.39	-2.28	-14.21	-6.74	1
7	9	0	26.74	21.17	-0.00	-21.17	5.57	1
7	9	1	26.75	17.07	17.01	-1.40	9.68	1
7	9	2	29.95	25.14	-1.46	25.10	4.81	1
7	9	4	16.50	18.21	-2.42	-18.05	-1.71	1
7	9	5	16.55	13.83	-11.88	7.92	2.72	1
7	9	6	19.19	28.53	-6.67	27.75	-9.34	1
7	9	7	27.22	22.24	5.55	-21.54	4.97	1
7	9	8	30.52	34.88	26.74	-21.92	-4.35	1
7	9	9	16.97	19.28	-15.28	-11.67	-2.31	1
7	9	11	13.62	15.43	15.43	0.34	-1.81	1
7	10	0	9.65	7.03	0.00	7.03	2.62	1
7	10	1	23.65	22.04	22.02	-1.05	1.61	1
7	10	2	30.54	22.92	-17.67	14.60	7.62	1
7	10	3	21.60	22.52	-18.94	12.18	-0.91	1
7	10	4	21.60	22.47	-5.35	-21.86	-0.86	1
7	10	5	13.67	15.72	5.17	-13.44	-2.06	1
7	10	7	27.27	25.75	-25.21	5.23	1.52	1
7	10	8	16.65	15.47	7.34	-13.78	1.18	1
7	10	9	27.00	22.79	22.75	-1.37	4.21	1
7	10	10	21.21	20.71	14.34	14.93	0.51	1
7	10	12	16.03	15.15	-4.15	14.57	0.89	1
7	10	13	15.75	23.85	23.62	3.26	-8.10	1
7	10	14	8.99	7.79	-5.64	5.38	1.19	1
7	11	0	30.31	31.83	0.00	31.83	-1.52	1
7	11	2	21.41	23.79	-14.21	-19.08	-2.39	1
7	11	3	27.02	26.95	-8.39	-25.61	0.07	1
7	11	4	16.51	10.83	-4.84	9.57	5.68	1
7	11	5	9.49	9.19	5.75	7.17	0.30	1
7	11	6	20.14	15.46	2.35	-15.31	4.68	1
7	11	11	12.58	11.16	-11.01	-1.87	1.42	1
7	11	12	15.27	17.82	-10.52	14.52	-2.55	1
7	11	14	11.59	8.61	-3.55	7.84	2.98	1
7	11	16	21.20	25.68	-13.99	-21.54	-4.49	1
7	12	0	15.41	11.85	-0.00	-14.85	3.56	1
7	12	1	13.01	11.17	-11.15	0.61	1.84	1
7	12	2	12.77	9.56	-5.54	7.75	3.41	1
7	12	3	12.92	14.21	2.11	-14.05	-1.29	1
7	12	4	15.76	14.21	11.02	5.26	3.55	1
7	12	5	9.03	7.36	4.36	5.96	1.67	1
7	12	7	17.68	16.87	16.65	2.74	0.80	1
7	12	8	12.32	12.42	11.29	-5.59	-0.10	1
7	12	9	14.80	20.49	-15.73	13.11	-5.69	1
7	13	0	8.49	3.47	0.00	3.47	5.02	1
7	13	1	16.96	14.54	-4.17	-16.01	3.42	1
7	13	2	15.91	16.09	15.77	3.22	-0.18	1
7	13	5	20.19	21.99	16.34	-14.65	-1.79	1
7	13	7	13.29	10.90	-0.58	10.89	2.39	1
7	13	8	7.80	14.70	-14.66	-1.12	-6.90	1
7	13	9	7.59	10.70	9.71	-4.49	-3.10	1
7	14	2	12.77	14.22	10.59	-9.49	-1.44	1
7	15	1	11.73	12.34	1.80	11.37	-0.61	1
7	0	4	40.45	46.63	46.63	-0.00	-6.18	1
7	0	5	23.27	24.76	-0.00	24.76	-1.49	1
7	0	6	65.53	56.72	-56.72	0.00	8.80	1
7	0	7	28.78	28.65	-0.00	-28.65	0.12	1
7	0	9	45.84	45.29	-0.00	-45.29	0.54	1
7	0	10	42.74	42.00	-42.00	0.00	0.74	1
7	0	12	32.43	33.59	33.59	-0.00	-1.49	1
7	0	13	16.91	7.13	0.00	7.13	9.78	1
7	0	14	19.63	19.58	-19.58	0.00	0.05	1
7	0	15	75.57	66.44	66.44	-0.00	9.13	1
7	0	17	7.48	10.13	-0.00	10.13	-2.65	1
7	0	18	45.09	37.60	-37.60	0.00	7.49	1
7	0	19	23.67	24.43	-0.00	-24.43	-0.76	1
7	0	20	19.25	13.20	-13.20	0.00	6.05	1
7	0	21	16.49	15.04	-0.00	-15.04	1.44	1
7	0	22	13.15	4.90	4.90	-0.00	8.25	1
8	0	7	44.73	40.63	-0.00	-40.63	4.09	1
8	0	10	31.26	26.82	-26.82	0.00	4.44	1
8	0	11	27.18	22.33	0.00	22.33	4.85	1
8	0	12	17.35	15.85	15.85	-0.00	1.50	1
8	0	13	49.80	41.08	0.00	41.08	8.72	1
8	0	15	21.90	20.17	-0.00	-20.17	1.73	1
8	0	16	24.90	17.05	-17.05	0.00	7.85	1
8	0	17	33.72	31.94	-0.00	-31.94	1.78	1
8	0	22	27.38	23.86	23.86	-0.00	3.52	1
8	1	2	15.73	24.04	-2.19	23.94	-8.32	1
8	1	4	12.93	11.18	5.94	9.54	1.75	1
8	1	5	31.10	28.53	-22.31	17.14	2.57	1
8	1	6	36.30	35.32	24.07	-25.85	0.98	1
8	1	7	44.27	55.11	5.40	-54.85	-10.85	1
8	1	8	18.45	11.19	-2.37	11.18	7.26	1
8	1	9	42.02	39.06	26.73	28.49	2.96	1
8	1	10	26.12	31.00	-27.19	14.89	-4.88	1
8	1	13	20.86	20.15	-11.91	16.25	0.71	1
8	1	14	26.29	21.84	-11.69	18.44	4.45	1
8	1	18	31.05	28.66	-23.80	-15.98	2.39	1
8	1	20	31.08	24.75	3.90	-24.44	6.33	1
8	1	22	23.05	19.36	-18.89	4.26	3.69	1
8	2	0	14.67	17.75	-17.75	0.00	-3.09	1
8	2	2	15.94	19.12	16.03	-10.43	-3.18	1
8	2	3	32.73	34.94	22.19	-26.99	-2.21	1
8	2	4	31.54	32.89	-8.25	-31.83	-1.35	1
8	2	5	34.72	36.94	-35.61	9.83	-2.22	1
8	2	7	28.04	34.97	29.54	18.73	-6.93	1
8	2	8	42.01	56.02	-22.25	51.41	-14.01	1
8	2	9	27.10	22.12	21.58	-4.85	4.98	1
8	2	10	23.18	21.28	15.68	-14.38	1.90	1
8	2	11	27.90	26.04	-26.02	1.04	1.87	1
8	2	14	18.76	17.99	-2.35	-17.84	0.77	1
8	2	15	27.06	24.86	-24.80	-1.63	2.20	1
8	2	16	25.02	17.32	17.32	0.01	7.70	1
8	2	17	19.50	15.31	15.24	-1.53	4.19	1
8	2	18	19.47	19.00	-1.64	-18.93	0.46	1
8	2	20	21.85	17.83	13.27	11.91	4.02	1
8	2	21	21.23	18.20	18.05	2.14	3.03	1
8	3	0	22.08	15.98	-15.98	0.00	6.10	1
8	3	1	32.24	38.60	31.56	22.23	-6.37	1
8	3	4	28.00	35.22	34.50	7.04	-7.22	1
8	3	5	33.32	36.62	34.90	-11.11	-3.30	1
8	3	6	28.55	26.24	17.87	-19.21	2.31	1
8	3	7	24.46	20.76	-1.69	-20.69	3.70	1
8	3	12	27.69	26.12	-25.89	-3.47	1.57	1
8	3	8	31.32	37.43	11.11	35.74	-6.11	1
8	3	14	38.00	36.19	-3.27	-36.04	1.81	1
8	3	15	19.28	16.97	16.55	3.62	2.31	1
8	3	16	27.52	26.23	23.99	10.61	1.29	1
8	3	18	19.40	15.16	15.07	-1.66	4.24	1
8	3	19	19.14	16.24	11.87	11.07	2.90	1
8	3	20	21.60	18.21	6.34	17.07	3.39	1
8	3	21	16.13	18.96	-18.93	-1.09	-2.84	1
8	4	0	52.51	54.64	-54.64	0.00	-2.13	1
8	4	1	39.33	45.68	24.59	-38.50	-6.35	1
8	4	3	18.23	22.57	-8.42	20.94	-4.33	1
8	4	4	32.46	22.46	12.59	-18.67	10.00	1
8	4	5	17.30	17.02	4.34	16.45	0.29	1
8	4	6	20.01	24.77	22.21	10.94	-4.76	1
8	4	7	30.72	25.29	-23.92	8.22	5.42	1
8	4	8	16.60	14.22	3.00	-13.90	2.37	1
8	4	9	17.14	9.67	-9.28	2.71	7.47	1
8	4	10	22.81	23.25	1.55	23.20	-0.44	1
8	4	11	18.16	15.07	5.10	-14.18	3.09	1
8	4	12	41.57	42.89	-28.32	-32.20	-1.31	1
8	4	13	18.96	22.90	-4.52	-22.45	-3.94	1
8	4	14	19.24	19.59	-19.26	3.60	-0.35	1
8	4	15	19.43	18.79	10.14	15.82	0.64	1
8	4	16	22.53	23.37	16.92	-16.12	-0.84	1
8	5	0	53.65	45.04	45.04	-0.00	8.61	1
8	5	1	26.56	27.03	-14.61	-22.74	-0.47	1
8	5	3	44.37	42.82	42.23	7.08	1.55	1
8	5	4	18.45	14.83	-4.91	-13.99	3.62	1
8	5	5	16.32	13.05	-0.47	13.04	3.27	1
8	5	6	40.92	39.36	-34.05	19.73	1.56	1
8	5	7	34.23	36.23	-9.20	35.04	-1.99	1
8	5	8	31.11	33.44	-15.91	-29.41	-2.33	1
8	5	10	29.98	27.57	21.72	16.99	2.41	1
8	5	11	19.45	13.51	-13.50	-0.43	5.94	1
8	5	12	26.15	24.35	-20.05	13.82	1.80	1
8	6	0	16.77	16.58	16.58	-0.00	0.20	1
8	6	1	16.81	8.59	5.91	6.24	8.22	1
8	6	2	35.52	33.82	-8.88	32.64	2.70	1
8	6	4	37.31	36.23	8.73	35.15	1.10	1
8	6	5	38.46	39.65	-39.53	-3.09	-1.19	1
8	6	8	30.05	23.76	13.92	-19.26	6.29	1
8	6	9	21.58	22.83	-16.85	15.40	-1.24	1
8	6	10	17.94	19.23	3.36	-19.09	-1.29	1
8	6	13	19.48	22.97	13.37	18.68	-3.49	1
8	6	14	24.84	26.42	-14.87	21.83	-1.58	1
8	6	19	17.88	13.86	-11.20	-8.17	4.02	1
8	6	20	19.79	18.27	-7.52	-16.59	1.58	1
8	7	2	36.21	42.16	26.97	32.40	-5.95	1
8	7	3	29.74	28.42	-24.17	-14.95	1.32	1
8	7	6	18.52	11.91	0.38	11.91	6.60	1
8	7	7	21.81	16.32	10.70	-12.32	5.49	1
8	7	8	24.63	27.53	-11.01	-25.21	-2.90	1
8	7	9	31.43	29.45	16.12	24.65	1.98	1
8	7	11	19.47	22.71	7.62	-21.60	-3.24	1
8	7	12	22.53	21.47	20.39	-6.75	1.05	1
8	7	13	17.73	15.26	-11.67	4.20	2.47	1
8	8	1	32.81	28.90	-26.68	11.10	3.92	1
8	8	3	29.00	22.26	22.12	-2.45	6.74	1
8	8	4	27.21	24.62	-24.40	-3.40	2.59	1
8	8	5	41.51	43.82	-25.58	-35.57	-2.31	1
8	8	6	25.17	21.90	20.66	-7.27	3.27	1
8	8	11	19.45	19.16	-7.79	17.52	0.29	1
8	8	17	26.61	24.90	12.36	-21.61	1.71	1
8	9	1	19.44	17.50	-5.64	16.57	1.94	1
8	9	2	19.45	15.19	-14.44	-4.70	4.26	1
8	9	3	29.79	24.27	-24.15	-1.94	5.52	1
8	9	4	27.56	24.74	23.94	-6.24	2.82	1
8	9	5	19.44	20.35	10.04	17.70	-0.91	1
8	9	6	22.36	20.55	15.15	-13.88	1.81	1
8	10	2	19.42	16.43	5.71	-16.41	2.99	1
8	10	4	19.35	18.69	14.84	-11.36	0.66	1
8	10	5	15.76	17.89	-1.62	17.82	-2.13	1
8	10	6	19.21	14.22	14.09	1.99	4.99	1
8	10	10	28.26	25.92	-2.65	25.78	2.34	1
8	11	3	35.89	33.53	30.46	14.74	2.36	1

Table 2.3

Fractional coordinates and thermal parameters ($Å^2$) with estimated standard deviations.

	x/a	y/b	z/c	Uiso
Br(1)	0.2698±03	0.1318±03	0.0855±01	*
Br(2)	0.8878±03	0.1724±02	0.2283±01	*
Cl(1)	0.8265±13	0.0923±07	0.3841±04	*
Cl(2)	1.0636±14	0.0106±12	0.3610±05	*
C(1)	0.1874±22	0.3775±15	0.2913±08	0.0326±50
C(2)	0.0911±23	0.3314±16	0.3303±08	0.0376±53
C(3)	0.1661±22	0.3142±15	0.3802±08	0.0322±53
C(4)	0.2521±27	0.2340±18	0.3690±09	0.0482±65
C(5)	0.2998±23	0.2322±15	0.3118±08	0.0364±56
C(6)	0.4178±25	0.1711±18	0.3093±09	0.0481±61
C(7)	0.4564±23	0.1640±16	0.2507±08	0.0391±55
C(8)	0.4639±21	0.2622±14	0.2288±08	0.0278±48
C(9)	0.3606±22	0.3261±15	0.2350±08	0.0326±50
C(10)	0.3120±22	0.3348±15	0.2916±08	0.0313±50
C(11)	0.3701±24	0.4243±16	0.2109±08	0.0411±58
C(12)	0.4077±23	0.4159±15	0.1528±08	0.0339±53
C(13)	0.5106±23	0.3548±15	0.1462±08	0.0358±54
C(14)	0.4868±20	0.2546±13	0.1716±07	0.0225±46
C(15)	0.5840±22	0.1910±14	0.1516±08	0.0322±52
C(16)	0.5752±19	0.2144±13	0.0916±07	0.0251±45
C(17)	0.5334±22	0.3234±15	0.0895±08	0.0344±50
C(18)	0.6383±27	0.3987±18	0.1680±09	0.0550±71
C(19)	0.3970±23	0.3899±15	0.3241±08	0.0352±52
C(20)	0.0087±26	0.4815±17	0.3732±09	0.0449±63
C(21)	0.7994±31	0.2349±22	0.0831±12	0.0719±84

Table 2.3 cont.

	x/a	y/b	z/c	Uiso
C(22)	-0.1249±28	0.3342±19	0.3555±09	0.0549±67
C(23)	-0.2459±28	0.3818±19	0.3601±10	0.0561±70
C(24)	-0.2790±27	0.4270±18	0.3058±10	0.0558±69
C(25)	-0.1750±27	0.4926±18	0.2860±09	0.0495±66
C(26)	-0.0607±25	0.4373±17	0.2846±09	0.0439±62
C(27)	0.7116±24	0.0772±16	0.0710±08	0.0402±59
C(28)	0.6012±26	0.0183±17	0.0505±09	0.0442±60
C(29)	0.5848±35	0.0341±24	-0.0075±13	0.0819±98
C(30)	0.5719±28	0.1475±19	-0.0158±10	0.0583±74
C(31)	0.6704±26	0.2036±17	0.0042±10	0.0514±66
C(32)	0.1308±27	0.2787±18	0.4686±09	0.0511±67
C(33)	0.0381±31	0.2396±24	0.5051±12	0.0674±84
C(34)	0.5601±32	0.4499±22	0.0303±11	0.0691±86
C(35)	0.6659±32	0.5176±22	0.0158±12	0.0714±86
C(36)	0.9148±45	0.0166±30	0.3466±16	0.1046±130
O(1)	0.0839±15	0.2779±10	0.4195±06	0.0389±36
O(2)	0.2245±21	0.3111±14	0.4772±07	0.0739±57
O(3)	0.6182±16	0.3844±11	0.0635±06	0.0429±39
O(4)	0.4705±24	0.4465±17	0.0147±09	0.0922±71
O(5)	0.0879±27	0.2807±18	0.1509±10	0.1068±81
N(1)	0.6884±19	0.1836±12	0.0624±07	0.0385±45
N(2)	-0.0240±19	0.3957±13	0.3374±07	0.0355±47

* Anisotropic thermal parameters Uij ($Å^2$) with e.s.d.'s.

	U 11	U 22	U 33	2U 23	2U 31	2U 12
Br(1)	0.0679 24	0.0897 20	0.0666 17	0.0249 35	0.0229 35	0.0591 38

Table 2.3 cont.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br(2)	0.0840 26	0.0700 17	0.0605 15	-0.0042 33	0.0053 35	-0.0474 38
Cl(1)	0.1601 114	0.0777 59	0.1063 70	0.0535 112	0.0193 149	0.0408 141
Cl(2)	0.1118 117	0.2047 134	0.1249 94	-0.0395 194	0.0275 164	0.1279 208

Table 2.4

a) Bond lengths and e.s.d.s (Å).

C(1) -C(2)	1.61 ± 3	C(16)-N(1)	1.53 ± 3
C(1) -C(10)	1.51 ± 3	C(17)-O(3)	1.44 ± 3
C(2) -C(3)	1.56 ± 3	C(20)-N(2)	1.56 ± 3
C(2) -N(2)	1.57 ± 3	C(21)-N(1)	1.52 ± 4
C(3) -C(4)	1.50 ± 3	C(22)-N(2)	1.49 ± 3
C(3) -O(1)	1.46 ± 3	C(22)-C(23)	1.50 ± 4
C(4) -C(5)	1.58 ± 3	C(23)-C(24)	1.59 ± 4
C(5) -C(6)	1.56 ± 4	C(24)-C(25)	1.56 ± 4
C(5) -C(10)	1.54 ± 3	C(23)-C(26)	1.49 ± 3
C(6) -C(7)	1.59 ± 3	C(26)-N(2)	1.55 ± 3
C(7) -C(8)	1.49 ± 3	C(27)-N(1)	1.53 ± 3
C(8) -C(9)	1.46 ± 3	C(27)-C(28)	1.57 ± 4
C(8) -C(14)	1.57 ± 3	C(28)-C(29)	1.54 ± 4
C(9) -C(10)	1.58 ± 3	C(29)-C(30)	1.61 ± 4
C(9) -C(11)	1.51 ± 3	C(30)-C(31)	1.44 ± 4
C(10)-C(19)	1.48 ± 3	C(31)-N(1)	1.56 ± 3
C(11)-C(12)	1.58 ± 3	C(32)-C(33)	1.51 ± 4
C(12)-C(13)	1.44 ± 4	C(32)-O(1)	1.38 ± 3
C(13)-C(14)	1.58 ± 3	C(32)-O(2)	1.16 ± 4
C(13)-C(17)	1.56 ± 3	C(34)-C(35)	1.56 ± 4
C(13)-C(18)	1.64 ± 4	C(34)-O(3)	1.42 ± 3
C(14)-C(15)	1.50 ± 3	C(34)-O(4)	1.08 ± 4
C(15)-C(16)	1.60 ± 3	C(36)-Cl(1)	1.74 ± 5
C(16)-C(17)	1.59 ± 3	C(36)-Cl(2)	1.70 ± 5

Table 2.4 cont.

b) Valency angles and e.s.d.s (°).

C(2) -C(1) -C(10)	116.6 ± 1.7	C(15)-C(16)-C(17)	104.3 ± 1.5
C(1) -C(2) -C(3)	103.6 ± 1.8	C(15)-C(16)-N(1)	112.3 ± 1.7
C(1) -C(2) -N(2)	112.7 ± 1.7	C(17)-C(16)-N(1)	119.4 ± 1.6
C(3) -C(2) -N(2)	114.9 ± 1.7	C(16)-C(17)-C(13)	106.5 ± 1.6
C(2) -C(3) -C(4)	107.0 ± 1.8	C(16)-C(17)-O(3)	113.1 ± 1.8
C(2) -C(3) -O(1)	107.8 ± 1.8	C(13)-C(17)-O(3)	112.6 ± 1.7
C(4) -C(3) -O(1)	105.8 ± 1.7	C(23)-C(22)-N(2)	116.2 ± 2.1
C(3) -C(4) -C(5)	114.0 ± 1.9	C(22)-C(23)-C(24)	108.2 ± 2.1
C(4) -C(5) -C(6)	109.1 ± 1.9	C(23)-C(24)-C(25)	110.8 ± 2.3
C(4) -C(5) -C(10)	109.7 ± 1.7	C(24)-C(25)-C(26)	109.5 ± 2.1
C(6) -C(5) -C(10)	115.0 ± 2.0	C(25)-C(26)-N(2)	113.4 ± 2.0
C(5) -C(6) -C(7)	107.4 ± 1.8	C(28)-C(27)-N(1)	109.2 ± 1.9
C(6) -C(7) -C(8)	109.1 ± 1.8	C(27)-C(28)-C(29)	110.6 ± 2.2
C(7) -C(8) -C(9)	118.5 ± 2.0	C(28)-C(29)-C(30)	106.5 ± 2.3
C(7) -C(8) -C(14)	108.8 ± 1.6	C(29)-C(30)-C(31)	114.9 ± 2.5
C(9) -C(8) -C(14)	106.4 ± 1.7	C(30)-C(31)-N(1)	110.5 ± 2.1
C(8) -C(9) -C(10)	114.8 ± 1.7	C(33)-C(32)-O(1)	108.9 ± 2.4
C(8) -C(9) -C(11)	117.0 ± 2.0	C(33)-C(32)-O(2)	129.4 ± 2.5
C(10)-C(9) -C(11)	110.0 ± 1.7	O(1) -C(32)-O(2)	121.5 ± 2.4
C(1) -C(10)-C(5)	106.9 ± 1.9	C(35)-C(34)-O(3)	101.5 ± 2.5
C(1) -C(10)-C(9)	109.8 ± 1.7	C(35)-C(34)-O(4)	129.3 ± 3.0
C(1) -C(10)-C(19)	112.5 ± 1.8	O(3) -C(34)-O(4)	128.5 ± 3.0
C(5) -C(10)-C(9)	106.2 ± 1.7	Cl(1)-C(36)-Cl(2)	116.9 ± 2.5
C(5) -C(10)-C(19)	110.3 ± 1.8	C(3) -O(1) -C(32)	114.3 ± 1.8
C(9) -C(10)-C(19)	110.9 ± 1.9	C(17)-O(3) -C(34)	112.0 ± 2.0
C(9) -C(11)-C(12)	110.5 ± 1.7	C(16)-N(1) -C(21)	110.7 ± 1.8
C(11)-C(12)-C(13)	111.8 ± 1.8	C(16)-N(1) -C(27)	109.9 ± 1.6
C(12)-C(13)-C(14)	110.1 ± 1.9	C(16)-N(1) -C(31)	109.2 ± 1.8

Table 2.4 cont.

b) cont.

C(12)-C(13)-C(17)	114.2 ± 1.8	C(21)-N(1) -C(27)	105.7 ± 1.9
C(12)-C(13)-C(18)	114.9 ± 1.9	C(21)-N(1) -C(31)	111.4 ± 1.9
C(14)-C(13)-C(17)	100.1 ± 1.6	C(27)-N(1) -C(31)	109.9 ± 1.6
C(14)-C(13)-C(18)	109.5 ± 1.8	C(2) -N(2) -C(20)	108.7 ± 1.8
C(17)-C(13)-C(18)	106.9 ± 1.9	C(2) -N(2) -C(22)	108.5 ± 1.7
C(8) -C(14)-C(13)	112.3 ± 1.6	C(2) -N(2) -C(26)	108.9 ± 1.6
C(8) -C(14)-C(15)	120.3 ± 1.7	C(20)-N(2) -C(22)	115.4 ± 1.8
C(13)-C(14)-C(15)	105.0 ± 1.7	C(20)-N(2) -C(26)	107.7 ± 1.6
C(14)-C(15)-C(16)	100.1 ± 1.6	C(22)-N(2) -C(26)	107.5 ± 1.9

Table 2.4 cont.

c) Some relevant intramolecular non-bonded distances (Å).

O(1) ...C(20)	3.20 ± 3
O(1) ...C(22)	2.96 ± 3
O(1) ...N(2)	2.96 ± 3
O(2) ...C(4)	3.04 ± 4
O(3) ...C(21)	2.95 ± 4
O(3) ...C(31)	3.02 ± 3
O(3) ...N(1)	2.92 ± 2
C(3) ...C(22)	3.31 ± 3
C(1) ...C(26)	2.88 ± 3
C(15)...C(27)	2.99 ± 3
C(17)...C(31)	3.17 ± 3

d) Intermolecular distances (Å) < 3.60 Å.

$Br(1)....C(31)^{I}$	3.46
$Br(1)....C(35)^{I}$	3.56
$Br(2)....O(5)^{II}$	3.36
$C(22)....Cl(1)^{III}$	3.51
$C(29)....Cl(1)^{IV}$	3.48
$C(36)....O(5)^{V}$	3.30
$O(2)....C(28)^{VI}$	3.56

The subscripts refer to the following equivalent positions:

I	1/2 + x,	1/2 - y,	-z;
II	-1 + x,	y,	z;
III	1 + x,	y,	z;
IV	1/2 - x,	-y,	-1 + z;
V	1 - x,	-1/2 + y,	1/2 - z;
VI	1 - x,	1/2 + y,	1/2 - z;

Figure 2.1

The atom numbering scheme.

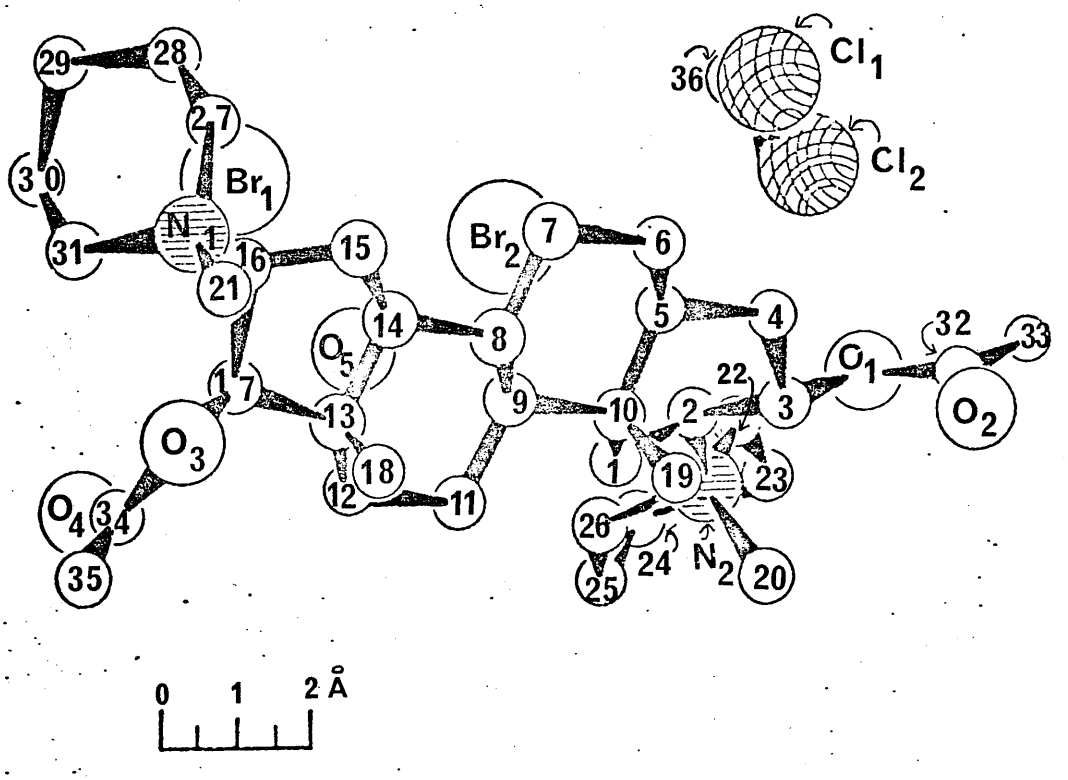

Cl1
Cl2
Br1
Br2
N1
N2
O1
O2
O3
O4
O5
0 1 2 Å

Figure 2.2

The molecular packing viewed down the b axis.

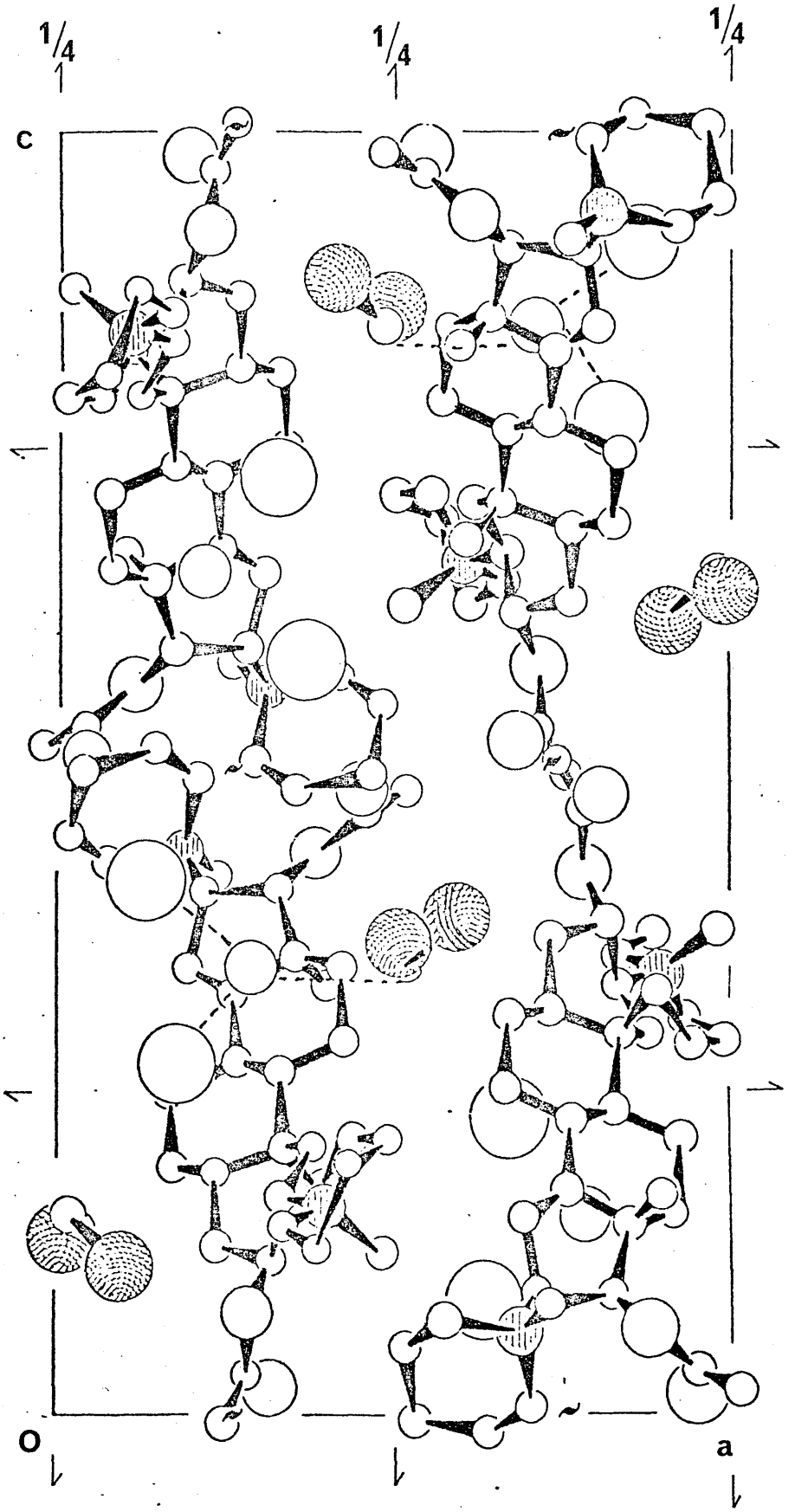
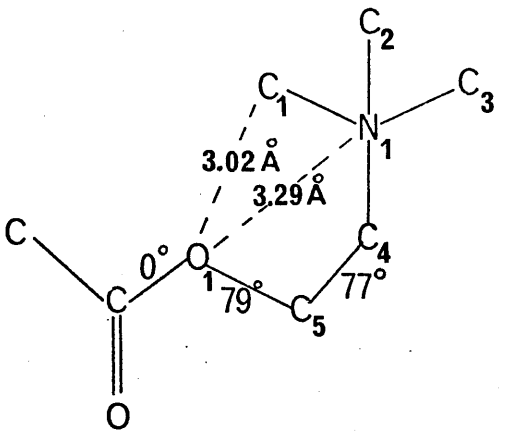
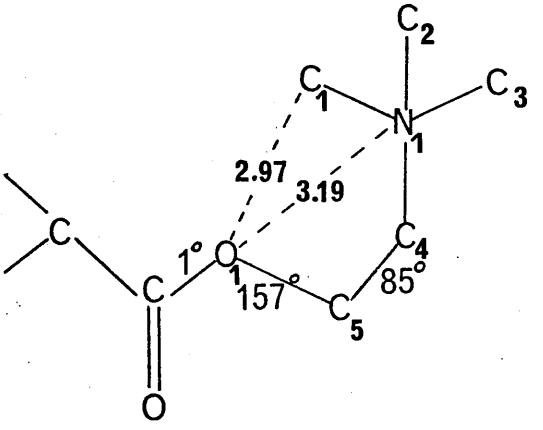

1/4
1/4
1/4
c
O
a

Figure 2.3

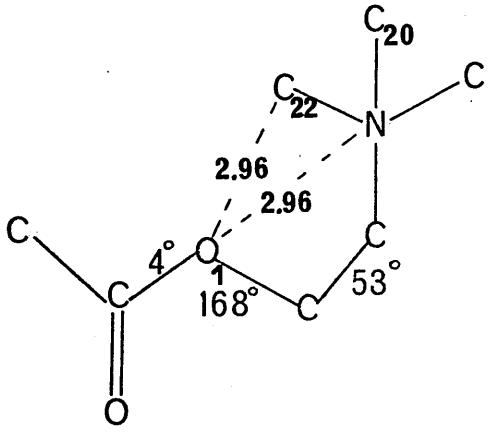
A comparison of torsional angles (°) and some intramolecular non-bonded distances (Å) in acetylcholine bromide, lactoylcholine iodide, and pancuronium bromide.



Acetylcholine bromide.

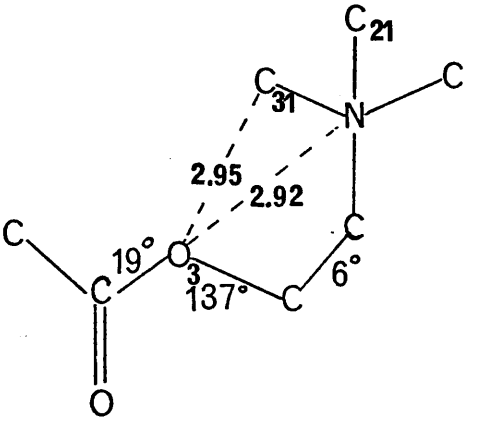


Lactoylcholine iodide.



Pancuronium bromide

Ring A.



Pancuronium bromide

Ring D.

2.3 DISCUSSION.

Considerable interest has been shown in the possible role of conformational isomerism in the biological actions of acetylcholine (II). Since pancuronium bromide (I) was discovered by the incorporation of acetylcholine-like fragments in 5α-androstane (Buckett et al., 1967) it is therefore pertinent to compare in some detail the geometries of the relevant moieties in pancuronium bromide with the geometries of acetylcholine bromide and lactoylcholine iodide, both of which have been studied by single-crystal X-ray analyses (Canepa et al., 1966; Chothia and Pauling, 1968).

In terms of the three torsion angles indicated in Figure 2.3, Kier (1967) has calculated that there is one "stable" conformation for acetylcholine. However, crystalline acetylcholine bromide does not possess this "stable" conformation whereas lactoylcholine iodide does. Comparison of values of the torsion angles, also presented in Figure2.3, reveals that the conformation of the ring D fragment differs markedly from the conformation of lactoylcholine iodide while the ring A fragment approximates to this "stable" conformation. In cholinergic molecules (Sundaralingam, 1968) angle (1) is normally 0°, angle (2) either 60° or 180°, and angle (3) in the range $60\text{-}85^{\circ}$.

Similar comparisons can be made of the inter-atomic non-bonded distances also shown in Figure 2.3. In both acetylcholine and lactoylcholine hydrogen bonding

has been postulated (Canepa et al., 1966; Chothia and Pauling, 1968) between a hydrogen on an N-carbon atom and the alcoholic oxygen C(1) ... H-C(1) ; O(1) ... C(1) distances which allow this hydrogen bonding are 3.02 and 2.97 Å in acetylcholine and lactoylcholine respectively. The hydrogen bonding has the effect of completing a hetero six-membered ring from the atoms O(1) - C(5) - C(4) - N(1) - C(1) - H in both acetylcholine and lactoylcholine. In pancuronium bromide the interatomic non-bonded distances in the ring D fragment again differ markedly from those of the ring A fragment, acetylcholine and lactoylcholine. O(3) of the ring D fragment is separated by only 2.95 Å and 2.92 Å from the two N-carbon atoms C(31) and C(21) respectively, whereas the corresponding distances between O(1), C(20) and C(22) in the ring A fragment are 3.20 Å and 2.96 Å respectively. Thus in the ring D fragment of pancuronium bromide O(3) may be involved in <u>two</u> hydrogen bonds of strengths similar to the hydrogen bonds in acetylcholine and lactoylcholine, forming <u>two</u> hetero six-membered rings of the atoms O(3) - C(17) - C(16) - N(1) - C(21) - H and O(3) - C(17) - C(16) - N(1) - C(31) - H. On the other hand, O(1) of the ring A fragment can be involved only in one comparable hydrogen bonding interaction with C(22), such that only <u>one</u> feasible six-membered ring may be constructed from the atoms O(1) - C(3) - C(2) - N(2) - C(22) - H since the O(1) - C(20) distance of 3.20 Å will not allow the same degree of hydrogen bonding.

Thus it is the hydrogen bonding of the ring D fragment which is the basic difference between it and the other cholinergic moieties which have been discussed. In addition, the abnormal torsion angles of the ring D fragment, which have already been discussed, may be explained in terms of double hydrogen bonding in this part of the molecule. Infrared evidence supports the interpretation of two quasi six-membered rings involving the C(17)-oxygen atom and tends to confirm that the O(1) ... C(20) distance of 3.20 Å does not lead to significant hydrogen bonding.

It is evident from Figure 2.1 that ring A exists in a twisted boat conformation which was expected from earlier studies (Hewett and Savage, 1968) of analogous non-quaternised 2β-piperidino-3α-ols. In addition both piperidino rings possess chair conformations which project into the α-face of the steroid molecule.

Since it was difficult to isolate the crystals without at least one molecule of water for every molecule of pancuronium bromide, the intermolecular contacts were examined for the posibility of hydrogen bond formation between the water molecule and the pancuronium bromide species. The O(5) ... Br(1) and O(5) ... Br(2) distances are 3.40 Å and 3.36 Å which are both shorter than the van der Waals' distances. These short contacts probably indicate the formation of hydrogen bonds between the water molecule and the two bromide ions. There is also the possibilty of hydrogen bonding between the methylene chloride and the pancuronium cation (Cl(1) ... C(22), 3.51 Å

and Cl(1) ... C(29), 3.48 Å). This explains why methylene chloride is an ideal solvent for giving pancuronium bromide in a crystalline form suitable for this study. Other intermolecular separations correspond to or are greater than van der Waals' distances.

Bonded distances and valency angles in the pancuronium cation are acceptably similar to literature values within the experimental limitaions of error. The Br(1) ... N(1) distance is 4.73 Å and the Br(2) ... N(2) distance is 4.37 Å.

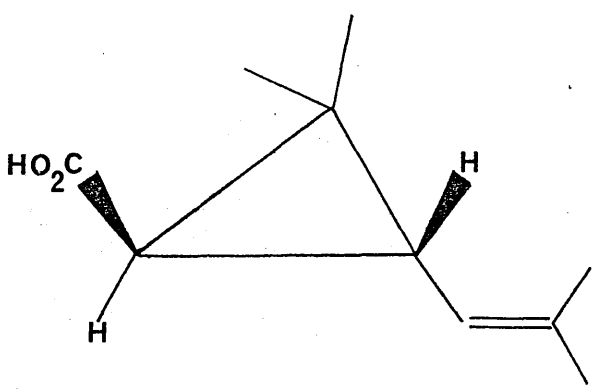
In conclusion, it is remarked that the potency and specific action of this agent may depend on both its rigidity and its ability by intramolecular hydrogen bonding to form three quasi six-membered rings of the type postulated in the crystal structures of both acetylcholine bromide (Canepa et al., 1966) and lactoylcholine iodide (Chothia and Pauling, 1968). It may also be important that the distance between the two quaternary nitrogen atoms in pancuronium bromide is 11.08 Å since it has been postulated (Barlow, 1960) that the interonium distance in neuromuscular blocking agents may approximate to that between regularly spaced anionic sites on the post-junctional membrane of the synaptic cleft.

THE ABSOLUTE CONFIGURATION OF (+) TRANS-CHRYSANTHEMIC ACID: CRYSTAL STRUCTURE ANALYSIS OF A p-BROMOANILIDE DERIVATIVE.

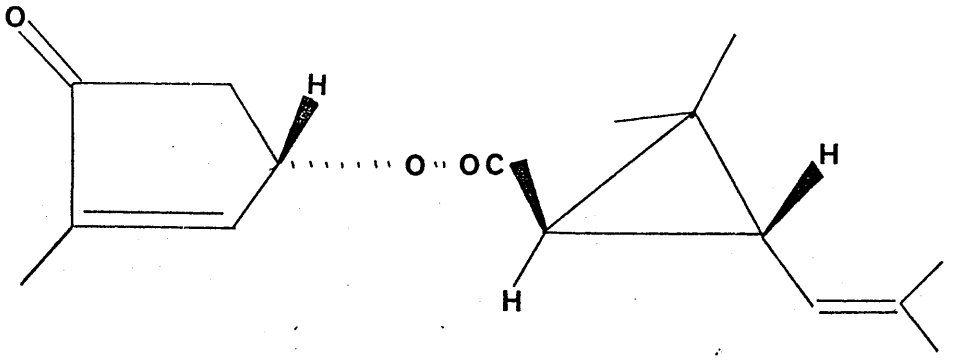
3.1 INTRODUCTION.

The chemistry of the natural pyrethrins has been the subject of considerable interest (Crombie and Elliott, 1961) and the absolute configuration of a key compound in pyrethrin chemistry, (+) trans-chrysanthemic acid (I), has been deduced as 1(R) - 2(R) from chemical considerations (Crombie and Harper, 1954).

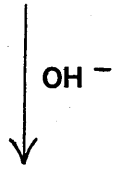
Chrysanthemic acid is formed by the action of base on natural pyrethrin I (II) and epimerisation takes place to from two isomers, 1(R) - 2(R)(+) trans- and 1(R) - 2(S)(+) - cis-chrysanthemic acid. Since both isomers are the precursors of many natural terpenes and take part in a number of important reactions (Crombie and Houghton, 1967), we undertook an X-ray determination of the absolute configuration of (+) trans-chrysanthemic acid using a p-bromoanilide derivative prepared by Professor L. Crombie.

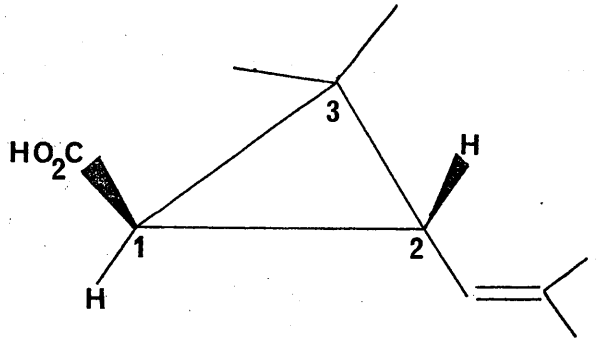


I

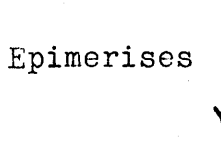


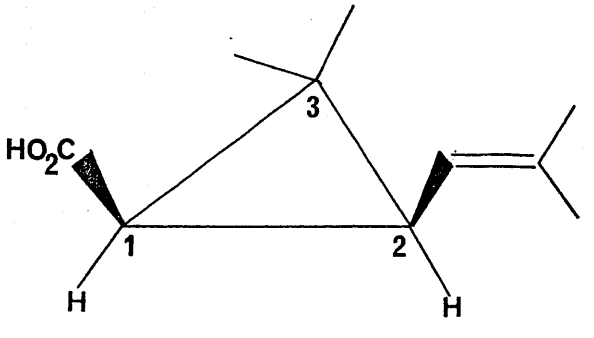
II





I





1(R)2(S) (+) cis-chrysanthemic acid.

3.2 EXPERIMENTAL.

Crystal Data.

(+) trans - chrysanthemic acid, p-bromoanilide derivative, $C_{16}H_{20}NOBr$, $M = 322.2$.

Orthorhombic,

$\underline{a} = 9.58 \pm 0.02$, $\underline{b} = 6.06 \pm 0.02$, $\underline{c} = 27.53 \pm 0.05$ Å.

$\underline{U} = 1601.6$ Å^3, $\underline{D}_m = 1.33$ (by flotation), $\underline{Z} = 4$, $\underline{D}_c = 1.34$.

$F(000) = 664$. Space group $P2_12_12_1$ (D_2^4, No. 19).

Linear absorption coefficient for X-rays ($\lambda = 1.5418$ Å), $\mu = 37.9$ cm^{-1}.

Crystallographic Measurements.

A crystal was mounted about the a axis and the unit cell parameters were determined from Weissenberg photographs taken with Cu-K_α ($\lambda = 1.5418$ Å) radiation and from precession photographs taken with Mo-K_α ($\lambda = 0.7107$ Å) radiation. The space group, $P2_12_12_1$, was uniquely determined from the systematic halvings in the axial reflexions. Equi-inclination Weissenberg photographs of the 0 - 4kℓ reciprocal lattice nets yielded some 400 independent reflexions, which proved to be a sufficient number of data for the determination of the structure and in particular the absolute configuration,

the latter representing the problem in hand.

The reflexions were estimated visually by comparison with a calibrated strip and were corrected for the appropriate Lorentz, polarisation and rotation factors. The various sets of structure amplitudes were placed on an approximate scale at a later stage in the analysis.

Structure Determination.

The position of the bromine atom (0.000, 0.187, 0.210) was found by Patterson methods. The initial (heavy-atom-phased) electron-density distribution was complicated by the presence of pseudo-mirror symmetry resulting from the bromine x-coordinate. Nevertheless, by careful selection of atomic sites from this distribution the entire structure was revealed and two further cycles of structure factor and electron density calculations lowered R to 0.29. In these calculations an overall isotropic parameter, $U_{iso} = 0.06$ Å^2, was used along with atomic scattering factors given in "International Tables for X-ray Crystallography", Vol. III. The structure amplitudes were placed on an approximate absolute scale by making $k \Sigma|F_o| = \Sigma|F_c|$ for each layer.

Structure Refinement.

Seven cycles of full-matrix least-squares calculations reduced R to its final value of 0.109. Details of the refinement are in Table 3.1. A weighting scheme of the form,

$$\sqrt{w} = \left\{[1 - \exp(-p_1(\sin\theta/\lambda)^2]/[1 + p_2|F_o| + p_3|F_o|^2]\right\}^{\frac{1}{2}},$$

was used in the calculations and the p-parameters were adjusted

so that constant averages for $w\Delta^2$, for reflexions batched according to $|F_o|$ and $\sin\theta/\lambda$, were obtained. The final values of p_1, p_2 and p_3 were 50, 0.0001, and 0.001 respectively.

Before anisotropic refinement of the bromine atom the data were put on one overall scale by use of the layer scale factors obtained at the end of the isotropic refinement. The agreement between the observed and calculated structure amplitudes at the conclusion of the refinement is shown in Table 3.2.

The final fractional coordinates, thermal parameters and their e.s.d.s are in Table 3.3. Interatomic distances and angles calculated from the coordinates in Table 3.3 are in Table 3.4. A view of the molecule along a and our numbering scheme is shown in Figure 3.1. The arrangement of the molecule in the unit cell projected down the b axis can be seen in Figure 3.2.

Absolute Configuration.

The absolute configuration of the p-bromoanilide of (+) trans-chrysanthemic acid was established by means of Bijvoet's anomalous-dispersion method (1949). The bromine atom scatters the X-rays anomalously thus resulting in a breakdown of Friedel's Law so that for space group $P2_12_12_1$

$$I(hk\ell) = I(\bar{h}k\bar{\ell}) = I(h\bar{k}\bar{\ell}) = I(\bar{h}\bar{k}\ell)$$

$$\neq I(\bar{h}\bar{k}\bar{\ell}) = I(\bar{h}k\ell) = I(h\bar{k}\ell) = I(hk\bar{\ell}).$$

The reflexions were indexed in a right-handed system (Peerdeman and Bijvoet, 1956) and the intensities of 33 Bijvoet pairs ($hk\ell$ and $hk\bar{\ell}$) were measured visually,

Using the complex scattering curve for bromine given in "International Tables for X-ray Crystallography", Vol. III, structure factors were calculated and the ratio of the observed intensities was compared with the ratio of the squares of the corresponding calculated structure factors for each pair of reflexions. Results of this calculation, shown in Table 3.5, reveal that all of the Bijvoet pairs with the exception of four, marked with an asterisk, have both ratios consistently greater than or less than unity, which implies that the molecule chosen (Figure 3.1) is the one with the correct absolute configuration which happily is identical with that deduced from the chemical work (Crombie and Harper, 1954).

Table 3.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-3}$	Final R′
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, full-matrix, unit weights.	1-3	0.170	35.8	-
As above but adjustments made to the weighting scheme.	4-5	0.154	5.3	0.04
x,y,z,Uij(i,j=1,2,3) for Br atom, x,y,z,Uiso for all other non-hydrogen atoms, one scale factor, full-matrix.	6-7	0.109	2.7	0.02.

Table 3.2

Observed and calculated structure amplitudes.

H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC
0	1	0	3.2	0.0	1	1	0	6.0	4.7	2	1	3	79.7	75.7	3	4	7	15.5	13.2
0	2	0	94.3	104.1	1	2	0	112.1	113.4	2	2	3	54.1	48.3	3	0	8	6.6	7.5
0	6	0	11.1	12.2	1	1	1	14.1	16.6	2	3	3	20.6	16.7	3	1	8	40.8	41.2
0	1	1	40.8	45.8	1	2	1	55.3	51.2	2	4	3	13.6	15.2	3	2	8	25.6	23.9
0	2	1	59.2	65.2	1	3	1	16.8	14.6	2	0	4	35.8	41.8	3	4	8	18.8	21.2
0	3	1	9.9	7.2	1	1	2	41.9	41.7	2	1	4	72.0	58.5	3	0	9	30.9	32.0
0	4	1	28.4	29.7	1	3	2	18.9	18.4	2	2	4	27.0	22.3	3	1	9	19.4	18.3
0	5	1	8.6	5.0	1	4	2	24.3	23.7	2	3	4	34.7	35.7	3	2	9	42.7	44.7
0	1	2	93.2	118.6	1	0	4	7.4	7.5	2	4	4	19.4	21.5	3	3	9	16.6	19.4
0	2	2	42.9	46.1	1	1	3	89.3	86.1	2	5	4	9.5	11.8	3	0	10	17.5	18.2
0	3	2	14.9	14.0	1	2	3	15.7	16.7	2	0	5	47.6	50.4	3	1	10	12.8	16.3
0	1	3	47.4	61.3	1	3	3	58.6	53.4	2	1	5	59.6	85.1	3	2	10	33.2	29.1
0	2	3	65.0	70.1	1	0	5	8.3	1.9	2	2	5	17.6	21.1	3	0	11	29.1	28.1
0	3	3	11.7	9.9	1	1	4	147.0	159.7	2	3	5	27.9	26.4	3	1	11	38.0	40.6
0	4	3	22.0	21.9	1	2	4	58.1	56.2	2	4	5	13.8	14.0	3	2	11	21.9	21.4
0	5	3	11.1	4.4	1	3	4	40.5	32.8	2	0	6	47.7	41.3	3	3	11	16.7	14.0
0	0	4	10.7	15.4	1	4	4	26.9	22.1	2	1	6	14.0	13.1	3	0	12	10.6	9.6
0	2	4	44.4	38.1	1	5	4	21.2	10.3	2	2	6	12.6	12.9	3	1	12	11.1	8.8
0	3	4	47.2	48.3	1	0	6	14.6	11.4	2	3	6	35.8	38.4	3	2	12	18.5	16.5
0	4	4	15.1	15.2	1	1	5	46.5	39.4	2	0	7	31.7	34.2	3	4	12	13.4	11.7
0	1	5	8.2	14.6	1	2	5	27.6	27.4	2	1	7	A6.0	87.3	3	0	13	53.9	57.5
0	2	5	10.5	12.3	1	3	5	28.4	26.9	2	2	7	11.0	11.0	3	1	13	7.1	8.7
0	3	5	20.6	21.7	1	0	7	32.7	25.6	2	4	7	8.6	9.4	3	2	13	19.2	21.6
0	4	5	15.2	13.5	1	1	6	81.0	82.0	2	0	8	13.4	15.0	3	2	14	22.5	21.0
0	5	5	11.2	2.9	1	2	6	26.5	25.1	2	1	8	26.3	24.3	3	3	14	9.0	7.9
0	0	6	5.6	4.3	1	3	6	26.7	24.0	2	2	8	32.4	36.0	3	4	14	9.6	11.3
0	1	6	19.4	21.7	1	4	6	9.5	4.8	2	3	8	30.5	31.9	3	0	15	34.0	35.7
0	2	6	11.6	5.9	1	0	8	32.6	26.4	2	4	8	8.7	7.4	3	2	15	20.0	22.3
0	3	6	34.9	33.1	1	1	7	51.1	48.6	2	0	9	7.3	10.9	3	3	15	9.2	8.5
0	4	6	12.6	11.0	1	2	7	28.2	25.9	2	1	9	23.4	24.0	3	1	16	25.2	28.8
0	5	6	14.2	9.0	1	3	7	58.5	57.5	2	2	9	37.7	39.6	3	2	16	10.0	12.1
0	1	7	112.9	134.7	1	4	7	17.5	15.5	2	3	9	14.0	14.2	3	3	16	13.2	12.5
0	2	7	16.4	12.1	1	0	9	41.4	40.7	2	4	9	22.3	23.6	3	0	17	21.7	22.9
0	3	7	8.5	2.1	1	1	8	68.9	63.0	2	0	10	49.7	52.6	3	1	17	11.9	14.0
0	5	7	12.3	15.6	1	2	8	37.2	29.3	2	1	10	22.7	19.8	3	3	17	17.3	20.8
0	0	8	36.5	37.0	1	3	8	17.8	14.2	2	2	10	20.1	22.7	3	1	18	12.3	9.1
0	1	8	22.5	25.9	1	4	8	9.7	7.5	2	3	10	19.7	19.5	3	2	18	11.8	14.2
0	2	8	20.6	24.1	1	5	8	13.8	8.6	2	0	11	19.7	12.8	3	0	19	10.2	11.4
0	3	8	31.8	33.1	1	1	9	19.0	16.2	2	1	11	51.8	55.7	3	1	19	12.7	11.8
0	4	8	17.1	16.5	1	2	9	27.3	22.7	2	2	11	27.6	27.7	3	1	20	18.4	18.5
0	0	9	7.6	0.0	1	3	9	23.4	23.5	2	3	11	8.0	10.8	3	0	21	12.0	13.8
0	1	9	39.5	42.9	1	4	9	9.9	7.9	2	4	11	16.6	19.6	4	1	0	13.5	11.7
0	2	9	37.4	41.0	1	5	9	13.9	9.5	2	0	12	32.6	39.4	4	2	0	33.4	29.2
0	3	9	11.9	11.3	1	0	11	71.7	69.8	2	1	12	13.5	15.5	4	1	1	36.0	31.3
0	4	9	13.1	12.0	1	1	10	42.2	43.5	2	2	12	28.6	29.7	4	2	1	17.9	15.9
0	0	10	54.2	69.6	1	2	10	56.4	52.9	2	3	12	9.5	9.3	4	3	1	7.8	6.2
0	1	10	9.5	11.2	1	3	10	8.7	7.9	2	0	13	7.5	5.4	4	1	2	31.1	25.9
0	2	10	45.6	43.4	1	4	10	26.5	25.2	2	1	13	21.5	24.1	4	2	2	20.4	20.0
0	3	10	24.4	22.8	1	5	10	10.8	12.5	2	2	13	22.1	24.9	4	0	3	33.3	30.3
0	5	10	10.1	7.9	1	0	12	18.5	12.2	2	0	14	44.2	53.1	4	1	3	20.4	20.4
0	1	11	36.4	39.1	1	1	11	45.9	43.1	2	1	14	8.2	10.7	4	2	3	31.2	29.9
0	2	11	41.1	39.7	1	2	11	55.6	52.2	2	2	14	16.2	17.9	4	3	3	11.9	8.5
0	4	11	23.3	28.7	1	3	11	36.7	37.1	2	4	14	12.2	11.5	4	0	4	19.6	19.8
0	0	12	25.2	27.0	1	0	13	74.8	64.3	2	1	15	21.0	19.4	4	1	4	59.0	52.1
0	1	12	28.1	30.0	1	1	12	11.7	9.6	2	2	15	20.8	21.9	4	2	4	7.9	6.2
0	2	12	36.8	32.9	1	2	12	30.9	31.2	2	3	15	16.2	17.6	4	3	4	36.9	38.9
0	3	12	16.6	13.5	1	3	12	9.1	8.2	2	4	15	12.3	13.1	4	0	5	25.7	29.8
0	5	12	11.3	6.1	1	4	12	23.8	21.5	2	0	16	22.6	23.0	4	1	5	66.7	65.9
0	1	13	29.5	31.5	1	1	13	19.5	16.0	2	1	16	18.5	21.5	4	2	5	14.0	14.1
0	2	13	23.6	27.5	1	2	13	25.6	24.5	2	3	16	20.9	21.2	4	3	5	12.2	13.3
0	4	13	13.9	14.7	1	3	13	15.3	16.4	2	1	17	28.3	26.6	4	0	6	4.2	3.0
0	0	14	73.3	82.2	1	4	13	10.4	10.1	2	2	17	15.7	15.2	4	1	6	27.3	22.7
0	2	14	13.9	12.3	1	0	15	49.5	50.8	2	3	17	10.7	12.0	4	2	6	14.1	12.6
0	3	14	18.0	20.6	1	1	14	17.0	13.5	2	0	18	16.4	19.4	4	3	6	24.2	26.7
0	4	14	17.2	16.6	1	2	14	27.6	25.6	2	1	18	15.3	14.1	4	1	7	51.1	50.8
0	5	14	8.7	6.4	1	3	14	15.7	13.6	2	1	19	18.0	16.4	4	2	7	16.9	17.1
0	1	15	29.0	26.0	1	0	16	8.3	2.2	2	0	20	18.3	22.2	4	3	7	11.9	14.7
0	2	15	24.7	25.3	1	1	15	11.6	10.6	2	1	20	8.9	10.3	4	0	8	11.0	9.5
0	3	15	21.7	23.0	1	2	15	21.8	17.6	2	3	20	9.5	11.6	4	1	8	16.0	17.8
0	4	15	14.2	10.8	1	0	17	10.1	7.2	2	1	21	20.5	21.7	4	2	8	16.3	13.8
0	0	16	32.9	32.2	1	1	16	21.0	18.2	2	2	23	9.6	8.9	4	3	8	10.5	12.2
0	1	16	22.3	26.4	1	2	16	15.1	11.5	3	1	0	25.0	26.5	4	0	9	15.2	16.3
0	2	16	12.2	14.0	1	4	16	10.7	11.4	3	2	0	52.7	50.7	4	1	9	19.8	19.8
0	3	16	23.2	25.5	1	0	18	10.5	11.3	3	3	0	12.9	12.4	4	2	9	18.1	13.7
0	4	16	8.8	11.3	1	1	17	21.9	19.7	3	1	1	12.6	8.6	4	0	10	40.8	43.1
0	1	17	32.9	32.6	1	3	17	16.8	15.4	3	2	1	40.6	39.4	4	1	10	18.5	16.2
0	2	17	16.1	15.8	1	1	18	23.4	19.1	3	3	1	12.9	10.6	4	2	10	18.7	15.2
0	3	17	9.7	1.0	1	2	18	17.0	15.3	3	1	2	5.1	10.0	4	3	10	17.4	15.3
0	4	17	8.6	6.9	1	1	19	9.6	5.6	3	2	2	31.5	33.6	4	0	11	6.9	8.2
0	0	18	19.5	19.7	1	2	19	11.7	11.3	3	3	2	17.0	15.7	4	1	11	20.4	20.0
0	3	18	12.1	5.8	1	3	19	17.4	15.4	3	0	3	59.3	79.4	4	2	11	17.1	15.9
0	4	18	8.8	9.6	1	0	21	20.2	15.7	3	1	3	25.8	24.1	4	0	12	26.3	27.7
0	1	19	21.2	18.8	1	1	20	26.3	25.8	3	2	3	31.0	32.8	4	2	12	20.0	18.7
0	2	19	10.6	10.9	1	2	20	12.0	13.4	3	3	3	21.6	22.6	4	1	13	11.8	13.2
0	3	19	12.3	12.2	1	1	21	17.7	16.9	3	0	4	16.3	15.5	4	2	13	17.8	19.8
0	0	20	13.7	12.7	1	2	21	14.9	12.4	3	1	4	49.4	52.0	4	0	14	13.8	10.9
0	1	20	13.2	14.2	1	3	21	10.8	8.9	3	2	4	55.5	52.0	4	1	14	7.1	9.9
0	3	20	14.3	17.0	1	0	23	18.3	19.7	3	4	4	14.2	12.0	4	2	14	7.7	8.6
0	1	21	19.2	18.6	1	1	22	18.1	16.0	3	0	5	20.7	13.1	4	1	15	10.5	7.8
0	3	21	10.2	10.4	1	2	24	12.4	12.3	3	1	5	49.0	43.1	4	2	15	14.5	14.1
0	0	22	9.7	7.2	2	1	0	32.1	38.1	3	2	5	6.9	7.2	4	0	16	23.4	27.1
0	2	22	10.1	9.8	2	2	0	52.5	58.6	3	3	5	22.1	24.8	4	1	17	17.8	18.2
0	3	22	8.8	8.7	2	3	0	15.6	13.7	3	0	6	30.9	32.9	4	2	17	8.4	10.1
0	2	23	15.2	20.9	2	1	1	52.4	47.8	3	1	6	80.3	80.3	4	3	17	10.1	10.6
0	0	24	14.3	10.5	2	2	1	51.1	47.8	3	2	6	8.7	10.5	4	1	18	15.0	12.0
0	2	24	8.8	3.7	2	3	1	14.1	9.9	3	3	6	22.1	20.8	4	3	18	11.4	13.2
0	1	25	8.8	12.6	2	4	1	22.4	22.6	3	4	6	10.2	10.8	4	1	19	16.8	15.0
0	0	26	13.4	10.7	2	1	2	47.4	47.2	3	1	7	14.5	15.2	4	0	20	17.7	20.6
0	2	26	8.6	9.4	2	2	2	45.7	42.8	3	2	7	41.0	41.2	4	2	20	10.1	12.9
0	0	28	9.8	9.1	2	3	2	21.1	23.8	3	3	7	32.2	33.1	4	1	21	12.3	10.8

Table 3.3

Fractional coordinates and thermal parameters ($Å^2$) with estimated standard deviations.

	x/a	y/b	z/c	Uiso
Br(1)	-0.0080±8	0.1809±9	0.2103±2	*
C(1)	0.139 ±5	-0.455 ±6	-0.052 ±1	0.064±11
C(2)	0.053 ±5	-0.476 ±6	-0.097 ±1	0.080±12
C(3)	0.104 ±5	-0.669 ±6	-0.072 ±1	0.065±10
C(4)	0.110 ±5	-0.405 ±7	-0.141 ±1	0.083±14
C(5)	0.049 ±5	-0.290 ±6	-0.175 ±1	0.077±12
C(6)	0.113 ±5	-0.198 ±7	-0.220 ±1	0.099±13
C(7)	-0.107 ±6	-0.166 ±8	-0.167 ±1	0.109±15
C(8)	0.238 ±6	-0.812 ±9	-0.093 ±1	0.114±15
C(9)	0.001 ±6	-0.830 ±6	-0.045 ±1	0.085±11
C(10)	0.082 ±8	-0.375 ±8	-0.012 ±2	0.061±15
C(11)	0.112 ±4	-0.175 ±6	0.066 ±1	0.056±09
C(12)	0.037 ±5	-0.274 ±5	0.098 ±1	0.061±10
C(13)	-0.016 ±6	-0.179 ±6	0.142 ±1	0.085±11
C(14)	0.046 ±5	0.030 ±6	0.154 ±1	0.065±10
C(15)	0.129 ±5	0.144 ±6	0.120 ±1	0.070±10
C(16)	0.165 ±5	0.033 ±6	0.077 ±1	0.078±12

* Anisotropic thermal parameters Uij ($Å^2$) with e.s.d.'s.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br(1)	0.165 9	0.130 4	0.119 3	-0.047 6	-0.025 10	0.023 13

Table 3.3 cont.

	x/a	y/b	z/c	U_{iso}
N(1)	0.156 ±4	-0.276 ±5	0.024 ±1	0.064±10
O(1)	-0.054 ±4	-0.379 ±5	-0.000 ±1	0.053±09

Table 3.4

a) Bond lengths and e.s.d.s (Å).

C(1) -C(2)	1.49 ± 5	C(10)-N(1)	1.34 ± 6
C(1) -C(3)	1.45 ± 5	C(10)-O(1)	1.34 ± 8
C(1) -C(10)	1.33 ± 6	N(1) -C(11)	1.39 ± 4
C(2) -C(3)	1.44 ± 5	C(11)-C(12)	1.28 ± 5
C(2) -C(4)	1.40 ± 5	C(12)-C(13)	1.44 ± 5
C(3) -C(8)	1.65 ± 7	C(13)-C(14)	1.43 ± 5
C(3) -C(9)	1.57 ± 6	C(14)-C(15)	1.39 ± 5
C(4) -C(5)	1.31 ± 6	C(15)-C(16)	1.41 ± 5
C(5) -C(6)	1.48 ± 5	C(16)-C(11)	1.39 ± 5
C(5) -C(7)	1.69 ± 7	C(14)-Br(1)	1.88 ± 3

b) Valency angles and e.s.d.s (°).

C(2) -C(1) -C(3)	58.6 ± 2.4	C(6) -C(5) -C(7)	108.4 ± 3.2
C(2) -C(1) -C(10)	120.0 ± 4.8	C(1) -C(10)-O(1)	126.2 ± 4.9
C(3) -C(1) -C(10)	122.8 ± 4.2	C(1) -C(10)-N(1)	123.3 ± 6.0
C(1) -C(2) -C(3)	59.2 ± 2.5	N(1) -C(10)-O(1)	110.5 ± 3.9
C(1) -C(2) -C(4)	118.4 ± 4.2	C(10)-N(1) -C(11)	130.3 ± 4.4
C(3) -C(2) -C(4)	122.5 ± 3.9	N(1) -C(11)-C(16)	117.7 ± 3.2
C(1) -C(3) -C(2)	62.2 ± 2.6	N(1) -C(11)-C(12)	123.0 ± 3.1
C(2) -C(3) -C(8)	121.6 ± 3.2	C(12)-C(11)-C(16)	118.9 ± 2.9
C(2) -C(3) -C(9)	121.3 ± 4.0	C(11)-C(12)-C(13)	126.1 ± 3.1
C(1) -C(3) -C(8)	114.6 ± 3.9	C(12)-C(13)-C(14)	113.0 ± 3.5
C(1) -C(3) -C(9)	121.9 ± 3.0	C(13)-C(14)-C(15)	122.3 ± 2.9
C(8) -C(3) -C(9)	108.7 ± 3.3	C(13)-C(14)-Br(1)	119.7 ± 2.8
C(2) -C(4) -C(5)	127.4 ± 4.7	C(15)-C(14)-Br(1)	117.3 ± 2.5
C(4) -C(5) -C(6)	127.1 ± 4.5	C(14)-C(15)-C(16)	117.2 ± 3.3
C(4) -C(5) -C(7)	122.8 ± 3.4	C(15)-C(16)-C(11)	121.4 ± 3.6

Table 3.4 cont.

c) Some intermolecular contacts < 4.0 Å.

Br(1)....Br(1)^{I}	3.74
N(1) ....O(1)^{II}	3.00
O(1) ....C(1)^{III}	3.85
O(1) ....C(9)^{IV}	3.59
O(1) ....C(10)^{III}	3.82
O(1) ....C(11)^{III}	3.70
O(1) ....C(16)^{III}	3.55
C(2) ....C(16)^{III}	3.78
C(4) ....C(13)^{II}	3.62
C(7) ....C(11)^{III}	3.97
C(7) ....C(12)^{III}	3.91
C(7) ....C(16)^{III}	3.97
C(8) ....C(14)^{II}	3.80
C(8) ....C(15)^{II}	3.96
C(9) ....C(10)^{V}	3.52
C(9) ....C(11)^{V}	3.87
C(9) ....C(16)^{V}	3.81
C(9) ....C(16)^{III}	3.79

The subscripts refer to the following equivalent positions:

I	-x,	1/2 + y,	1/2 - z;
II	1/2 + x,	-1/2 - y,	-z;
III	-1/2 + x,	-1/2 - y,	-z;
IV	x,	1 + y,	z;
V	x,	-y,	z;

Table 3.5

Bijvoet pairs used in the anomalous-dispersion calculation.

h	k	l	$I_l/I_{\bar{l}}$	$F_l/F_{\bar{l}}^2$		h	k	l	$I_l/I_{\bar{l}}$	$F_l/F_{\bar{l}}^2$	
1	2	1	0.85	0.88		2	2	10	1.13	1.13	
1	1	3	0.87	0.96		2	3	10	0.89	0.84	
1	2	3	0.55	0.61		2	2	12	0.83	0.93	
1	3	3	0.89	0.92		3	1	1	0.69	0.78	
1	1	5	1.18	1.12		3	1	3	0.85	0.86	
1	1	6	1.18	1.01		3	2	3	0.89	0.87	
1	1	7	0.85	0.93		3	3	3	0.82	0.81	
1	2	8	0.82	0.85		3	2	4	0.64	0.96	
1	1	9	0.78	0.62		3	3	5	0.89	0.92	
1	1	10	0.85	0.91		3	1	7	0.65	0.89	
2	1	3	0.69	0.86		3	1	9	0.80	0.78	
2	2	3	0.80	0.95		4	2	2	0.75	1.17	*
2	1	4	0.89	1.05	*	4	1	4	0.64	0.96	
2	2	5	0.89	1.16	*	4	1	5	0.86	0.96	
2	2	8	1.13	1.10		4	1	6	0.83	1.16	*
2	1	9	0.87	0.93		4	2	11	1.13	1.18	
2	2	9	0.85	0.95							

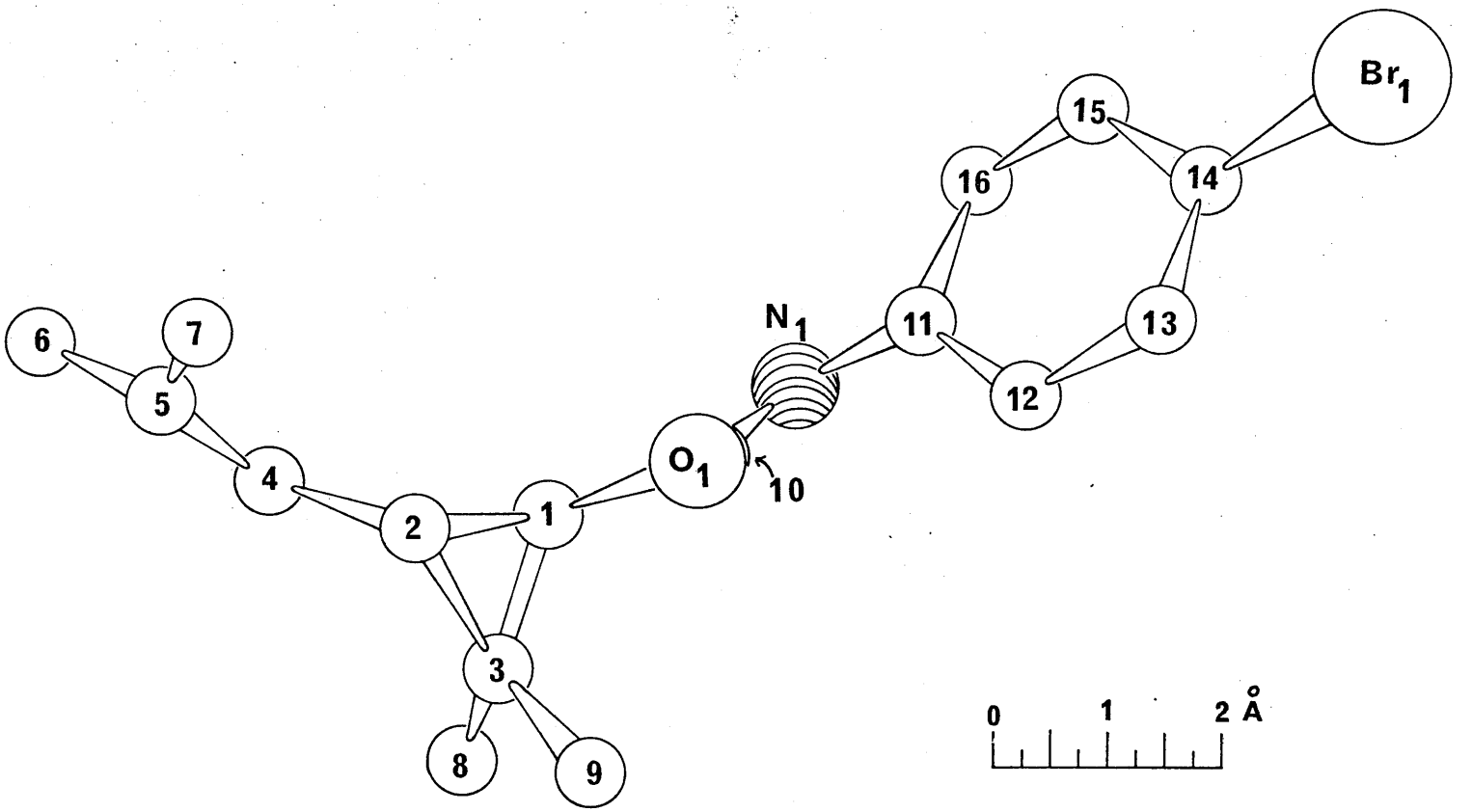
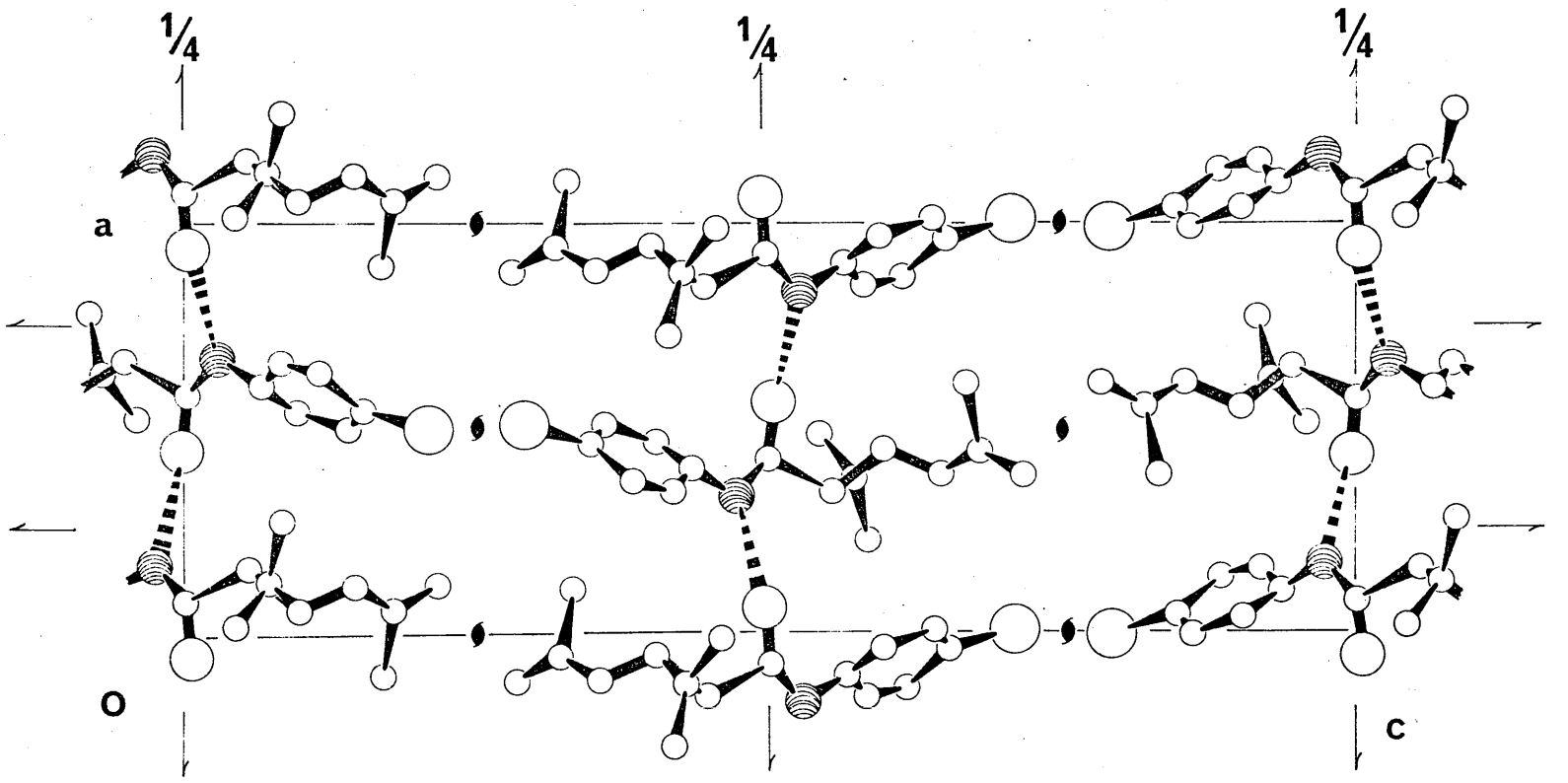

Br1
15
14
16
N1
11
13
12
6
7
5
4
O1
10
2
1
3
8
9
0
1
2 Å

Figure 3.2

A molecular-packing diagram viewed along the b axis.


1/4
1/4
1/4
a
O
c

3.3 DISCUSSION.

The restricted number of data in the x-direction has, not unexpectedly, led to poor resolution in that direction, which can in this instance be ignored since the sole object of the analysis was the determination of the absolute configuration of the molecule. After due consideration of the standard deviations none of the bond lengths and angles differ significantly from those listed in "Tables of Interatomic Distances in Molecules and Ions", Chem. Soc. Special Publ., No. 18, 1965 and in view of the limited accuracy little would be gained by dwelling upon them in detail.

The molecules of the derivative are maximally extended in the crystal and are held by a spiral system of -C – O ... H - N - (O ... N 3.00 ± 0.05 Å) hydrogen bonds about a two-fold screw axis. This can be seen in Figure 3.2. All the other intermolecular distances correspond to, or are larger than, van der Waal distances.

PART IV.

CRYSTAL STRUCTURE ANALYSIS OF A CYCLOPENTADIENYLCARBONYLIRON MERCAPTIDE.

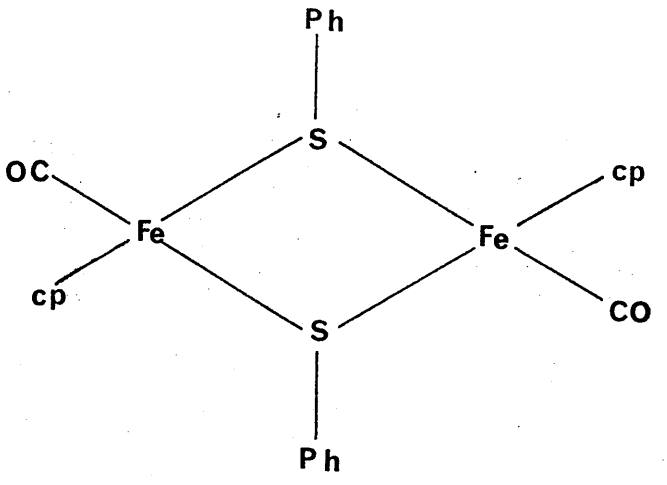
THE CRYSTAL STRUCTURE OF DI-μ-PHENYLTHIO-BIS(CYCLOPENTADIENYLCARBONYLIRON) AT -160°.

1.1 INTRODUCTION.

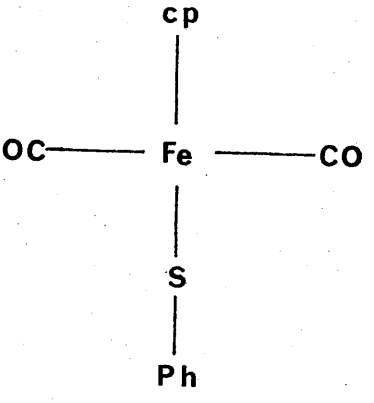
During their investigations of cyclopentadienylcarbonyliron mercaptides, Knox and his co-workers (Ahmad et al., 1966) prepared di-μ-phenylthio-bis(cyclopentadienylcarbonyliron), (I), and, from an examination of this preparation and others, they suggested possible mechanisms which gave an insight into the bonding in hydrocarbon metal sulphide complexes.

The preparation involved a controlled dimerisation of the mononuclear terminal mercaptide complex, $C_5H_5Fe(CO)_2SPh$, (II), and resulted in two isomers of constitution $(C_5H_5FeCO\ SC_6H_5)_2$, (I). The stabilities of both isomers are almost equivalent although it would seem that one isomer (m.p. 170°) is thermodynamically more stable than the other (m.p. 166°) but there is no evidence of an equilibrium between the two.

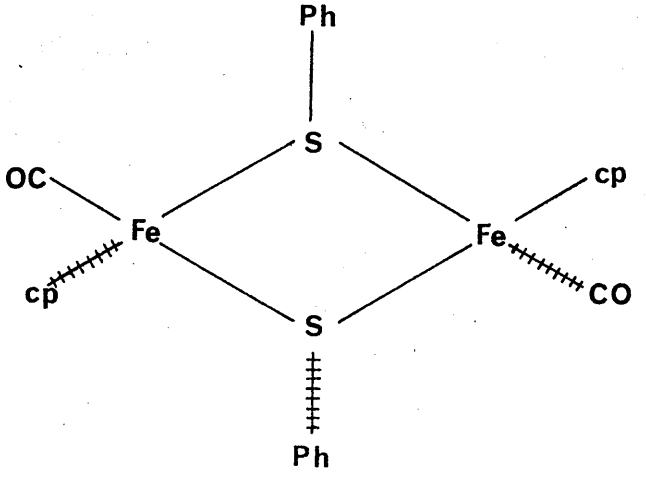
Although only two isomers were found, at least five geometrical isomers of (I) could exist depending on the geometry of the iron - sulphur cycle. Examination of the p.m.r. spectra enabled two of the isomers to be eliminated but spectrochemical evidence alone did not allow an unequivocal establishment of stereochemistry. It was conceivable that the more stable isomer was the all-trans system (III) but as this was by no means certain the more stable crystalline material was examined by single crystal X-ray analysis.



I



II



III

1.2 EXPERIMENTAL.

Crystal Data.

Di-μ-phenylthio-bis(cyclopentadienylcarbonyliron),

$C_{24}H_{20}Fe_2S_2O_2$, $M = 516.0$.

Monoclinic,

$\underline{a} = 10.13 \pm 0.02$, $\underline{b} = 23.22 \pm 0.03$, $\underline{c} = 17.89 \pm 0.03$ Å,

$\beta = 97.30^{\circ}$, $\underline{U} = 4171$ Å^3, $\underline{D}_m = 1.55$ (by flotation), $\underline{Z} = 8$,

$\underline{D}_c = 1.64$, $F(000) = 2112$.

Space group $P2_1/c$ (C_{2h}^5, No. 14), 2 molecules per asymmetric unit.

Linear absorption coefficient for X-rays ($\lambda = 1.5418$ Å),

$\mu = 133.2$ cm^{-1}.

Black crystals of di-μ-phenylthio-bis(cyclopentadienyl-carbonyliron) were formed from methylene chloride/ligroin.

Crystallographic Measurements.

Oscillation, rotation and Weissenberg photographs were taken with Cu-K_α ($\lambda = 1.5418$ Å) radiation at -160°. The unit cell parameters were evaluated from rotation and equatorial layer line Weissenberg photographs. The space group was determined from the systematic absences ($h0\ell$ absent when ℓ is odd, and $0k0$ absent when k is odd). The intensity data, consisting of layer lines $0k\ell$ - $7k\ell$ were

collected by means of equi-inclination multiple-film Weissenberg exposures (Robertson, 1943) taken with Cu-K_α radiation at -160° of a crystal rotating about a. The data were estimated visually by comparison with a calibrated wedge and corrected for Lorentz, polarisation and rotation factors. A total of 3713 independent structure amplitudes were derived. Unobserved reflexions were not included in any of the calculations and no absorption corrections were applied.

Initially the data were put on an approximate absolute scale by making $k\ \Sigma|F_o| = \Sigma|F_c|$ for each layer. The layer scale factors were later refined by least-squares methods. During the refinement stages of the analysis 9 reflexions with low order indices were discarded since they were suffering from extinction effects and had very large delta values. The Patterson and first four cycles of structure factor calculations were carried out using only the $0 - 4k\ell$ data.

Structure Determination.

A three-dimensional Patterson synthesis was computed with data sharpened to point atom at rest with respect to the iron atoms. In the space group $P2_1/c$ the equivalent positions are,

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

such that an atom situated in a general position will give rise to vector peaks at

$$0, \quad \tfrac{1}{2} - 2y, \quad \tfrac{1}{2};$$

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

$$-2x, \quad -2y, \quad -2z;$$

in the Patterson distribution. As there were four iron atoms in the asymmetric unit the Patterson function was difficult to solve unambiguously. Four dominating peaks were found on the line $x = 0$, $z = \frac{1}{2}$, and eight larger peaks on the Harker section, $y = \frac{1}{2}$. The Harker line peak at $\frac{1}{2} - 2y = 0$ suggested that the corresponding general and Harker peaks both lay on the Harker section, $y = \frac{1}{2}$, and were related by two-fold symmetry through the Harker section. The coordinates of the two iron atoms were calculated using these two peaks and were found to be almost 3 Å apart. This suggested that they were both in the same molecule and this was confirmed when an Fe(1) - Fe(2) vector peak was found in the correct location. The other Harker line and Harker section peaks did not lead to any clear general vector peaks.

The first set of structure factors phased on these two iron atoms resulted in a discrepancy factor, R, of 0.67. In the subsequent Fourier summation all the iron and sulphur atoms were revealed. The next set of structure factors phased on these eight atoms gave an R-factor of 0.37 and in the subsecuent Fourier synthesis 59 non-hydrogen atoms were identified, a carbonyl carbon atom being the only one not definitely distinguished, C(13'). Two further cycles of

structure factor and Fourier calculations reduced the R-factor to 0.21. At this point the structure factors derived from the $5k\ell$, $6k\ell$, and $7k\ell$ sets of reflexions were included in the structure factor calculations and two more rounds of Fourier refinement were carried out reducing the R-factor to 0.14.

Structure Refinement.

The positional and thermal parameters of the atoms and the individual layer scale factors and, in the last three cycles, an overall scale factor were refined by least-squares methods.

Nine cycles of block-diagonal least-squares calculations minimising the function,

$$M = \sum w(|F_o| - |F_c|)^2,$$

were carried out until R was reduced to 0.102. The progress of the refinement is shown in Table 1.1. In the first three cycles of refinement unit weights were applied and the R-factor was reduced to 0.119. Thereafter the weighting scheme employed was of the form,

$$w = \{(1 - \exp(-p_1(\sin\theta/\lambda)^2)/(1 + p_2|F_o| + p_3|F_o|^2)\}^{\frac{1}{2}} .$$

After each refinement cycle an analysis of the weighting scheme was examined and the values of p_1, p_2, and p_3 were adjusted to achieve appropriate weights by ensuring that averages for $w\Delta^2$ were constant for reflexions batched according to $|F_o|$ and $\sin\theta/\lambda$. The final values of p_1, p_2, and p_3 were 100, 0.001, and 0.0001 respectively.

After the third cycle it was noted that five of

the carbon atoms, C(8'), C(9'), C(10'), C(11'), and C(12'), forming one of the cyclopentadienyl rings, had noticeably higher values for their temperature factors (0.07, 0.05, 0.04, 0.07, and 0.08 $Å^2$) compared with the average value of 0.03 $Å^2$ for the other carbon atoms. A Fourier summation calculated over the volume containing this ring was computed using the phases derived from the structure factors calculated with all the atoms except C(8'), C(9'), C(10'), C(11'), and C(12') and new coordinates found for these atoms. However, these proved to be almost identical to the coordinates obtained in the third cycle of the least-squares refinement so that the high U_{iso} values must have been due to disorder of the cyclopentadienyl ring. This was confirmed in a difference synthesis in which positive peaks were found in the region of these five atoms. At room temperature the whole molecule is disordered and for this reason the data were collected at -160^{o}. It is therefore not surprising that some traces of disorder in the structure still remain.

Before anisotropic refinement of the iron and sulphur atoms, the data were put on a common scale by use of the layer scale factors obtained at the end of the isotropic refinement. After the last cycle of refinement the parameter shifts were all less than one-fifth of the estimated standard deviations. The theoretical scattering factors used in the analysis are those given in "International Tables for X-ray Crystallography", Vol. III.

The agreement between the observed amplitudes

and final calculated structure factors can be seen in Table 1.2. Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1.3. The anisotropic thermal parameters in Table 1.3 are values of U_{ij} in the expression,

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)].$$

Intramolecular bonded distances and valence angles are shown in Figure 1.1 and 1.2 respectively. Average e.s.d.s in bond lengths and angles are given in Table 1.4. Some intramolecular non-bonded distances and intermolecular contacts <4.0 Å are listed in Table 1.5. Equations of various planes in the molecule and displacements of atoms from them are shown in Table 1.6. The packing arrangement of the molecules in the crystal projected down the a-axis is illustrated in Figure 1.3. Figure 1.4 shows a view of molecule I along the line joining the mid-points of the iron-iron and oxygen-oxygen separations and Figure 1.5 shows a view of molecule II along the line joining the mid-points of the bonds Fe(1') to S(2') and Fe(2') to S(1'). Both these figures give an explanation of the atom numbering scheme used in both molecules.

Table 1.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-4}$	Final R'
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, block-diagonal, unit weights.	1-3	0.119	37.2	-
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, block-diagonal, weighting scheme adjusted.	4-6	0.110	-	0.020
x,y,z,Uij(i,j=1,2,3) for Fe and S atoms, x,y,z,Uiso for all other non-hydrogen atoms, one scale factor, block-diagonal, weighting scheme applied.	7-9	0.103	15.1	0.018

Table 1.2

Observed and calculated structure amplitudes.

H	K	L	F OBS	F CALC
0	4	0	362.8	391.5
0	6	0	122.5	-121.5
0	10	0	178.6	-154.3
0	12	0	41.4	-46.5
0	14	0	44.3	-37.5
0	16	0	94.0	-77.7
0	18	0	33.4	24.6
0	20	0	68.1	-55.8
0	26	0	108.4	-100.9
0	3	1	25.3	-17.4
0	4	1	239.4	224.2
0	5	1	220.4	223.7
0	6	1	97.9	99.1
0	7	1	25.5	-24.0
0	8	1	175.8	-141.4
0	9	1	34.6	-18.5
0	10	1	61.1	-44.0
0	11	1	89.6	62.7
0	12	1	41.8	35.2
0	13	1	53.3	50.0
0	14	1	54.4	-49.6
0	15	1	111.6	-104.5
0	18	1	64.9	-57.5
0	19	1	44.5	-61.1
0	1	2	157.3	-206.4
0	2	2	203.7	-237.0
0	3	2	358.7	367.5
0	4	2	46.7	37.9
0	5	2	59.1	47.7
0	6	2	59.4	-41.4
0	7	2	196.3	180.5
0	12	2	33.7	-30.3
0	13	2	46.7	-38.2
0	14	2	55.0	44.8
0	16	2	51.7	-47.2
0	18	2	55.8	41.7
0	19	2	67.0	-56.9
0	20	2	55.7	-53.5
0	22	2	43.3	42.1
0	27	2	42.2	37.3
0	28	2	50.8	46.2
0	29	2	62.6	-65.3
0	1	3	187.3	-221.2
0	3	3	184.8	-189.0
0	4	3	40.8	39.5
0	5	3	92.4	-91.9
0	6	3	129.7	-122.9
0	8	3	156.6	131.8
0	9	3	137.3	119.6
0	10	3	71.7	55.6
0	11	3	93.7	-83.4
0	12	3	91.9	87.6
0	14	3	80.2	65.3
0	16	3	93.3	83.1
0	18	3	44.8	-37.0
0	24	3	33.2	-36.9
0	27	3	74.1	69.1
0	1	4	152.4	-182.5
0	2	4	33.3	37.8
0	3	4	44.9	-48.8
0	4	4	160.1	-176.2
0	5	4	106.4	-112.7
0	6	4	76.9	73.0
0	7	4	102.8	-90.6
0	8	4	54.9	-52.4
0	9	4	52.2	-46.3
0	10	4	82.4	79.8
0	11	4	45.7	-34.8
0	12	4	62.6	-53.6
0	13	4	145.7	130.9
0	14	4	149.2	136.2
0	17	4	72.3	66.2
0	18	4	66.2	55.2
0	19	4	39.1	-29.2
0	21	4	35.5	33.5
0	24	4	43.4	-47.8
0	1	5	75.2	77.9
0	2	5	23.3	15.6
0	3	5	153.2	172.6
0	4	5	55.6	-51.6
0	6	5	32.5	-31.9
0	7	5	78.5	62.3
0	8	5	63.1	-63.0
0	9	5	107.8	-111.1
0	10	5	62.5	-54.0
0	11	5	47.3	-42.0
0	12	5	56.5	-48.7
0	14	5	47.6	-46.4
0	15	5	91.5	77.3
0	16	5	43.1	-34.7
0	17	5	33.7	26.3
0	18	5	48.9	37.9
0	19	5	46.6	39.7
0	23	5	65.4	-65.1
0	25	5	36.9	-37.3
0	1	6	109.7	-103.8
0	2	6	36.4	40.7
0	4	6	66.3	61.1
0	5	6	66.1	59.8
0	6	6	50.4	51.5
0	7	6	62.8	46.5
0	8	6	100.8	87.1
0	9	6	33.1	29.2
0	10	6	59.9	-55.0
0	11	6	191.7	-178.7
0	14	6	92.9	-94.2
0	15	6	227.3	-216.0
0	18	6	46.2	-39.8
0	21	6	70.4	68.7
0	1	7	55.5	76.7
0	3	7	67.6	-56.9
0	4	7	54.3	-40.3
0	5	7	16.1	-16.0
0	6	7	39.0	37.6
0	7	7	27.3	26.0
0	10	7	53.0	59.9
0	11	7	55.4	81.6
0	12	7	82.5	-66.3
0	15	7	94.6	-80.9
0	16	7	56.2	-47.9
0	17	7	34.7	-24.6
0	19	7	56.1	-47.9
0	20	7	53.1	56.9
0	1	8	41.3	32.2
0	2	8	76.7	-80.1
0	3	8	23.5	20.1
0	4	8	50.9	-45.8
0	7	8	50.3	43.8
0	9	8	69.3	67.5
0	11	8	144.2	140.1
0	12	8	201.9	193.1
0	13	8	69.4	69.7
0	14	8	121.8	-107.6
0	15	8	99.4	130.4
0	16	8	54.6	52.3
0	18	8	107.9	-130.9
0	20	8	43.0	37.3
0	24	8	54.5	49.8
0	25	8	42.3	-39.0
0	1	9	49.6	42.0
0	3	9	31.0	-33.1
0	5	9	69.1	-51.4
0	6	9	55.4	52.6
0	8	9	31.7	-31.5
0	9	9	67.0	-57.2
0	10	9	54.3	51.6
0	12	9	91.9	86.4
0	13	9	59.3	54.9
0	14	9	95.6	69.1
0	15	9	91.7	49.8
0	16	9	74.4	75.2
0	17	9	56.0	49.0
0	22	9	45.3	-49.9
0	0	10	116.3	-109.4
0	1	10	40.1	30.9
0	2	10	126.9	125.4
0	3	10	27.2	-20.4
0	4	10	74.2	-65.8
0	5	10	28.0	-22.7
0	6	10	47.4	-46.0
0	7	10	29.3	-24.5
0	8	10	68.7	-66.9
0	9	10	85.6	-82.4
0	10	10	35.3	-24.5
0	11	10	39.6	37.7
0	13	10	73.9	-71.9
0	15	10	80.4	75.6
0	16	10	39.6	36.0
0	17	10	35.5	-24.7
0	18	10	55.5	50.7
0	19	10	38.8	42.0
0	20	10	56.0	56.4
0	21	10	45.9	-46.9
0	25	10	34.4	-32.9
0	1	11	82.3	-72.4
0	2	11	49.9	44.5
0	5	11	63.3	-57.2
0	6	11	75.8	63.8
0	7	11	65.6	-62.3
0	8	11	131.9	-114.2
0	11	11	55.7	-45.7
0	12	11	104.0	-103.1
0	14	11	30.4	-71.5
0	5	11	36.5	-57.2
0	16	11	53.3	-58.9
0	18	11	52.1	-49.1
0	19	11	56.2	54.2
0	24	11	67.4	68.3
0	0	12	178.4	-165.3
0	1	12	85.0	83.0
0	2	12	40.6	38.8
0	4	12	38.2	-32.6
0	5	12	49.9	47.5
0	6	12	39.2	42.7
0	7	12	26.1	-21.3
0	9	12	37.5	-29.9
0	10	12	51.1	47.9
0	11	12	64.7	-62.3
0	12	12	74.3	-70.1
0	13	12	35.3	-24.4
0	17	12	42.5	-35.1
0	23	12	40.3	39.1
0	24	12	34.9	-33.9
0	2	13	42.9	35.1
0	4	13	43.4	-31.5
0	5	13	106.1	105.3
0	6	13	23.7	31.5
0	8	13	41.9	36.4
0	9	13	103.9	104.0
0	10	13	42.7	36.9
0	11	13	43.2	-37.1
0	12	13	46.9	42.6
0	14	13	53.1	46.3
0	17	13	41.1	-39.0
0	18	13	45.8	41.7
0	21	13	86.4	-84.4
0	0	14	124.1	125.4
0	1	14	67.6	64.9
0	3	14	109.0	-103.6
0	4	14	99.7	88.1
0	5	14	34.4	30.5
0	6	14	34.7	37.6
0	8	14	60.9	57.8
0	9	14	55.9	50.9
0	13	14	46.5	40.9
0	16	14	33.2	-35.7
0	19	14	47.7	42.2
0	20	14	40.0	-39.5
0	1	15	55.2	37.3
0	2	15	60.6	-52.9
0	4	15	30.5	25.1
0	5	15	43.2	41.3
0	6	15	35.4	-22.2
0	7	15	56.8	-57.6
0	8	15	47.0	45.7
0	12	15	46.0	38.6
0	15	15	39.8	-41.3
0	17	15	63.4	50.2
0	0	16	68.7	59.2
0	2	16	100.4	-87.4
0	6	16	85.1	-84.3
0	8	16	35.2	-36.7
0	10	16	38.7	-39.1
0	13	16	51.6	-51.2
0	16	16	52.1	42.8
0	18	16	41.7	39.4
0	1	17	39.5	-27.8
0	3	17	52.8	-46.0
0	6	17	46.0	-42.4
0	7	17	42.2	-35.5
0	8	17	56.6	49.4
0	10	17	73.9	-71.0
0	14	17	52.4	-46.9
0	1	18	45.3	-43.2
0	2	18	34.1	25.9
0	3	18	29.4	23.4
0	4	18	16.9	-20.6
0	5	18	29.1	-25.7
0	6	18	33.2	-19.9
0	9	18	54.6	-54.2
0	10	18	43.5	37.6
0	16	18	42.4	-37.5
0	3	19	85.9	85.2
0	8	19	75.2	-7.9
0	7	19	54.4	51.3
0	10	19	33.9	-35.0
0	11	19	26.5	25.6
0	12	19	39.8	34.9
0	13	19	39.1	-34.6
0	2	20	66.8	53.1
0	4	20	55.3	42.0
0	12	20	64.9	-72.5
0	13	20	33.8	44.4
0	6	21	36.8	32.9
0	9	21	53.6	-60.7
0	2	22	42.8	-45.4
0	5	22	34.2	33.0
0	7	22	26.9	34.8
0	1	23	6.5	-20.3
1	1	19	40.0	-44.9
1	2	19	31.5	-40.0
1	3	19	23.5	-25.0
1	4	19	54.1	60.2
1	5	19	35.0	-37.3
1	11	19	33.7	35.2
1	12	19	22.5	27.5
1	1	18	22.4	-30.9
1	3	18	25.7	27.1
1	4	18	15.0	19.9
1	5	18	33.4	34.6
1	7	18	30.1	28.9
1	8	18	27.0	15.4
1	9	18	28.9	33.1
1	10	18	34.4	-41.1
1	13	18	36.4	-35.6
1	1	17	61.6	65.6
1	3	17	32.8	26.8
1	4	17	23.1	29.1
1	5	17	54.7	61.1
1	8	17	28.8	36.7
1	11	17	50.0	-54.4
1	0	16	52.7	59.1
1	3	16	36.0	-32.6
1	4	16	38.5	39.4
1	5	16	35.9	-37.4
1	6	16	33.2	31.7
1	7	16	35.7	-40.8
1	1	15	30.1	-32.0
1	4	15	52.5	-55.8
1	5	15	81.5	85.7
1	6	15	56.1	-59.4
1	7	15	13.6	-25.7
1	8	15	23.6	-31.2
1	9	15	30.3	30.6
1	10	15	30.2	-35.9
1	12	15	43.8	47.8
1	14	15	49.0	60.4
1	0	14	116.4	-109.2
1	1	14	75.3	73.4
1	2	14	45.5	-44.3
1	3	14	18.6	28.4
1	4	14	76.1	-70.8
1	9	14	47.1	-49.8
1	10	14	47.2	45.0
1	11	14	43.0	-45.8
1	14	14	47.6	48.4
1	18	14	32.3	33.4
1	1	13	45.3	-46.3
1	2	13	63.0	65.0
1	3	13	56.7	-57.7
1	4	13	18.0	22.5
1	5	13	44.6	-47.6
1	6	13	63.5	61.9
1	7	13	77.6	-77.4
1	10	13	55.6	-65.5
1	13	13	47.1	46.0
1	16	13	41.3	-45.4
1	18	13	34.5	-35.3
1	19	13	34.8	39.5
1	0	12	86.6	86.7
1	2	12	113.5	110.7
1	3	12	51.1	42.2
1	4	12	21.1	24.2
1	6	12	42.2	-67.3
1	7	12	78.9	83.3
1	8	12	40.5	-47.2
1	11	12	32.7	34.0
1	13	12	74.4	-77.6
1	1	11	99.6	100.0
1	2	11	39.0	-33.0
1	3	11	55.6	62.0
1	4	11	32.5	-35.2
1	5	11	46.6	51.1
1	6	11	55.5	59.5
1	7	11	26.7	-27.9
1	10	11	132.6	132.9
1	11	11	46.9	-52.3
1	16	11	52.6	60.5
1	20	11	56.5	64.6
1	22	11	40.7	-47.6
1	23	11	24.3	-30.5
1	0	10	52.3	55.4
1	1	10	44.6	-54.9
1	3	10	35.3	-42.2
1	4	10	105.9	107.1
1	7	10	30.2	-32.4
1	8	10	54.8	55.0
1	9	10	31.7	24.6
1	10	10	21.2	-33.2
1	11	10	73.2	77.2
1	12	10	34.0	34.0
1	14	10	97.1	-93.8
1	15	10	52.3	55.3
1	18	10	35.6	-40.2
1	19	10	29.5	26.8
1	22	10	43.3	-51.0
1	1	9	59.2	-58.4
1	2	9	57.2	-64.5
1	3	9	65.1	-65.9
1	4	9	136.0	-130.1
1	6	9	29.7	29.8
1	7	9	84.2	92.6
1	8	9	138.3	-145.9
1	11	9	36.2	37.3
1	12	9	57.8	-85.6
1	16	9	30.2	-35.0
1	18	9	10.2	10.6
1	19	9	35.6	-35.3
1	0	8	165.9	-172.7
1	1	8	103.9	100.6
1	2	8	28.7	-26.2
1	3	8	29.1	-40.8
1	4	8	32.5	-39.1
1	6	8	81.3	71.2
1	7	8	56.3	-60.0
1	8	8	23.4	-13.4
1	10	8	33.6	-33.4
1	11	8	129.9	-133.3
1	12	8	35.9	43.3
1	13	8	21.4	-23.3
1	14	8	45.8	-54.2
1	15	8	145.8	-145.6
1	16	8	65.3	72.1
1	20	8	32.8	30.0
1	2	7	130.5	127.1
1	3	7	51.8	52.6
1	4	7	59.4	-50.5
1	5	7	55.6	-61.6
1	6	7	77.7	74.7
1	7	7	25.2	27.7
1	8	7	40.8	-46.0
1	9	7	80.2	-82.3
1	10	7	28.2	-24.3
1	11	7	19.2	12.8
1	12	7	65.1	-63.9
1	13	7	66.6	-69.2
1	14	7	46.2	45.0
1	15	7	65.0	66.8
1	16	7	75.2	-81.9
1	17	7	64.1	69.7
1	19	7	43.1	43.3
1	0	6	156.9	-159.6
1	1	6	68.4	-64.1
1	2	6	103.3	132.7
1	3	6	11.1	27.6
1	4	6	91.2	-74.1
1	7	6	60.2	55.9
1	8	6	56.1	-57.5
1	10	6	26.9	27.7
1	12	6	40.0	-40.4
1	13	6	228.1	223.4
1	14	6	66.8	62.5
1	15	6	46.6	45.6
1	17	6	54.4	62.0
1	18	6	45.5	51.2
1	20	6	33.3	27.4
1	2	5	93.8	88.2
1	3	5	119.2	123.5
1	4	5	61.5	65.0
1	5	5	155.5	-155.4
1	6	5	38.6	-46.2
1	7	5	96.2	93.7
1	8	5	99.3	103.0
1	9	5	92.8	-87.3
1	10	5	35.1	34.2
1	11	5	56.7	63.0
1	12	5	165.4	165.5
1	13	5	35.4	-20.1
1	14	5	26.1	29.0
1	16	5	103.9	109.2
1	17	5	50.3	-44.6
1	21	5	46.9	45.5
1	22	5	49.7	-56.2
1	23	5	18.2	-30.2
1	25	5	34.2	44.3
1	0	4	121.5	142.3
1	1	4	176.6	-230.0
1	2	4	189.2	-205.5
1	3	4	24.2	19.9
1	5	4	56.2	-57.4
1	7	4	114.5	102.6
1	8	4	53.8	55.8
1	9	4	103.8	-90.8
1	10	4	53.7	51.1
1	11	4	40.6	36.1
1	14	4	30.1	29.7
1	15	4	20.6	23.8
1	16	4	96.7	-100.2
1	18	4	75.7	-74.2
1	19	4	19.0	-26.7
1	20	4	35.0	-39.1
1	26	4	34.0	37.6
1	27	4	33.2	40.2
1	1	3	47.0	-43.5
1	2	3	28.6	18.9
1	3	3	107.6	-112.0
1	4	3	242.7	263.6
1	5	3	22.9	32.1
1	6	3	67.4	-67.8
1	8	3	104.6	87.1
1	9	3	24.1	22.1
1	10	3	143.4	-136.7
1	11	3	39.4	32.8
1	12	3	66.7	-63.7
1	13	3	25.1	32.3
1	14	3	189.1	-185.4
1	17	3	33.5	-27.1
1	18	3	85.6	-81.7
1	19	3	89.7	-94.9
1	22	3	72.6	79.9
1	1	2	116.2	-153.3
1	2	2	155.3	-163.1
1	3	2	46.1	44.7
1	4	2	106.7	111.3
1	5	2	75.2	-63.1
1	6	2	175.9	-166.6
1	7	2	145.8	-136.5
1	8	2	27.9	26.4
1	11	2	34.9	-42.9
1	12	2	24.2	30.4
1	13	2	113.7	-103.7
1	15	2	129.3	-129.0
1	18	2	57.9	61.7
1	21	2	66.7	79.1
1	23	2	29.6	31.9
1	25	2	38.1	41.2
1	26	2	57.0	-65.1
1	27	2	28.5	21.6
1	2	1	176.3	-193.7
1	3	1	55.6	-52.2
1	4	1	31.6	24.8
1	5	1	53.4	45.5
1	6	1	86.7	72.6
1	7	1	140.0	-131.5
1	8	1	25.2	28.8
1	9	1	59.4	-45.8
1	11	1	57.5	-63.7
1	12	1	56.6	56.2
1	13	1	103.5	99.6
1	17	1	136.3	139.4
1	18	1	87.4	94.2
1	19	1	88.9	104.8
1	21	1	30.4	30.1
1	22	1	35.3	47.6
1	23	1	39.0	45.2
1	24	1	51.3	-58.9
1	25	1	28.2	-31.2
1	3	0	183.7	-198.5
1	4	0	177.7	-170.6
1	5	0	49.1	46.1
1	6	0	107.2	96.0
1	7	0	77.0	59.7
1	8	0	69.1	40.4
1	9	0	142.5	126.8
1	11	0	41.8	44.3
1	12	0	58.9	-59.5
1	13	0	174.6	171.9
1	14	0	161.6	154.2
1	15	0	49.5	40.0
1	17	0	24.8	29.1
1	18	0	129.3	141.1
1	22	0	40.6	49.7
1	23	0	61.0	-69.5
1	27	0	60.8	-59.5
1	28	0	43.1	47.2
1	3	-1	65.2	-73.7
1	4	-1	162.6	-139.5
1	5	-1	69.4	80.5
1	6	-1	215.7	-202.0
1	7	-1	49.2	-52.5
1	8	-1	71.4	62.9
1	9	-1	93.3	86.5
1	10	-1	29.7	-23.5
1	11	-1	40.9	-36.7
1	12	-1	67.2	70.4
1	14	-1	102.7	100.1
1	15	-1	46.4	43.3
1	19	-1	26.5	25.1
1	20	-1	42.7	-42.3
1	21	-1	43.0	-41.3
1	22	-1	50.7	-53.6
1	23	-1	37.6	40.0
1	24	-1	49.7	-46.3
1	25	-1	32.2	-42.0
1	27	-1	73.2	77.9
1	28	-1	40.1	-41.5
1	2	-2	133.9	152.8
1	3	-2	120.4	121.9
1	4	-2	90.7	89.8
1	5	-2	204.2	197.8
1	6	-2	109.7	97.0
1	7	-2	87.5	86.4
1	8	-2	38.1	30.5
1	10	-2	50.8	60.5
1	12	-2	124.4	-130.7
1	13	-2	106.1	-101.1
1	15	-2	45.6	45.8
1	16	-2	142.4	-139.4
1	17	-2	124.9	-115.2
1	18	-2	31.7	-30.8
1	19	-2	46.0	51.7
1	20	-2	117.1	-124.9
1	21	-2	52.7	-55.2
1	24	-2	55.7	-56.9
1	2	-3	50.3	-57.9
1	3	-3	50.9	57.6
1	4	-3	60.7	66.9
1	5	-3	124.6	130.2
1	6	-3	80.0	84.4
1	7	-3	41.1	34.6
1	8	-3	45.3	-39.9
1	9	-3	32.5	20.3
1	10	-3	54.2	-51.8
1	11	-3	95.4	-96.4
1	12	-3	24.4	9.6
1	15	-3	44.9	-40.7
1	16	-3	43.7	36.3
1	17	-3	73.4	-70.7
1	18	-3	70.0	-68.1
1	20	-3	30.3	30.4
1	21	-3	47.2	-49.9
1	23	-3	37.5	-37.0
1	24	-3	69.8	68.9
1	25	-3	46.4	-54.4
1	26	-3	39.6	40.4
1	3	-4	127.9	124.1
1	4	-4	74.5	84.7
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1	6	-4	22.0	-31.3
1	7	-4	90.2	-86.7
1	8	-4	105.6	-101.8
1	9	-4	175.4	-155.6
1	10	-4	91.5	-91.3
1	11	-4	88.5	81.0
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1	13	-4	163.4	-149.7
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1	17	-4	31.2	-27.8
1	18	-4	73.5	64.6
1	20	-4	47.1	43.6
1	21	-4	19.2	5.9
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1	27	-4	35.1	35.3
1	28	-4	39.1	-45.7
1	2	-5	103.6	-107.7
1	3	-5	169.5	-178.7
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1	5	-5	54.7	-57.3
1	6	-5	107.7	-101.4
1	8	-5	152.9	-139.0
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1	15	-5	36.1	-28.9
1	18	-5	53.0	-55.2
1	21	-5	79.1	76.5
1	23	-5	26.9	27.7
1	25	-5	47.6	50.4
1	28	-5	43.9	52.1
1	2	-6	90.8	-113.3
1	3	-6	72.1	-91.4
1	4	-6	186.8	-169.3
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1	7	-6	31.5	-34.5
1	8	-6	36.5	35.7
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1	11	-6	28.6	-15.9
1	12	-6	209.2	197.1
1	13	-6	114.1	-102.3
1	14	-6	83.6	-83.3
1	15	-6	17.4	22.0
1	16	-6	99.4	95.9
1	18	-6	51.8	-53.2
1	20	-6	52.7	50.4
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1	7	-7	92.8	87.0
1	8	-7	104.3	102.2
1	10	-7	40.5	44.9
1	11	-7	55.0	77.1
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1	16	-7	82.1	-75.2
1	18	-7	35.7	31.2
1	19	-7	36.0	-36.4
1	21	-7	46.3	-40.3
1	22	-7	31.8	38.3
1	2	-8	240.4	262.7
1	5	-8	91.2	99.2
1	6	-8	149.2	148.3
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1	10	-8	63.9	-61.5
1	12	-8	16.6	-16.2
1	13	-8	110.8	94.3
1	14	-8	113.7	-107.2
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1	18	-8	38.4	-37.6
1	21	-8	39.5	30.0
1	22	-8	38.1	-44.0
1	24	-8	40.6	-44.1
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1	3	-9	90.1	82.6
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1	15	-9	66.0	60.8
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1	23	-9	36.7	-39.0
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1	8	-10	45.6	-51.1
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1	13	-10	127.0	102.1
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1	19	-10	56.6	-53.3
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1	1	-11	54.4	-56.3
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1	4	-11	36.7	-37.0
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1	9	-11	49.1	44.0
1	10	-11	112.2	-105.5
1	11	-11	25.6	-21.1
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1	2	-12	129.8	-114.4
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1	8	-12	76.5	66.9
1	9	-12	78.9	-76.3
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1	13	-12	52.4	-45.7
1	14	-12	73.6	23.7
1	15	-12	45.1	-47.6
1	17	-12	29.8	23.2
1	18	-12	31.9	-27.6
1	19	-12	73.3	-70.3
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1	2	-13	17.4	-8.7
1	3	-13	37.2	-35.4
1	4	-13	117.3	101.3
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1	14	-13	23.5	-23.2
1	15	-13	26.8	-20.2
1	16	-13	35.1	30.8
1	17	-13	31.7	32.3
1	20	-13	28.2	21.5
1	21	-13	25.6	32.9
1	22	-13	26.9	25.8
1	23	-13	26.3	23.8
1	0	-14	193.9	192.1
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1	9	-14	138.9	123.0
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1	13	-14	52.3	46.0
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1	17	-14	46.2	42.8
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1	3	-15	30.0	25.8
1	4	-15	50.6	-70.8
1	7	-15	33.3	-24.5
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1	1	-16	63.7	51.6
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1	4	-16	54.5	48.0
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1	10	-16	49.9	53.0
1	11	-16	37.2	-35.8
1	12	-16	70.7	-64.6
1	13	-16	17.8	24.1
1	14	-16	17.3	24.6
1	15	-16	20.4	-22.3
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1	20	-16	54.6	-59.7
1	1	-17	33.2	-27.8
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1	8	-17	43.7	-39.9
1	9	-17	29.1	25.1
1	12	-17	38.5	-33.0
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1	1	-19	33.0	-27.4
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1	0	-22	24.7	27.6
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2	8	18	26.9	-31.7
2	9	18	19.8	22.2
2	10	18	25.7	-30.9
2	11	18	30.5	-31.0
2	12	18	15.2	23.9
2	13	18	21.8	22.5
2	14	18	13.3	-0.6
2	15	18	21.9	-19.5
2	16	18	43.3	55.9
2	3	17	36.5	-30.0
2	6	17	27.7	-22.5
2	7	17	40.2	-39.4
2	8	17	34.8	37.3
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2	4	16	69.0	-67.5
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2	10	16	38.9	43.3
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2	13	16	63.9	63.7
2	15	16	19.0	23.8
2	16	16	25.7	-31.6
2	17	16	29.7	31.9
2	2	15	51.8	52.0
2	3	15	23.8	-22.4
2	4	15	50.5	55.8
2	5	15	35.8	32.8
2	6	15	55.4	56.8
2	7	15	16.8	-13.8
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2	15	15	20.7	-21.9
2	16	15	24.2	-24.7
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2	3	14	45.3	46.4
2	4	14	45.5	47.8
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2	6	14	20.5	-14.8
2	7	14	44.5	43.1
2	8	14	23.5	24.8
2	9	14	23.8	-20.0
2	10	14	29.1	28.6
2	11	14	31.3	-33.7
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2	6	12	73.1	-72.1
2	7	12	65.8	-62.3
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2	12	12	29.1	-19.9
2	14	12	23.1	-24.5
2	16	12	43.6	49.4
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2	10	11	74.6	60.1
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2	14	11	60.7	65.3
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2	17	11	70.9	81.4
2	21	11	27.9	29.2
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2	0	10	119.8	-121.0
2	1	10	106.9	106.1
2	2	10	35.7	-43.6
2	4	10	23.9	13.6
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2	1	9	91.0	112.7
2	2	9	128.0	130.2

H	K	L	F OBS	F CALC
2	3	9	61±0	67±6
2	4	9	128±0	115±1
2	5	9	95±6	-54±2
2	6	9	103±2	114±6
2	7	9	191±6	121±6
2	8	9	30±0	-25±0
2	9	9	92±4	-82±5
2	10	9	48±3	50±5
2	11	9	73±2	77±3
2	12	9	47±8	54±3
2	13	9	44±5	-51±7
2	14	9	23±7	-20±3
2	15	9	39±0	-39±2
2	16	9	40±8	43±3
2	17	9	81±5	77±6
2	18	9	176±5	188±3
2	19	9	50±2	47±4
2	20	9	42±6	-40±4
2	21	9	42±6	-42±8
2	22	9	72±6	-73±8
2	23	9	48±4	46±9
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2	0	10	44±5	-41±6
2	1	10	37±7	-43±4
2	2	10	144±9	153±3
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2	7	10	31±1	34±5
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2	10	10	134±9	-136±3
2	11	10	101±9	-103±8
2	12	10	38±5	37±3
2	13	10	59±8	-79±0
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2	16	10	87±0	-70±9
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2	14	11	59±8	-79±0
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2	17	11	87±0	-70±9
2	18	11	28±6	-31±5
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2	20	11	37±7	39±8
2	21	11	32±1	40±6
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2	8	12	31±1	34±5
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2	10	12	29±3	-24±2
2	11	12	134±9	-136±3
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3	4	-9	13.0	11.0
3	6	-9	95.7	-84.0
3	7	-9	138.7	139.2
3	8	-9	35.2	32.1
3	9	-9	14.0	19.7
3	10	-9	34.2	-30.4
3	11	-9	33.5	32.1
3	12	-9	30.4	-32.2
3	13	-9	39.1	[illegible]
3	14	-9	81.9	-80.7
3	19	-9	80.0	-84.5
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3	23	-9	95.6	-91.0
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3	0	-10	76.5	-89.0
3	2	-10	122.3	-125.9
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3	5	-10	70.8	72.3
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3	7	-10	59.2	-50.7
3	9	-10	64.1	57.7
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3	11	-10	108.6	-103.4
3	15	-10	69.4	-69.4
3	16	-10	46.5	55.7
3	17	-10	39.6	39.4
3	19	-10	74.7	-80.4
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3	21	-10	98.3	90.9
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3	1	-11	40.8	-47.1
3	3	-11	62.9	-72.1
3	4	-11	111.3	105.6
3	5	-11	106.8	-95.8
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3	8	-11	27.6	-22.0
3	9	-11	174.3	-111.4
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3	17	-11	99.9	102.5
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3	22	-11	69.6	58.9
3	23	-11	25.6	30.2
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3	10	-12	38.3	45.3
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3	16	-12	47.9	-47.8
3	17	-12	71.8	67.5
3	18	-12	127.0	111.7
3	19	-12	51.9	-54.1
3	22	-12	46.1	46.9
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3	1	-13	42.9	32.6
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3	5	-13	44.0	45.7
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3	13	-13	28.0	27.0
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3	17	-13	33.2	-31.5
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3	19	-14	19.9	26.2
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3	1	-20	25.9	25.0
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4	1	13	20.5	-17.1
4	2	13	55.5	-61.9
4	3	13	37.5	-37.4
4	4	13	44.5	-47.7
4	6	13	37.7	-34.5
4	7	13	26.7	22.6
4	8	13	54.7	-60.6
4	11	13	37.2	36.7
4	12	13	41.8	-52.0
4	2	12	41.9	-42.9
4	5	12	71.1	73.2
4	6	12	37.2	39.1
4	7	12	69.0	71.4
4	9	12	20.7	20.0
4	10	12	31.6	34.3
4	11	12	29.2	30.6
4	13	12	76.1	-88.2
4	14	12	20.0	13.6
4	15	12	15.9	19.1
4	16	12	24.4	-31.2
4	18	12	19.9	26.1
4	19	12	49.0	58.4
4	20	12	26.9	-31.0
4	2	11	44.2	49.0
4	3	11	19.3	-23.9
4	6	11	49.8	56.8
4	8	11	52.1	53.3
4	9	11	37.2	-38.3
4	10	11	46.0	54.8
4	12	11	29.3	28.9
4	15	11	40.3	45.1
4	17	11	51.7	65.5
4	19	11	22.4	22.3
4	20	11	24.7	33.9
4	0	10	45.5	48.5
4	1	10	67.0	70.8
4	2	10	27.8	-24.0
4	3	10	21.2	-17.3
4	4	10	47.8	52.8
4	6	10	21.9	-16.7
4	8	10	22.6	-27.8
4	9	10	39.7	-42.6
4	10	10	54.6	-58.6
4	11	10	40.8	47.5
4	14	10	23.9	-24.5
4	15	10	70.2	73.5
4	16	10	49.6	54.4
4	17	10	37.9	-38.5
4	19	10	46.2	56.6
4	20	10	33.2	34.0
4	21	10	43.6	-49.7
4	3	9	76.0	77.9
4	4	9	83.4	-83.3
4	5	9	14.5	15.3
4	6	9	66.1	-71.0
4	7	9	49.9	47.3
4	8	9	56.4	-51.8
4	10	9	29.9	-29.5
4	13	9	41.0	-45.4
4	14	9	77.3	81.0
4	15	9	43.1	-44.0
4	16	9	20.6	-27.1
4	17	9	33.2	-44.6
4	18	9	45.8	-52.3
4	19	9	53.0	-58.5
4	20	9	33.4	-42.6
4	22	9	33.4	-38.9
4	23	9	50.2	-58.4
4	0	8	57.2	-68.1
4	1	8	87.1	94.4
4	2	8	55.5	60.5
4	3	8	82.1	-93.8
4	5	8	25.6	29.2
4	7	8	71.7	-106.2
4	8	8	78.5	96.9
4	9	8	31.9	-31.8
4	10	8	46.3	55.5
4	11	8	42.2	-45.5
4	12	8	25.6	21.3
4	14	8	28.9	-32.7
4	15	8	23.8	27.4
4	16	8	33.8	-37.3
4	17	8	20.6	-34.1
4	18	8	51.1	-90.1
4	22	8	37.7	-37.4
4	1	7	38.1	-39.8
4	3	7	34.9	45.5
4	4	7	47.8	52.9
4	5	7	62.9	-64.9
4	7	7	62.8	57.4
4	8	7	22.1	-25.7
4	11	7	52.9	50.9
4	12	7	65.7	-72.4
4	14	7	43.9	-44.0
4	16	7	20.7	-23.2
4	17	7	23.9	-25.1
4	18	7	51.7	57.6
4	19	7	32.9	-37.2
4	22	7	63.8	70.0
4	0	6	84.1	-85.0
4	1	6	47.7	57.9
4	2	6	102.7	109.5
4	4	6	145.8	-153.3
4	5	6	111.6	116.2
4	8	6	189.8	-197.5
4	10	6	50.3	-43.2
4	12	6	50.6	54.5

H	K	L	F OBS	F CALC
4	16	6	68.0	68.1
4	18	6	26.7	30.2
4	20	6	70.2	81.1
4	21	6	49.8	54.4
4	22	6	29.9	35.9
4	23	6	34.3	43.8
4	2	5	27.1	-29.9
4	3	5	91.4	-102.5
4	4	5	34.1	31.0
4	5	5	54.1	-65.4
4	7	5	105.2	-122.8
4	8	5	106.0	101.3
4	9	5	106.9	-98.1
4	10	5	42.1	44.0
4	11	5	46.1	54.1
4	12	5	75.3	70.5
4	15	5	59.6	62.3
4	17	5	65.1	66.4
4	19	5	82.4	92.0
4	23	5	79.3	80.1
4	24	5	50.1	-56.1
4	0	4	78.1	-55.0
4	1	4	99.2	-121.9
4	2	4	22.6	27.8
4	4	4	68.1	-67.8
4	5	4	144.3	-153.5
4	6	4	68.3	76.8
4	7	4	94.3	89.7
4	8	4	28.0	-26.9
4	9	4	33.2	31.9
4	11	4	93.1	86.1
4	12	4	21.7	24.3
4	13	4	63.3	61.2
4	14	4	64.7	-58.1
4	16	4	44.9	45.2
4	23	4	40.7	-46.2
4	25	4	35.5	-53.6
4	3	3	33.5	22.5
4	4	3	42.2	44.1
4	5	3	139.7	155.1
4	6	3	26.9	22.5
4	7	3	44.6	43.5
4	8	3	121.6	127.1
4	9	3	82.4	74.8
4	10	3	86.3	-72.6
4	12	3	127.4	129.2
4	15	3	62.7	-64.1
4	17	3	35.2	-34.5
4	19	3	41.4	-38.8
4	21	3	64.9	-71.3
4	25	3	36.7	-46.4
4	26	3	25.7	-33.5
4	0	2	24.1	41.2
4	1	2	51.5	-59.3
4	2	2	31.7	-35.7
4	3	2	168.9	187.7
4	4	2	111.7	109.2
4	5	2	52.9	-52.1
4	6	2	76.7	70.9
4	7	2	157.7	151.8
4	8	2	141.7	131.7
4	9	2	28.4	-28.9
4	10	2	30.1	31.9
4	11	2	15.9	-15.7
4	12	2	16.7	22.3
4	13	2	36.4	31.5
4	14	2	52.5	-57.7
4	15	2	43.9	-43.7
4	18	2	75.9	-71.2
4	20	2	53.3	-59.2
4	22	2	63.4	-65.5
4	23	2	28.8	30.3
4	24	2	20.4	-19.0
4	25	2	26.6	25.4
4	1	1	23.5	48.7
4	2	1	45.6	45.9
4	3	1	22.9	-31.5
4	4	1	27.0	18.5
4	5	1	38.0	39.4
4	6	1	65.1	-62.4
4	7	1	124.5	-124.8
4	9	1	65.7	62.8
4	10	1	66.1	-79.4
4	11	1	156.5	-141.4
4	12	1	69.6	-62.4
4	13	1	38.6	41.2
4	15	1	21.7	-25.0
4	16	1	47.7	-47.2
4	17	1	23.1	30.8
4	18	1	20.4	19.2
4	19	1	41.3	45.1
4	20	1	31.6	35.9
4	24	1	29.3	32.0
4	26	1	45.3	50.4
4	3	0	62.2	-61.5
4	4	0	61.5	51.8
4	5	0	30.0	-32.2
4	6	0	171.6	-169.1
4	7	0	105.7	-92.4
4	8	0	26.4	-21.4
4	10	0	52.7	-82.1
4	11	0	171.7	-148.1
4	12	0	57.0	-50.4
4	13	0	67.5	63.1
4	14	0	43.9	48.0
4	15	0	55.0	-55.2
4	16	0	22.4	33.0
4	18	0	83.8	76.7
4	19	0	86.8	-84.8
4	20	0	37.5	40.1
4	22	0	23.0	22.2
4	23	0	22.1	-25.8
4	27	0	34.1	39.4
4	3	-1	105.4	-85.0
4	4	-1	72.3	-75.8
4	6	-1	15.1	10.2
4	7	-1	42.5	-40.6
4	8	-1	259.9	-237.6
4	9	-1	36.6	36.7
4	10	-1	55.2	53.4
4	11	-1	36.4	-34.7
4	12	-1	18.7	-13.9
4	13	-1	69.6	76.9
4	14	-1	71.5	69.3
4	15	-1	21.5	19.4
4	17	-1	23.3	-21.2
4	19	-1	37.7	34.9
4	20	-1	26.7	-34.4
4	22	-1	25.7	-23.5
4	23	-1	45.6	49.9
4	3	-2	26.2	-30.7
4	4	-2	74.6	-75.6
4	5	-2	112.3	110.6
4	7	-2	50.0	-45.8
4	9	-2	76.2	65.3
4	10	-2	145.7	127.8
4	11	-2	108.4	89.7
4	13	-2	95.8	87.1
4	14	-2	73.2	64.7
4	15	-2	38.9	32.9
4	16	-2	85.3	-76.2
4	17	-2	73.0	79.8
4	18	-2	28.9	29.4
4	19	-2	23.7	-24.4
4	20	-2	53.4	-56.9
4	22	-2	32.5	32.0
4	25	-2	31.9	-31.7
4	2	-3	92.4	84.7
4	3	-3	37.8	-38.1
4	4	-3	58.4	48.9
4	5	-3	60.6	59.7
4	6	-3	245.2	229.0
4	8	-3	91.4	83.0
4	10	-3	123.9	110.8
4	11	-3	140.4	120.6

H	K	L	F OBS	F CALC
4	12	-3	45.4	-37.8
4	17	-3	56.7	-54.9
4	20	-3	53.6	56.8
4	21	-3	47.1	-45.8
4	23	-3	42.5	42.3
4	24	-3	46.2	54.4
4	2	-4	64.2	75.5
4	3	-4	18.6	11.2
4	4	-4	73.2	23.8
4	6	-4	28.3	36.3
4	7	-4	95.7	92.6
4	8	-4	91.1	-82.5
4	9	-4	56.0	-49.2
4	10	-4	32.7	-25.5
4	11	-4	91.3	84.8
4	13	-4	105.9	-100.7
4	15	-4	47.9	-41.0
4	16	-4	19.7	-25.8
4	17	-4	115.9	-97.0
4	18	-4	37.5	33.9
4	19	-4	123.0	105.3
4	20	-4	20.6	-26.0
4	23	-4	43.4	44.9
4	1	-5	91.3	112.7
4	3	-5	71.0	75.8
4	4	-5	142.8	-167.7
4	7	-5	55.6	62.3
4	8	-5	55.7	-61.2
4	9	-5	111.7	-104.2
4	10	-5	61.1	-56.0
4	11	-5	72.1	-67.8
4	12	-5	63.4	-71.1
4	13	-5	65.3	-75.9
4	14	-5	51.6	-43.4
4	15	-5	29.5	-32.6
4	16	-5	71.7	-62.0
4	17	-5	40.7	36.9
4	18	-5	37.6	-40.7
4	19	-5	20.7	-16.8
4	20	-5	41.1	45.2
4	21	-5	32.9	30.1
4	22	-5	62.5	-55.3
4	23	-5	44.1	-52.5
4	24	-5	34.6	44.2
4	26	-5	37.8	-43.0
4	27	-5	36.0	-43.9
4	2	-6	25.5	-29.0
4	3	-6	73.0	-79.9
4	4	-6	40.4	49.7
4	5	-6	137.9	-150.9
4	7	-6	59.9	-55.4
4	8	-6	91.5	77.7
4	9	-6	101.9	-92.8
4	10	-6	60.6	-61.3
4	11	-6	61.8	-56.8
4	12	-6	22.8	-9.0
4	13	-6	42.4	-41.0
4	14	-6	24.6	-32.6
4	16	-6	55.1	54.2
4	17	-6	41.0	-34.5
4	18	-6	41.4	-41.6
4	19	-6	31.6	32.1
4	20	-6	37.1	36.6
4	21	-6	43.0	-48.4
4	22	-6	41.4	-42.9
4	26	-6	27.7	-28.9
4	1	-7	110.1	-139.1
4	2	-7	41.6	-46.0
4	3	-7	85.6	83.3
4	4	-7	48.5	-59.2
4	5	-7	66.1	-67.3
4	6	-7	32.2	-32.2
4	7	-7	116.5	119.4
4	8	-7	45.5	-63.9
4	9	-7	40.8	-35.9
4	10	-7	43.7	38.8
4	11	-7	83.5	74.6
4	14	-7	75.9	74.8
4	15	-7	51.5	45.0
4	19	-7	37.6	-41.6
4	21	-7	35.8	40.0
4	23	-7	89.9	-89.2
4	25	-7	54.5	63.4
4	1	-8	76.9	79.4
4	2	-8	36.1	-46.5
4	4	-8	55.7	-57.9
4	5	-8	168.8	182.2
4	6	-8	53.2	42.6
4	7	-8	65.9	-74.2
4	8	-8	83.7	92.3
4	9	-8	101.0	97.4
4	12	-8	34.3	29.1
4	13	-8	79.7	79.4
4	14	-8	25.6	28.3
4	15	-8	30.9	16.0
4	17	-8	66.5	62.6
4	18	-8	46.2	-44.6
4	19	-8	37.2	-32.1
4	20	-8	12.5	21.3
4	21	-8	42.9	41.6
4	22	-8	33.2	-36.1
4	24	-8	32.3	33.2
4	26	-8	35.8	41.7
4	2	-9	40.0	41.6
4	4	-9	131.1	151.9
4	5	-9	140.2	-157.1
4	6	-9	58.2	54.3
4	7	-9	65.6	60.0
4	8	-9	37.3	39.5
4	9	-9	100.7	-100.3
4	10	-9	44.9	39.6
4	11	-9	43.5	42.7
4	12	-9	44.7	44.1
4	13	-9	47.2	-53.7
4	15	-9	41.0	34.4
4	18	-9	29.0	-25.2
4	19	-9	50.6	44.4
4	20	-9	68.4	-65.5
4	22	-9	60.6	58.2
4	23	-9	15.7	20.1
4	24	-9	42.1	-42.6
4	25	-9	28.2	39.4
4	0	-10	42.6	47.3
4	2	-10	124.5	139.5
4	4	-10	52.7	-44.7
4	5	-10	41.6	37.6
4	6	-10	62.5	69.3
4	7	-10	35.4	-31.0
4	8	-10	123.1	-120.7
4	10	-10	22.0	21.8
4	11	-10	43.6	-34.1
4	13	-10	47.2	-42.4
4	14	-10	52.1	-56.5
4	17	-10	39.3	34.3
4	19	-10	45.4	-43.3
4	1	-11	145.4	147.9
4	2	-11	103.2	-109.0
4	3	-11	52.5	53.7
4	4	-11	25.1	14.7
4	5	-11	29.6	30.1
4	6	-11	142.4	-150.5
4	7	-11	32.2	26.0
4	8	-11	24.5	27.0
4	9	-11	54.7	-44.8
4	10	-11	78.0	-76.9
4	11	-11	47.7	43.9
4	12	-11	51.2	47.9
4	13	-11	33.6	-37.0
4	14	-11	47.8	-45.7
4	15	-11	20.7	-11.8
4	17	-11	25.6	-35.2
4	19	-11	47.8	-49.3
4	20	-11	27.6	-31.5
4	21	-11	31.0	-39.6
4	0	-12	59.7	58.4

H	K	L	F OBS	F CALC
4	1	-12	81.9	-87.2
4	5	-12	109.8	-104.0
4	6	-12	38.9	39.4
4	7	-12	44.9	44.2
4	9	-12	23.1	-16.9
4	10	-12	48.2	49.1
4	11	-12	33.4	34.9
4	12	-12	29.2	30.2
4	13	-12	33.8	-36.4
4	17	-12	37.7	-28.9
4	19	-12	37.8	42.3
4	20	-12	39.5	-44.3
4	1	-13	106.1	-110.0
4	2	-13	22.3	-24.1
4	3	-13	99.1	-104.3
4	6	-13	51.4	-50.7
4	8	-13	103.5	93.1
4	9	-13	59.1	55.5
4	10	-13	58.2	-79.8
4	13	-13	76.2	73.2
4	14	-13	48.6	-53.1
4	16	-13	29.9	-29.0
4	18	-13	25.6	32.0
4	20	-13	41.0	43.9
4	22	-13	28.4	32.6
4	0	-14	73.1	-58.8
4	1	-14	38.4	35.6
4	2	-14	124.9	-127.4
4	6	-14	80.9	-76.3
4	7	-14	61.7	60.5
4	10	-14	53.4	-47.8
4	12	-14	26.4	-20.6
4	13	-14	30.9	-29.4
4	16	-14	51.8	59.7
4	17	-14	41.3	-44.
4	18	-14	33.8	25.0
4	20	-14	55.7	53.6
4	21	-14	18.5	23.6
4	22	-14	17.0	26.1
4	3	-15	29.1	-31.2
4	4	-15	33.7	37.6
4	5	-15	23.9	31.4
4	6	-15	16.9	24.2
4	7	-15	74.6	-74.4
4	9	-15	29.1	34.0
4	10	-15	45.7	37.7
4	11	-15	103.2	-105.7
4	15	-15	36.7	35.2
4	17	-15	33.1	36.0
4	19	-15	43.1	49.2
4	20	-15	24.9	-29.7
4	0	-16	23.9	24.5
4	1	-16	31.6	33.4
4	2	-16	43.1	40.2
4	3	-16	52.0	-54.2
4	4	-16	47.7	47.1
4	5	-16	63.0	59.8
4	7	-16	69.9	-74.1
4	9	-16	36.7	36.4
4	11	-16	46.4	42.3
4	13	-16	56.4	49.2
4	15	-16	54.6	49.5
4	19	-16	34.4	-42.6
4	1	-17	40.6	44.2
4	5	-17	64.8	61.0
4	7	-17	19.8	12.8
4	8	-17	59.7	-57.6
4	9	-17	64.7	54.8
4	10	-17	67.0	69.0
4	14	-17	60.1	62.5
4	15	-17	35.3	-33.3
4	16	-17	47.7	48.4
4	17	-17	55.8	-57.2
4	0	-18	37.8	-25.8
4	4	-18	44.8	-46.7
4	6	-18	42.5	43.9
4	7	-18	21.6	-25.5
4	8	-18	18.4	-11.2
4	9	-18	20.7	-30.5
4	10	-18	40.2	41.6
4	11	-18	16.8	-7.8
4	13	-18	30.5	-26.3
4	2	-19	42.4	41.[illegible]
4	3	-19	37.9	-42.0
4	6	-19	35.0	29.7
4	7	-19	35.7	-33.3
4	8	-19	34.8	-35.4
4	12	-19	69.3	-72.6
4	14	-19	39.1	-43.9
4	2	-20	23.9	30.9
4	4	-20	20.9	-29.7
4	5	-20	48.7	-49.8
4	6	-20	32.4	-26.9
4	7	-20	19.5	21.5
4	8	-20	32.6	-39.1
4	9	-20	25.4	-22.3
4	10	-20	17.0	-21.8
4	13	-20	29.6	-36.9
4	3	-21	30.5	31.7
4	4	-21	51.8	-51.9
5	3	16	36.8	-26.7
5	7	16	36.9	-34.0
5	8	16	26.9	-24.6
5	12	16	39.4	-39.9
5	1	15	41.7	-36.0
5	2	15	27.7	-25.3
5	6	15	30.1	-30.1
5	7	15	26.6	28.5
5	8	15	22.6	20.2
5	9	15	22.1	24.6
5	10	15	17.6	19.4
5	12	15	25.8	18.4
5	3	14	34.9	20.4
5	4	14	31.8	29.1
5	5	14	28.3	25.7
5	6	14	31.9	32.6
5	7	14	50.3	43.2
5	10	14	44.2	42.4
5	11	14	56.6	56.9
5	12	14	35.6	-35.2
5	13	14	24.3	-34.8
5	14	14	16.4	18.5
5	15	14	56.8	53.1
5	16	14	36.6	-31.1
5	2	13	40.8	35.0
5	4	13	55.8	41.5
5	5	13	49.9	53.9
5	6	13	32.1	27.3
5	8	13	45.0	36.5
5	0	12	47.6	82.4
5	1	12	49.4	51.7
5	4	12	62.5	62.1
5	6	12	43.2	-44.6
5	9	12	43.1	-39.7
5	10	12	49.5	-37.3
5	13	12	23.7	-14.7
5	15	12	30.6	40.2
5	17	12	48.0	-47.7
5	18	12	21.7	21.6
5	19	12	34.4	34.7
5	1	11	49.9	35.4
5	4	11	72.8	-64.4
5	6	11	47.1	-40.2
5	8	11	74.6	-73.0
5	10	11	72.1	-67.3
5	11	11	28.1	-36.5
5	12	11	42.9	-44.0
5	13	11	20.0	22.3
5	16	11	34.6	-39.1
5	17	11	21.7	22.7
5	20	11	22.4	-23.5
5	1	10	128.1	128.2
5	3	10	120.8	-112.1
5	6	10	41.4	-41.8
5	7	10	48.4	-59.9

H	K	L	F OBS	F CALC
5	6	10	46.7	43.5
5	12	10	81.5	74.1
5	18	10	43.6	-42.4
5	20	10	32.1	26.1
5	21	10	40.0	-40.9
5	1	9	70.3	-67.8
5	2	9	25.4	34.2
5	3	9	31.3	-24.9
5	5	9	32.1	-28.2
5	6	9	53.1	54.9
5	7	9	46.7	-53.5
5	8	9	43.3	39.5
5	9	9	59.5	60.2
5	10	9	69.0	69.7
5	11	9	49.4	39.3
5	13	9	35.3	34.0
5	0	8	168.4	-167.6
5	2	8	66.5	72.5
5	3	8	24.1	-21.1
5	4	8	117.3	-112.9
5	5	8	132.7	134.7
5	7	8	36.6	30.2
5	9	8	86.2	84.0
5	11	8	19.6	28.2
5	13	8	40.5	-35.8
5	14	8	40.8	-40.4
5	16	8	35.0	35.9
5	18	8	30.5	-33.5
5	19	8	29.4	35.7
5	20	8	25.0	32.6
5	21	8	53.4	49.2
5	1	7	41.8	42.2
5	2	7	52.3	-49.7
5	3	7	56.5	56.4
5	4	7	28.2	26.6
5	6	7	36.0	42.2
5	9	7	74.5	-61.8
5	10	7	78.7	70.1
5	11	7	38.5	-36.8
5	12	7	48.2	-37.4
5	13	7	70.7	-64.3
5	14	7	62.4	-59.3
5	1	6	75.9	-73.5
5	2	6	109.0	116.8
5	3	6	37.9	31.7
5	4	6	38.8	45.6
5	5	6	134.9	-124.5
5	6	6	143.3	133.8
5	7	6	40.4	-32.4
5	8	6	45.2	-55.0
5	9	6	93.9	-72.5
5	10	6	64.2	-57.6
5	13	6	77.3	-63.2
5	14	6	66.4	-81.0
5	15	6	32.1	25.3
5	22	6	33.7	-26.8
5	1	5	57.8	59.8
5	2	5	52.9	-80.0
5	3	5	25.7	22.2
5	4	5	99.7	-90.1
5	5	5	64.2	53.9
5	6	5	183.5	-184.0
5	7	5	56.3	47.1
5	8	5	81.9	-70.5
5	10	5	94.9	-85.5
5	11	5	51.2	44.8
5	12	5	26.4	26.5
5	13	5	38.5	-34.2
5	14	5	45.3	42.5
5	17	5	28.8	38.7
5	18	5	28.7	-26.0
5	19	5	28.2	-26.0
5	21	5	57.2	-58.8
5	22	5	27.7	-24.7
5	23	5	34.4	-36.4
5	0	4	50.7	-82.1
5	1	4	75.5	-79.4
5	2	4	95.1	-96.0
5	3	4	99.4	83.0
5	4	4	26.0	29.7
5	5	4	103.6	-92.7
5	8	4	96.9	90.7
5	9	4	37.8	-33.3
5	11	4	103.0	-86.9
5	12	4	106.9	89.6
5	13	4	90.3	77.6
5	14	4	76.3	-71.3
5	16	4	47.3	37.8
5	17	4	20.4	24.9
5	18	4	62.7	-55.3
5	24	4	23.1	26.8
5	25	4	45.0	48.4
5	1	3	58.0	-118.3
5	2	3	74.4	97.1
5	3	3	93.8	-107.8
5	4	3	68.7	73.0
5	5	3	47.6	-50.0
5	6	3	55.1	50.7
5	7	3	61.3	-79.1
5	8	3	33.4	31.8
5	9	3	13.3	19.9
5	10	3	24.1	-19.7
5	12	3	34.0	31.3
5	13	3	91.5	90.4
5	16	3	24.3	-25.0
5	17	3	42.6	39.7
5	19	3	36.8	34.6
5	21	3	65.6	62.8
5	23	3	29.5	33.0
5	24	3	28.8	34.0
5	25	3	26.3	31.7
5	0	2	75.2	104.5
5	1	2	39.0	51.9
5	2	2	66.9	-77.9
5	3	2	18.6	29.2
5	4	2	31.8	-36.0
5	5	2	96.2	91.8
5	6	2	133.9	-140.5
5	7	2	29.1	33.2
5	8	2	79.4	-25.9
5	9	2	62.8	56.7
5	10	2	30.2	-29.0
5	11	2	110.5	-115.3
5	13	2	116.7	114.7
5	14	2	34.2	25.5
5	15	2	129.4	-121.6
5	16	2	34.1	25.8
5	17	2	94.9	89.5
5	18	2	46.2	47.5
5	19	2	75.9	-71.6
5	20	2	45.4	46.2
5	21	2	37.3	38.0
5	22	2	39.1	39.3
5	23	2	35.3	-27.6
5	24	2	29.5	30.7
5	25	2	25.0	7.8
5	1	1	112.8	119.0
5	5	1	39.8	34.7
5	6	1	41.9	40.7
5	7	1	113.2	-106.0
5	8	1	40.5	37.7
5	10	1	33.6	27.4
5	11	1	32.7	-31.3
5	14	1	22.5	-16.9
5	17	1	40.5	-38.7
5	20	1	24.4	-32.6
5	24	1	46.9	-49.8
5	25	1	26.5	-24.8
5	1	0	54.7	-78.8
5	2	0	73.1	79.1
5	3	0	137.0	-105.5
5	4	0	118.9	87.0
5	5	0	25.2	-23.7
5	6	0	67.1	65.0
5	7	0	23.7	-22.8

H	K	L	F OBS	F CALC
5	8	0	49.8	-44.2
5	9	0	80.5	77.5
5	10	0	143.7	140.3
5	11	0	80.9	81.0
5	12	0	97.1	-87.5
5	13	0	55.7	47.3
5	14	0	33.5	37.9
5	16	0	125.7	-127.7
5	17	0	42.2	41.7
5	20	0	131.0	-130.0
5	23	0	47.4	-43.2
5	24	0	50.5	-53.9
5	25	0	41.9	-48.5
5	5	-1	119.7	127.0
5	6	-1	42.0	35.1
5	7	-1	92.3	78.4
5	8	-1	22.6	-22.5
5	9	-1	74.4	67.7
5	10	-1	48.3	44.3
5	13	-1	23.9	-19.4
5	14	-1	27.3	-30.9
5	15	-1	53.0	-44.5
5	16	-1	20.6	14.7
5	17	-1	60.9	-60.6
5	19	-1	21.4	-39.0
5	20	-1	42.4	51.0
5	21	-1	75.6	-80.2
5	23	-1	42.2	29.0
5	25	-1	40.0	-34.4
5	3	-2	157.6	124.9
5	4	-2	23.1	-19.8
5	5	-2	23.4	-23.5
5	6	-2	42.4	44.1
5	7	-2	89.0	89.3
5	9	-2	98.2	-97.4
5	10	-2	36.6	30.2
5	12	-2	35.4	-33.3
5	13	-2	124.9	-107.4
5	14	-2	51.2	49.4
5	16	-2	26.7	-27.2
5	17	-2	70.3	-68.3
5	18	-2	79.9	91.0
5	19	-2	50.9	50.8
5	20	-2	35.7	-40.8
5	22	-2	35.1	39.4
5	23	-2	71.3	74.0
5	3	-3	22.9	-34.7
5	4	-3	97.5	-89.0
5	5	-3	14.6	-19.6
5	6	-3	24.6	28.9
5	7	-3	39.1	-35.7
5	8	-3	56.5	-81.2
5	9	-3	96.3	-94.1
5	10	-3	37.1	-35.0
5	12	-3	108.7	-97.2
5	16	-3	26.8	-22.6
5	17	-3	115.2	121.4
5	19	-3	60.5	65.8
5	20	-3	36.6	31.2
5	21	-3	53.2	54.1
5	22	-3	39.6	-41.5
5	24	-3	55.9	56.8
5	1	-4	89.1	100.2
5	2	-4	103.3	-107.4
5	3	-4	53.4	-55.0
5	4	-4	40.5	56.8
5	5	-4	26.1	28.2
5	6	-4	122.0	-118.8
5	7	-4	33.8	-27.1
5	8	-4	35.0	-30.8
5	10	-4	126.0	-120.0
5	13	-4	47.7	49.9
5	14	-4	35.9	34.2
5	15	-4	26.2	17.1
5	16	-4	72.2	76.0
5	17	-4	53.4	-54.9
5	18	-4	91.6	96.4
5	19	-4	44.4	42.6
5	20	-4	50.1	52.3
5	21	-4	90.5	-56.7
5	23	-4	40.0	-38.0
5	1	-5	65.3	-59.9
5	3	-5	26.1	30.4
5	4	-5	74.0	-76.9
5	5	-5	81.0	-80.4
5	6	-5	69.3	82.7
5	7	-5	69.8	78.6
5	10	-5	53.0	47.2
5	12	-5	96.4	109.0
5	14	-5	170.4	152.9
5	16	-5	28.2	30.4
5	19	-5	32.4	-37.6
5	20	-5	35.2	-47.8
5	21	-5	35.7	34.2
5	22	-5	52.0	-58.0
5	23	-5	48.8	-59.0
5	1	-6	194.4	208.9
5	2	-6	36.8	47.5
5	3	-6	77.4	-103.5
5	4	-6	42.5	-40.0
5	5	-6	129.4	145.5
5	6	-6	13.6	11.3
5	7	-6	45.0	-35.0
5	8	-6	47.1	56.2
5	9	-6	42.2	47.6
5	10	-6	37.6	39.5
5	11	-6	43.9	49.9
5	12	-6	25.0	24.4
5	13	-6	57.5	56.4
5	15	-6	52.3	52.3
5	16	-6	41.0	-43.4
5	17	-6	39.8	37.6
5	18	-6	115.4	-116.1
5	1	-7	12.7	14.5
5	2	-7	14.8	22.0
5	3	-7	42.9	51.3
5	4	-7	93.9	103.1
5	5	-7	56.4	-59.9
5	6	-7	52.2	57.8
5	7	-7	54.9	63.1
5	11	-7	77.7	57.8
5	12	-7	33.1	-33.5
5	13	-7	63.8	-61.1
5	14	-7	70.0	-69.0
5	16	-7	42.6	-41.6
5	17	-7	77.1	-89.5
5	18	-7	25.3	28.8
5	19	-7	39.3	-43.5
5	22	-7	54.4	57.9
5	1	-8	81.4	-73.8
5	2	-8	118.2	153.0
5	4	-8	69.5	-79.7
5	6	-8	82.3	66.1
5	8	-8	74.8	-91.9
5	9	-8	51.0	-51.2
5	11	-8	57.2	-52.7
5	13	-8	130.5	-163.2
5	15	-8	32.3	-21.7
5	17	-8	42.8	-55.9
5	1	-9	31.2	34.2
5	2	-9	87.4	-111.4
5	3	-9	41.5	35.8
5	4	-9	12.8	16.3
5	5	-9	44.2	-49.2
5	6	-9	125.9	-139.0
5	7	-9	47.5	46.5
5	8	-9	90.4	-95.7
5	10	-9	77.2	-74.7
5	11	-9	44.4	52.6
5	13	-9	27.5	-28.8
5	14	-9	56.9	-66.7
5	15	-9	41.6	47.9
5	16	-9	39.1	-33.1
5	17	-9	22.8	29.2
5	22	-9	44.0	47.7
5	0	-10	29.4	-35.3
5	1	-10	63.1	-79.9
5	4	-10	27.2	-33.0
5	5	-10	107.5	-123.4
5	6	-10	34.5	43.7
5	7	-10	20.4	20.5
5	11	-10	97.8	102.8
5	14	-10	69.8	-71.1
5	15	-10	66.0	64.7
5	16	-10	22.8	25.2
5	19	-10	44.8	41.4
5	20	-10	34.5	32.4
5	1	-11	64.3	-60.7
5	2	-11	22.3	-29.3
5	3	-11	95.4	-118.0
5	4	-11	60.2	59.4
5	5	-11	32.6	41.5
5	8	-11	119.5	130.2
5	9	-11	31.1	27.7
5	12	-11	71.3	81.6
5	13	-11	25.1	34.6
5	16	-11	33.7	37.9
5	17	-11	32.9	39.1
5	18	-11	33.6	38.4
5	0	-12	56.3	-55.1
5	1	-12	34.7	31.2
5	2	-12	57.6	-66.7
5	3	-12	52.9	63.2
5	4	-12	30.2	30.2
5	5	-12	37.3	35.3
5	8	-12	55.8	55.6
5	10	-12	62.4	-59.9
5	11	-12	45.6	-53.1
5	12	-12	34.5	35.8
5	13	-12	45.9	55.8
5	14	-12	46.9	-52.8
5	15	-12	25.1	-32.1
5	16	-12	21.9	30.5
5	17	-12	21.2	27.6
5	18	-12	26.8	-29.4
5	1	-13	102.1	115.7
5	2	-13	54.9	63.2
5	3	-13	44.1	57.7
5	4	-13	24.8	18.1
5	5	-13	40.3	51.2
5	7	-13	64.1	-65.9
5	8	-13	45.6	-37.0
5	10	-13	34.5	-46.6
5	11	-13	113.1	-126.0
5	12	-13	25.6	-25.8
5	16	-13	42.2	-46.9
5	20	-13	38.5	-39.2
5	0	-14	67.7	73.3
5	2	-14	62.0	65.5
5	3	-14	27.8	-32.3
5	4	-14	49.6	55.8
5	5	-14	25.5	29.8
5	6	-14	25.6	-35.2
5	7	-14	55.1	-59.1
5	11	-14	39.3	-42.6
5	12	-14	38.8	-37.9
5	15	-14	32.9	-31.0
5	16	-14	24.4	-29.7
5	19	-14	58.1	-63.5
5	1	-15	36.3	42.2
5	2	-15	48.7	-47.5
5	3	-15	16.3	-17.0
5	4	-15	36.3	-34.7
5	5	-15	26.1	22.7
5	6	-15	47.3	-50.2
5	7	-15	44.3	-48.0
5	8	-15	72.1	-75.3
5	9	-15	56.6	59.7
5	10	-15	25.0	31.7
5	14	-15	24.9	29.5
5	16	-15	48.1	51.1
5	17	-15	40.6	-42.2
5	18	-15	17.8	22.9
5	0	-16	47.2	-56.5
5	1	-16	28.0	-38.2
5	2	-16	49.9	-53.6
5	4	-16	65.5	-71.1
5	5	-16	19.7	5.0
5	7	-16	27.5	-30.8
5	10	-16	53.9	63.4
5	11	-16	25.8	31.2
5	12	-16	25.0	30.0
5	13	-16	22.0	-27.7
5	14	-16	49.9	43.6
5	15	-16	35.7	35.9
5	1	-17	41.8	-47.8
5	3	-17	74.6	-89.2
5	6	-17	51.0	57.8
5	7	-17	32.2	-33.8
5	9	-17	29.3	30.6
5	10	-17	72.1	71.4
5	11	-17	27.7	35.1
5	12	-17	49.0	-51.9
5	13	-17	38.2	36.1
5	14	-17	20.8	-21.5
5	7	-18	59.3	65.9
5	9	-18	21.3	15.0
5	10	-18	20.6	-26.9
5	13	-18	37.8	-38.5
5	1	-19	22.0	26.2
5	2	-19	38.0	43.5
5	3	-19	32.3	34.4
5	4	-19	43.0	-44.8
5	7	-19	25.7	28.2
5	9	-19	32.8	-34.7
5	10	-19	49.9	51.6
5	11	-19	33.3	-37.7
5	0	-20	50.7	51.4
5	1	-20	37.3	39.5
5	2	-20	21.4	21.6
5	4	-20	37.1	44.1
5	10	-20	34.6	-42.5
5	1	-21	45.1	-51.0
5	4	-21	23.3	-29.3
5	5	-21	15.2	-25.7
5	8	-21	41.7	-57.4
5	0	-22	29.0	-40.9
5	4	-22	20.3	-35.7
6	3	15	36.5	-39.4
6	4	15	46.2	44.3
6	6	15	35.3	-37.2
6	0	14	35.4	27.0
6	2	14	59.3	-52.2
6	6	14	60.0	-51.5
6	12	14	44.8	46.5
6	13	14	26.5	-31.4
6	3	13	73.8	-63.2
6	4	13	36.2	-34.2
6	7	13	82.4	-82.6
6	11	13	32.9	-33.8
6	13	13	41.2	45.3
6	1	12	36.8	34.1
6	3	12	74.0	-68.9
6	9	12	35.8	37.0
6	3	11	36.6	39.2
6	4	11	31.7	-25.6
6	5	11	45.0	44.8
6	6	11	60.4	54.5
6	8	11	26.3	13.3
6	9	11	64.2	61.4
6	10	11	73.1	66.3
6	14	11	62.4	62.4
6	0	10	49.5	-72.2
6	1	10	96.5	105.2
6	2	10	59.9	92.5
6	5	10	67.2	59.3
6	8	10	26.0	31.5
6	9	10	44.5	59.6
6	11	10	40.9	28.1
6	12	10	36.3	-35.9
6	1	9	38.2	-38.9
6	2	9	29.7	26.5
6	3	9	34.5	32.9
6	6	9	54.4	35.6
6	7	9	35.8	-27.8
6	8	9	31.4	-27.2
6	11	9	49.7	-38.4
6	12	9	75.9	-80.7
6	13	9	69.0	-66.7
6	14	9	36.0	-32.0
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6	1	8	53.4	-53.2
6	2	8	73.5	67.3
6	3	8	52.9	45.7
6	7	8	30.1	-14.0
6	8	8	75.4	-72.4
6	9	8	78.5	-85.5
6	10	8	62.2	-57.2
6	11	8	40.9	-44.4
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6	13	8	61.8	-47.8
6	16	8	64.4	68.8
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6	5	7	46.6	-35.0
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6	9	7	53.4	-36.3
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6	5	6	58.5	-60.6
6	7	6	53.7	50.9
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6	12	6	128.8	137.8
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6	14	6	42.7	-35.6
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6	14	4	52.4	-45.8
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6	12	2	134.1	-131.9
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6	13	-14	65.6	65.8
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6	16	-14	44.8	-42.1
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7	3	14	51.3	-53.4
7	4	14	36.6	35.8
7	4	13	74.4	-77.2
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7	4	-5	96.5	114.8
7	5	-5	96.9	98.1
7	6	-5	56.9	54.0
7	7	-5	46.0	27.6
7	9	-5	39.6	21.6
7	12	-5	39.5	-25.3
7	13	-5	61.4	-47.7
7	18	-5	59.5	-55.1
7	21	-5	42.8	-43.7
7	2	-6	113.1	163.9
7	3	-6	31.6	29.1
7	4	-6	25.5	18.1
7	5	-6	46.6	31.8
7	6	-6	54.8	42.9
7	7	-6	62.9	-57.7
7	9	-6	101.2	-102.9
7	10	-6	64.4	-55.1
7	11	-6	55.2	35.7
7	12	-6	44.8	26.3
7	13	-6	69.6	-82.1
7	14	-6	107.0	-96.9
7	15	-6	98.7	92.1
7	16	-6	50.8	44.3
7	18	-6	56.4	-47.7
7	1	-7	57.6	70.1
7	2	-7	43.2	-45.3
7	6	-7	49.7	-42.4
7	8	-7	89.5	-56.2
7	9	-7	44.2	-56.2
7	13	-7	46.1	38.1
7	16	-7	59.0	53.9
7	0	-8	62.5	-71.8
7	2	-8	53.3	-57.7
7	3	-8	47.1	-51.6
7	4	-8	83.6	-80.4
7	5	-8	82.8	-83.2
7	6	-8	40.1	-34.1
7	7	-8	75.8	-76.1
7	8	-8	42.3	-27.9
7	12	-8	150.5	141.7
7	14	-8	77.8	-76.5
7	16	-8	81.9	58.7
7	18	-8	43.0	-39.4
7	1	-9	67.5	-74.4
7	2	-9	35.1	-34.3
7	3	-9	84.4	-87.5
7	4	-9	40.4	-44.8
7	5	-9	71.4	-67.9
7	10	-9	40.6	-32.8
7	11	-9	84.6	78.4
7	12	-9	53.8	-44.7
7	16	-9	91.1	-81.0
7	0	-10	56.1	-51.8
7	2	-10	66.2	70.6
7	3	-10	57.0	50.2
7	5	-10	55.3	51.3
7	6	-10	43.5	29.8
7	7	-10	57.1	76.0
7	9	-10	82.7	78.3
7	11	-10	69.2	-56.7
7	13	-10	59.3	48.4
7	15	-10	112.8	-124.2
7	17	-10	42.1	39.7
7	1	-11	83.5	89.1
7	2	-11	43.7	31.1
7	3	-11	74.9	75.0
7	6	-11	61.3	54.8
7	8	-11	105.6	92.3
7	9	-11	46.3	-42.7
7	10	-11	63.1	49.3
7	11	-11	69.3	-64.0
7	12	-11	50.7	42.8
7	15	-11	43.8	35.7
7	19	-11	35.1	41.5
7	20	-11	31.6	26.5
7	0	-12	49.4	-41.7
7	1	-12	93.9	-97.0
7	3	-12	58.2	50.3
7	5	-12	71.1	-57.1
7	6	-12	41.3	41.5
7	7	-12	50.5	56.6
7	12	-12	77.5	-73.1
7	13	-12	87.6	90.1
7	14	-12	29.0	29.9
7	16	-12	38.7	22.6
7	6	-13	92.3	-90.7
7	8	-13	70.6	-60.4
7	9	-13	58.3	29.1
7	11	-13	45.1	-41.4
7	19	-13	35.3	-15.0
7	1	-14	73.8	-75.2
7	2	-14	119.5	-124.1
7	3	-14	73.8	66.9
7	4	-14	41.5	42.6
7	8	-14	76.2	61.1
7	9	-14	81.6	-86.3
7	13	-14	62.2	-59.4
7	2	-15	46.0	32.2
7	3	-15	56.2	-42.6
7	4	-15	50.0	46.5
7	6	-15	49.4	36.8
7	9	-15	36.3	-37.8
7	13	-15	57.4	57.5
7	15	-15	33.3	-12.7
7	0	-16	151.1	164.0
7	1	-16	44.6	43.7
7	2	-16	57.3	-56.7
7	4	-16	52.1	35.2
7	5	-16	55.8	48.5
7	6	-16	73.4	-67.8
7	8	-16	40.6	29.8
7	7	-17	43.1	-36.7
7	13	-17	69.5	73.9
7	1	-18	49.8	43.9
7	3	-18	61.4	-65.2
8	6	19	49.2	93.6
0	6	19	75.1	-68.8

Table 1.3

Fractional coordinates and thermal parameters ($Å^2$) with estimated standard deviations.

	x/a	y/b	z/c	Uiso
Fe(1)	0.25922±26	0.44554±09	0.30409±12	*
Fe(2)	0.59133±25	0.47389±09	0.34581±12	*
S(1)	0.43695±42	0.41292±15	0.38151±18	*
S(2)	0.40464±42	0.51874±15	0.29049±19	*
O(1)	0.3194 ±13	0.3817 ± 5	0.1788 ±06	0.038±3
O(2)	0.6213 ±13	0.4034 ± 5	0.2207 ±06	0.034±3
C(1)	0.2983 ±17	0.4073 ± 6	0.2295 ±08	0.022±3
C(2)	0.6097 ±18	0.4308 ± 6	0.2712 ±08	0.025±4
C(3)	0.0576 ±19	0.4322 ± 7	0.2703 ±09	0.030±4
C(4)	0.0815 ±20	0.4943 ± 7	0.2824 ±10	0.035±4
C(5)	0.1367 ±21	0.5006 ± 8	0.3554 ±10	0.040±5
C(6)	0.1399 ±19	0.4459 ± 7	0.3914 ±09	0.031±4
C(7)	0.0943 ±19	0.4033 ± 7	0.3372 ±08	0.028±4
C(8)	0.6317 ±21	0.5276 ± 8	0.4361 ±10	0.039±4
C(9)	0.7056 ±21	0.4722 ± 8	0.4481 ±10	0.043±5
C(10)	0.7900 ±21	0.4668 ± 8	0.3941 ±10	0.041±5
C(11)	0.7727 ±20	0.5173 ± 8	0.3477 ±09	0.036±4
C(12)	0.6789 ±19	0.5546 ± 7	0.3745 ±09	0.030±4
C(13)	0.4745 ±17	0.3383 ± 6	0.3658 ±08	0.022±3
C(14)	0.3730 ±20	0.2973 ± 8	0.3565 ±10	0.037±4
C(15)	0.4012 ±21	0.2373 ± 8	0.3527 ±10	0.042±5
C(16)	0.5341 ±19	0.2201 ± 7	0.3599 ±09	0.029±4
C(17)	0.6441 ±19	0.2596 ± 7	0.3727 ±09	0.031±4
C(18)	0.6064 ±18	0.3201 ± 7	0.3746 ±08	0.027±4
C(19)	0.4196 ±17	0.5327 ± 6	0.1986 ±07	0.019±3
C(20)	0.3017 ±19	0.5334 ± 7	0.1485 ±09	0.031±4
C(21)	0.3109 ±20	0.5477 ± 7	0.0753 ±09	0.033±4
C(22)	0.4334 ±20	0.5609 ± 7	0.0542 ±09	0.035±4
C(23)	0.5495 ±19	0.5607 ± 7	0.1050 ±09	0.029±4
C(24)	0.5436 ±20	0.5477 ± 7	0.1772 ±09	0.033±4

Table 1.3 cont.

	x/a	y/b	z/c	Uiso
Fe(1′)	0.00608±26	0.22055±09	0.06959±12	*
Fe(2′)	-0.29341±26	0.24434±10	0.13005±12	*
S(1′)	-0.13789±43	0.17296±15	0.13164±19	*
S(2′)	-0.16931±42	0.28241±15	0.04903±18	*
O(1′)	0.1322 ±14	0.2819 ±06	0.1956 ±07	0.042±3
O(2′)	-0.1556 ±13	0.3062 ±05	0.2524 ±06	0.032±3
C(1′)	0.0778 ±18	0.2586 ±07	0.1448 ±08	0.027±4
C(2′)	-0.2112 ±17	0.2815 ±06	0.2029 ±07	0.020±3
C(3′)	0.0362 ±20	0.2247 ±08	-0.0402 ±10	0.036±4
C(4′)	-0.0247 ±20	0.1699 ±07	-0.0238 ±09	0.034±4
C(5′)	0.0714 ±20	0.1433 ±07	0.0294 ±09	0.034±4
C(6′)	0.1823 ±19	0.1795 ±07	0.0476 ±09	0.031±4
C(7′)	0.1539 ±21	0.2306 ±08	0.0002 ±10	0.041±5
C(8′)	-0.4458 ±31	0.1884 ±12	0.0792 ±16	0.083±8
C(9′)	-0.4712 ±26	0.2457 ±11	0.0541 ±14	0.067±7
C(10′)	-0.4840 ±22	0.2840 ±09	0.1095 ±10	0.044±5
C(11′)	-0.4762 ±24	0.2511 ±09	0.1719 ±12	0.052±5
C(12′)	-0.4498 ±30	0.1923 ±12	0.1548 ±15	0.077±8
C(13′)	-0.0621 ±16	0.1568 ±06	0.2215 ±07	0.017±3
C(14′)	0.0729 ±18	0.1421 ±07	0.2335 ±08	0.026±4
C(15′)	0.1325 ±19	0.1266 ±07	0.3013 ±09	0.029±4
C(16′)	0.0551 ±20	0.1277 ±07	0.3595 ±09	0.033±4
C(17′)	-0.0728 ±19	0.1425 ±07	0.3478 ±09	0.030±4
C(18′)	-0.1388 ±18	0.1576 ±07	0.2789 ±08	0.028±4
C(19′)	-0.1162 ±17	0.3557 ±06	0.0691 ±08	0.021±3
C(20′)	0.0041 ±18	0.3748 ±06	0.0519 ±08	0.024±3
C(21′)	0.0450 ±19	0.4326 ±07	0.0619 ±09	0.029±4
C(22′)	-0.0434 ±19	0.4720 ±07	0.0891 ±09	0.032±4
C(23′)	-0.1605 ±18	0.4536 ±07	0.1082 ±08	0.028±4
C(24′)	-0.2008 ±18	0.3941 ±07	0.0979 ±08	0.026±4

Table 1.3 cont.

* Anisotropic thermal parameters Uij ($Å^2$) with e.s.d.'s.

	U 11	U 22	U 33	2U 23	2U 31	2U 12
Fe(1)	0.0207 18	0.0228 11	0.0234 10	0.0030 17	0.0214 20	0.0003 21
Fe(2)	0.0205 18	0.0228 11	0.0245 10	-0.0047 18	0.0190 19	-0.0022 22
S(1)	0.0109 29	0.0198 17	0.0183 16	-0.0005 26	0.0187 30	-0.0020 32
S(2)	0.0103 28	0.0180 17	0.0223 17	-0.0017 27	0.0191 31	-0.0006 32
Fe(1′)	0.0267 19	0.0216 11	0.0268 11	-0.0030 18	0.0238 20	0.0036 22
Fe(2′)	0.0195 18	0.0250 11	0.0266 11	-0.0075 18	0.0238 20	-0.0054 21
S(1′)	0.0145 29	0.0156 16	0.0228 16	-0.0047 27	0.0219 31	-0.0044 32
S(2′)	0.0126 29	0.0191 16	0.0200 16	-0.0046 26	0.0213 31	0.0007 33

Table 1.4

a) Average bond lengths with e.s.d.s (Å).

Fe-S	2.261 ± 5	C -O	1.133 ± 19
Fe-C	1.693 ± 15	C -S	1.761 ± 14

C - C	for atoms C(3) - C(7)	1.412 ± 24
C - C	for atoms C(8) - C(12)	1.424 ± 26
C - C	for atoms C(3′)- C(7′)	1.413 ± 26
C - C	for atoms C(8′)- C(12′)	1.382 ± 34
C - C	for atoms C(13)- C(18)	1.418 ± 25
C - C	for atoms C(19)- C(24)	1.379 ± 25
C - C	for atoms C(13′)-C(18′)	1.364 ± 23
C - C	for atoms C(19′)-C(24′)	1.393 ± 23

b) Average valency angles with e.s.d.s (°).

Fe-S -Fe	97.67 ± 0.16	S -Fe-C	93.74 ± 0.56
S -Fe-S	81.09 ± 0.16	Fe-C -O	177.78 ± 1.47
Fe-S -C	112.07 ± 0.54	S -C -C	119.44 ± 1.24

C-C-C	for atoms C(3) - C(7)	107.96 ± 1.46
C-C-C	for atoms C(8) - C(12)	107.99 ± 1.58
C-C-C	for atoms C(3′)- C(7′)	107.98 ± 1.59
C-C-C	for atoms C(8′)- C(12′)	107.96 ± 2.16
C-C-C	for atoms C(13)- C(18)	120.03 ± 1.57
C-C-C	for atoms C(19)- C(24)	119.99 ± 1.60
C-C-C	for atoms C(13′)-C(18′)	119.99 ± 1.56
C-C-C	for atoms C(19′)-C(24′)	119.99 ± 1.52

Table 1.5

a) Some intramolecular non-bonded distances (Å).

Fe(1) ...Fe(2)	3.416	S(1) ...S(2)	2.943
Fe(1')...Fe(2')	3.393	S(1')...S(2')	2.937
O(1) ...O(2)	3.096	C(1) ...C(2)	3.195
O(1') ...O(2')	3.256	C(1')...C(2')	3.272

b) Some intermolecular contacts < 4.0 Å.

O(1) ....O(1')$_I$	3.03	C(15)....O(1')$_I$	3.80
O(2) ....O(2')$_I$	3.19	C(17)....O(2')$_I$	3.32
O(1) ....C(1')	3.76	C(18)....O(2')$_I$	3.47
O(2) ....C(2')$_I$	3.34	O(1) ....C(10')$_I$	3.36
C(1) ....O(1')	3.38	O(2) ....C(10')$_I$	3.50
C(2) ....O(2')$_I$	3.79	O(1) ....C(11')$_I$	3.68
C(3) ....O(1')	3.85	O(2) ....C(11')$_I$	3.76
C(3) ....O(2')	3.63	O(1) ....C(20')	3.68
C(7) ....O(1')	3.84	O(1) ....C(21')	3.47
C(7) ....O(2')	3.58	O(2) ....C(23')	3.38
C(14)....O(1')	3.55	O(2) ....C(24')	3.02

The subscript refers to the following equivalent position:

I 1 + x, y, z:

Table 1.6

Least-Squares Planes.

Plane No.	Atoms in Plane	Average Δ of atoms in plane	Atoms out of plane
1	C(3), C(4), C(5), C(6), C(7).	0.016 Å.	Fe(1) ...1.711 Å.
2	C(8), C(9), C(10), C(11), C(12).	0.008	Fe(2) ...1.683
3	C(3'),C(4'),C(5'), C(6'),C(7').	0.008	Fe(1')...1.675
4	C(8'),C(9'),C(10'), C(11'),C(12').	0.014	Fe(2')...1.751
5	C(13),C(14),C(15), C(16),C(17),C(18).	0.009	S(1) ...0.199
6	C(19),C(20),C(21), C(22),C(23),C(24).	0.008	S(2) ...0.081
7	C(13'),C(14'), C(15'),C(16'), C(17'),C(18').	0.005	S(1') ...0.071
8	C(19'),C(20'), C(21'),C(22'), C(23'),C(24').	0.009	S(2') ...0.143
9	Fe(1), Fe(2), S(1).		
10	Fe(1), Fe(2), S(2).		

Table 1.6 cont.

Plane No.	Atoms in Plane	Average Δ of atoms in plane	Atoms out of plane
11	Fe(1'), Fe(2'), S(1').		
12	Fe(1'), Fe(2'), S(2').		
13	S(1), S(2), Fe(1).		
14	S(1), S(2), Fe(2).		
15	S(1'), S(2'), Fe(1').		
16	S(1'), S(2'), Fe(2').		
17	Fe(1),Fe(2),C(2), O(2),C(1),O(1).	0.024	S(1) ...1.463 S(2) ...1.477
18	Fe(1'),Fe(2'), C(2'),O(2'), C(1'),O(1').	0.011	S(1') ...1.473 S(2') ...1.461

Plane Equations.

Plane 1: $0.9232X' - 0.1233Y - 0.3641Z' = -2.4414$ Å

Plane 2: $-0.7236X' - 0.4540Y - 0.5199Z' = -13.7987$

Plane 3: $0.4320X' - 0.4279Y - 0.7939Z' = -1.4721$

Plane 4: $-0.9849X' - 0.1725Y - 0.0149Z' = 3.6359$

Plane 5: $0.0001X' + 0.0665Y - 0.9978Z' = -5.4117$

Plane 6: $0.1462X' - 0.9619Y - 0.2310Z' = -11.9909$

Table 1.6 cont.

Plane 7:	-0.2472X'	- 0.9563Y	- 0.1562Z'	=	-3.9642
Plane 8:	-0.4209X'	+ 0.2039Y	- 0.8839Z'	=	0.9426
Plane 9:	0.1984X'	- 0.6509Y	- 0.7328Z'	=	-9.9587
Plane 10:	0.1604X'	- 0.3697Y	- 0.9152Z'	=	-8.0802
Plane 11:	-0.4616X'	- 0.3508Y	- 0.8148Z'	=	-2.8327
Plane 12:	-0.4365X'	- 0.6017Y	- 0.6688Z'	=	-3.9357
Plane 13:	0.3222X'	- 0.4832Y	- 0.8141Z'	=	-8.3165
Plane 14:	0.0372X'	- 0.5386Y	- 0.8417Z'	=	-10.2726
Plane 15:	-0.3387X'	- 0.4947Y	- 0.8003Z'	=	-3.5444
Plane 16:	-0.5624X'	- 0.4589Y	- 0.6879Z'	=	-2.8060
Plane 17:	-0.0856X'	+ 0.8161Y	- 0.5716Z'	=	5.3323
Plane 18:	-0.0972X'	+ 0.8445Y	- 0.5267Z'	=	3.6650

X', Y, and Z' (in Å) are referred to the orthogonal axes a', b, and c.

Table 1.7

Comparison of Molecular Parameters.

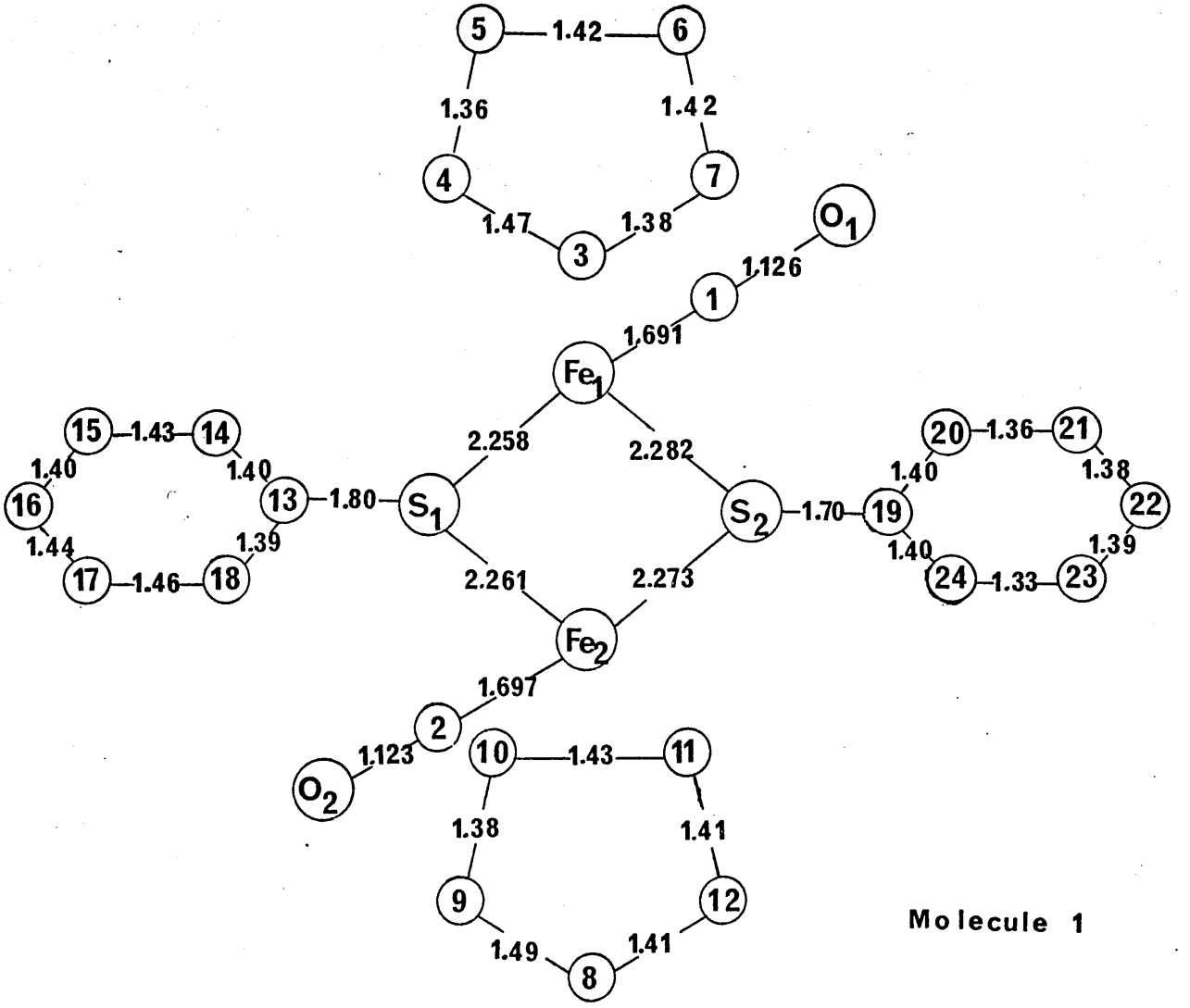
	Fe...Fe	Fe-S	S...S	Fe-C
$[C_2H_5SFe(CO)_3]_2$	2.537(10)Å	2.259(7)Å	2.932(14)Å	1.81(2)Å
$[C_2H_5SFe(NO)_2]_2$	2.720(3)	2.270(4)	3.633(4)	-
$[SFe(CO)_3]_2$	2.552(2)	2.228(2)	2.007(5)	1.776(5)
$[C_5H_5FeS]_4$	3.368(2) 2.631(2)	2.231(2)	2.884(3)	-
$[C_5H_5Fe(CO)_2]_2$	2.49 (2)	-	-	1.75 (3)
$[C_5H_5FeCO.SPh]_2$	3.405(5)	2.261(5)	2.940(5)	1.693(15)

	C-O	Fe-S-Fe	S-Fe-S
$[C_2H_5SFe(CO)_3]_2$	1.15 (2)Å	68.3(0.3)°	81.0(0.3)°
$[C_2H_5SFe(NO)_2]_2$	-	73.7(0.1)°	106.3(0.1)°
$[SFe(CO)_3]_2$	1.142(6)	69.9(0.1)°	53.5(0.1)°
$[C_5H_5FeS]_4$	-	98.0° 73.3°	99.1° 80.5°
$[C_5H_5Fe(CO)_2]_2$	1.12	-	-
$[C_5H_5FeCO.SPh]_2$	1.133(19)	97.7(0.2)°	81.1(0.2)°

	Dihedral Angle between the (S-Fe-S) planes	Distance of Fe atom from Cp plane.
$[C_2H_5SFe(CO)_3]_2$	95.2(0.5)°	-
$[C_2H_5SFe(NO)_2]_2$	Planar	-
$[SFe(CO)_3]_2$	79.8(0.1)°	-
$[C_5H_5FeS]_4$	-	1.757(5)Å
$[C_5H_5Fe(CO)_2]_2$	-	1.75(3)
$[C_5H_5FeCO.SPh]_2$	16.8°	1.71
Ferrocene	-	1.66(0.02)

Figure 1.1

Bond lengths (Å).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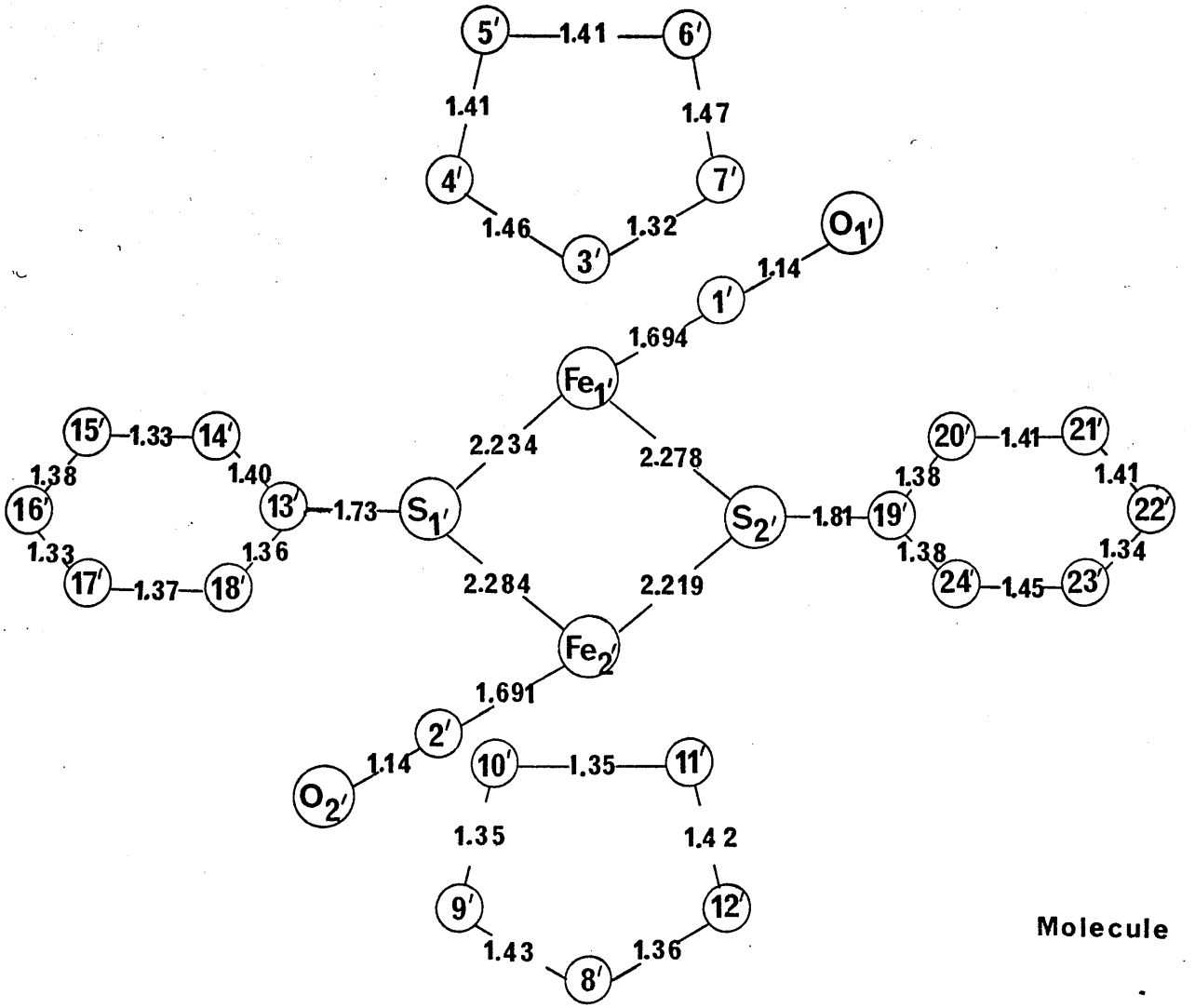
Molecule 1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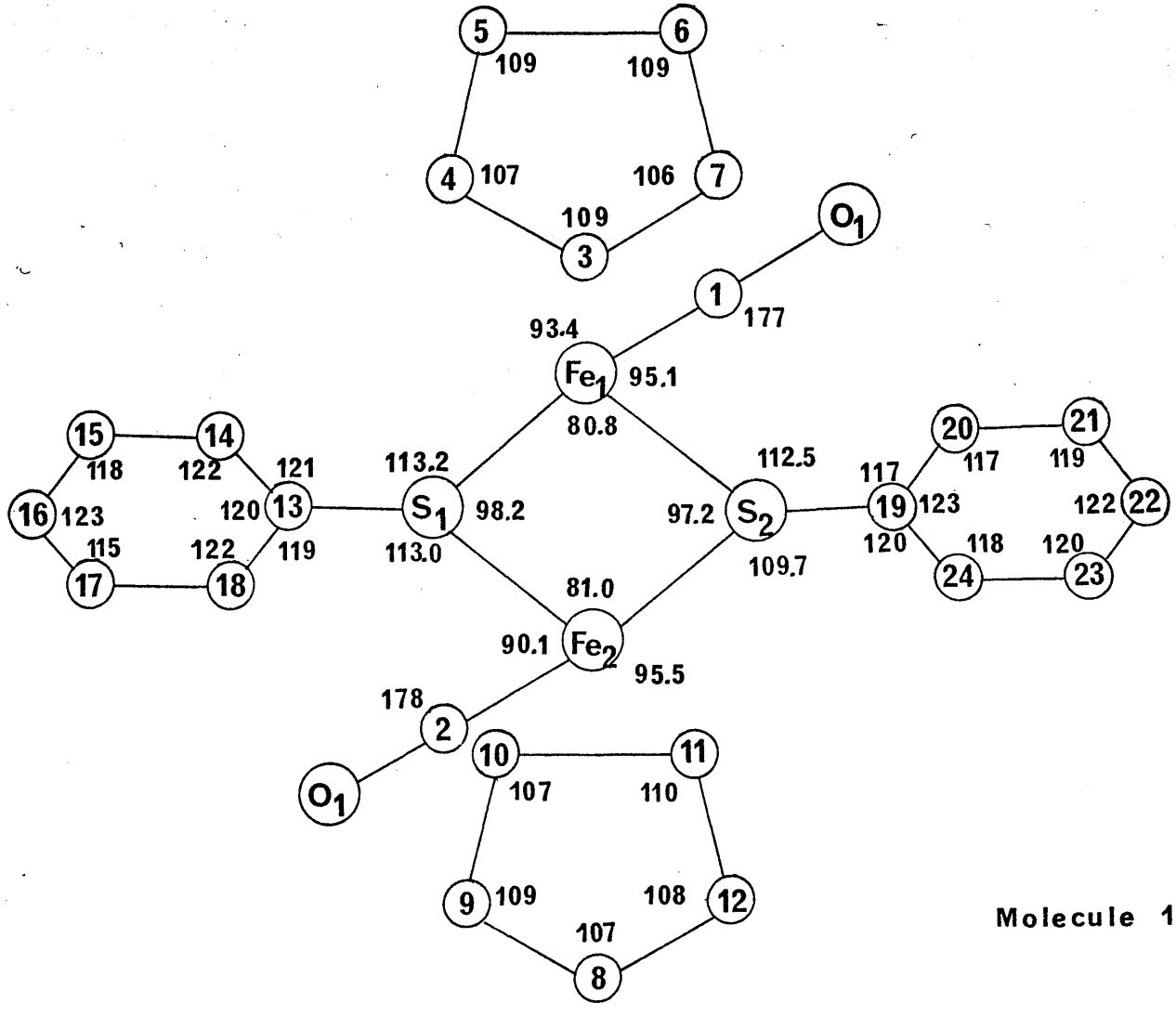
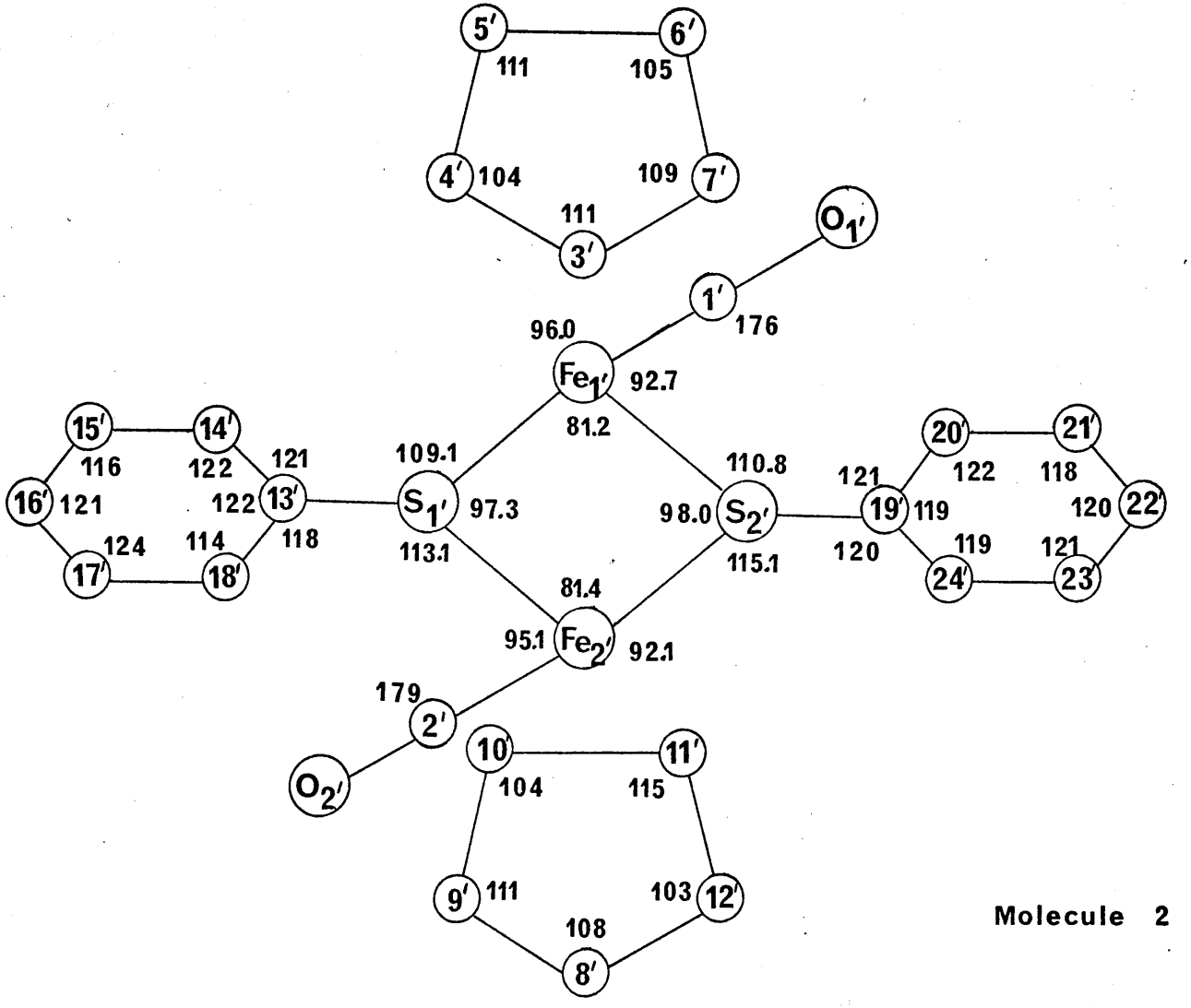
1.38
1.41
16′
13′
1.73
S1′
S2′
1.81
19′
22′
1.33
1.36
1.38
1.34
17′
1.37
18′
2.284
2.219
24′
1.45
23′
Fe2′
1.691
2′
1.14
O2′
10′
1.35
11′
1.35
1.42
9′
12′
1.43
1.36
8′

Molecule 2


5
6
109
109
4
107
106
7
109
3
O1
1
177
93.4
Fe1
95.1
80.8
15
14
118
122
121
113.2
112.5
117
20
117
21
119
16
123
120
13
S1
98.2
97.2
S2
19
123
122
22
115
122
119
113.0
109.7
120
118
120
17
18
24
23
81.0
90.1
Fe2
95.5
178
2
O1
10
11
107
110
9
109
108
12
107
8

Molecule 1


5′
6′
111
105
4′
104
109
7′
111
3′
O1′
1′
176
96.0
Fe1′
92.7
81.2
15′
14′
116
122
121
109.1
110.8
16′
121
122
13′
S1′
97.3
98.0
S2′
121
20′
21′
122
118
19′
119
120
22′
124
114
118
113.1
115.1
120
119
121
17′
18′
24′
23′
81.4
95.1
Fe2′
92.1
179
2′
O2′
10′
11′
104
115
9′
111
103
12′
108
8′

Molecule 2

Figure 1.3

A molecular-packing diagram viewed along the a axis.

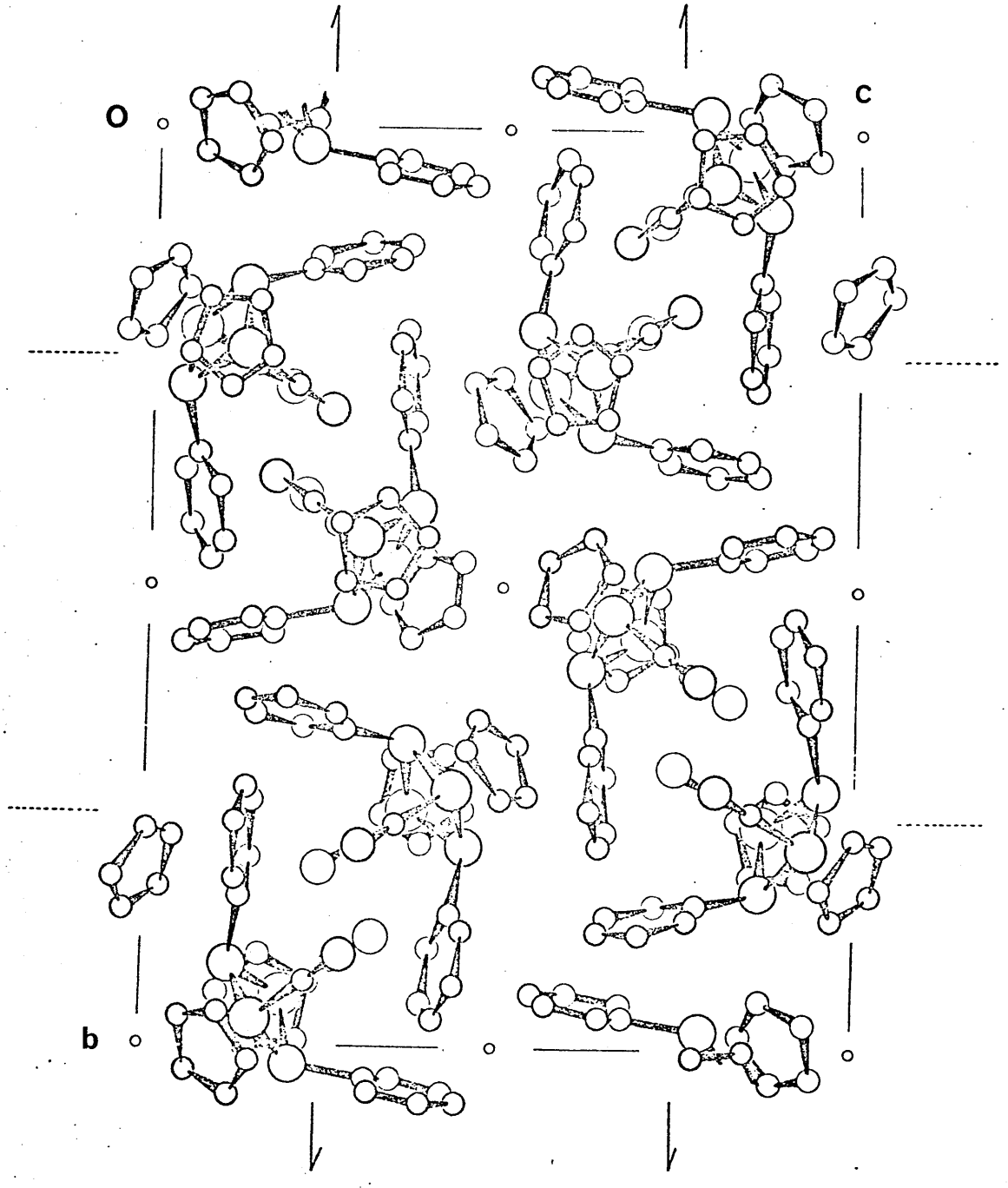

O
c
b

Figure 1.4

A view of molecule 1 along the line joining the mid-points of the iron-iron and oxygen-oxygen separations.

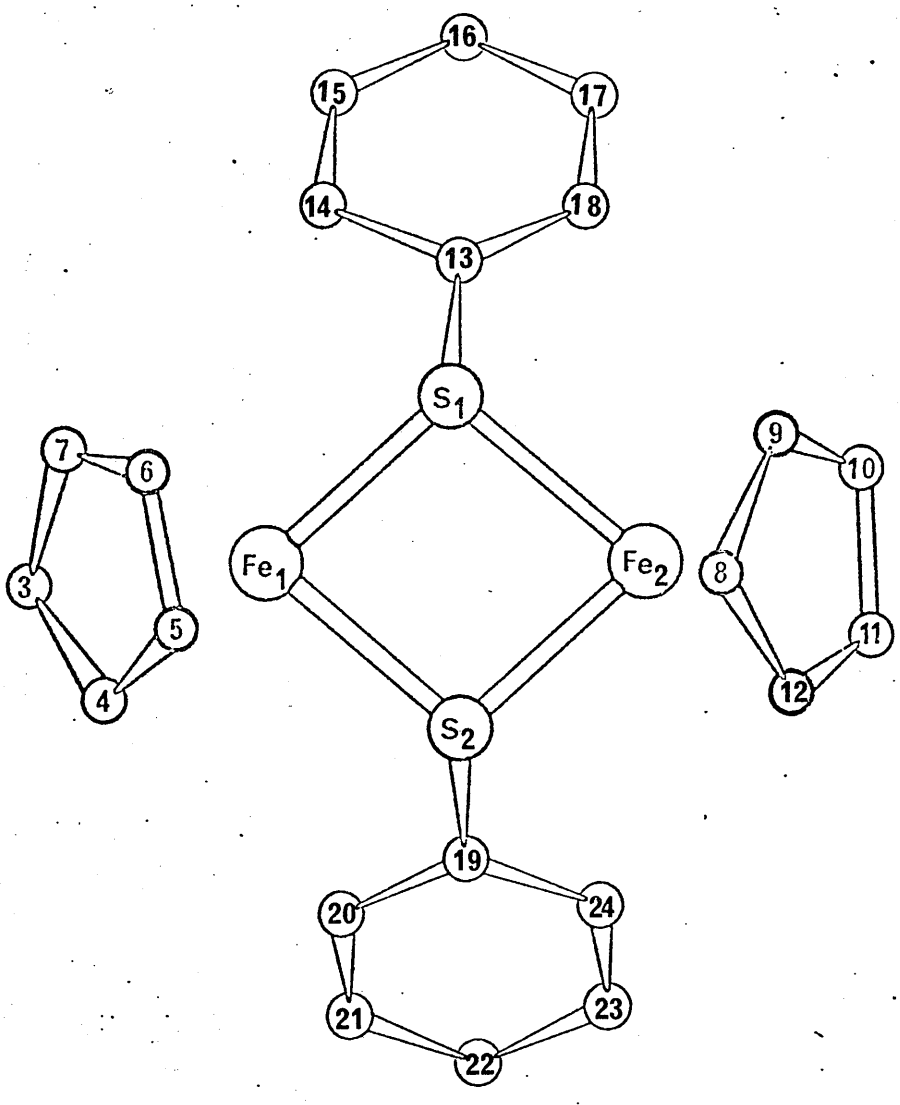
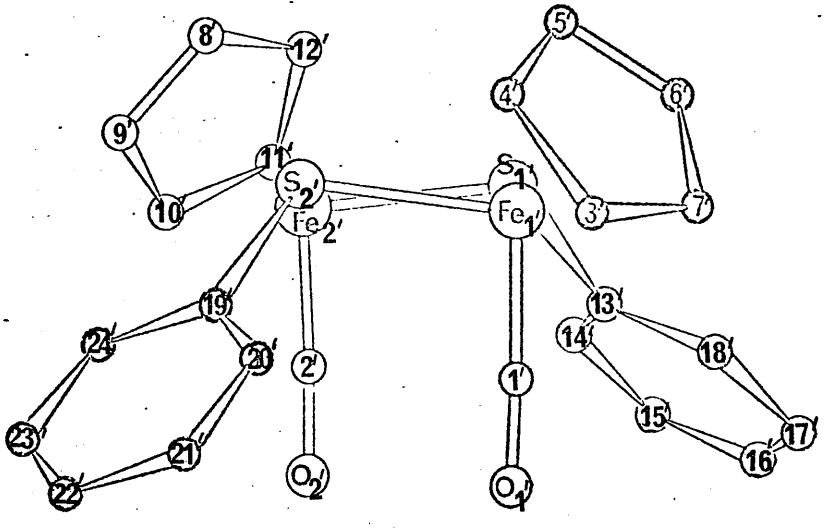

16
15
17
14
18
13
S1
7
6
9
10
3
Fe1
Fe2
8
5
11
4
12
S2
19
20
24
21
23
22

Figure 1.5

A view of molecule 2 along the line joining the mid-points of the bonds Fe(1′) to S(2′) and Fe(2′) to S(1′).

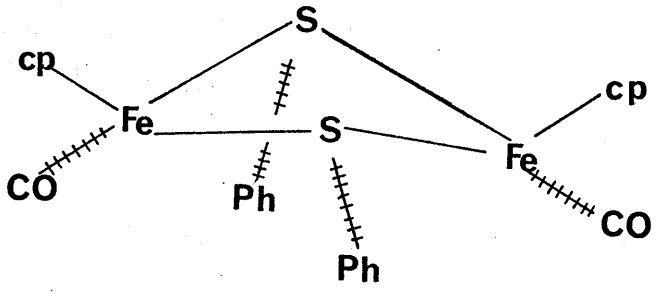

8'
12'
5'
4'
6'
9'
11'
S2'
S1'
10'
Fe2'
Fe1'
3'
7'
19'
13'
14'
24'
20'
2'
1'
18'
15'
23'
21'
17'
16'
22'
O2'
O1'

1.3 DISCUSSION.

The results of the crystal structure analysis of di-μ-phenylthio-bis(cyclopentadienylcarbonyliron) show that the most stable isomer obtained from the dimerisation of (II) has the cis-configuration (IV). The two independent molecules in the asymmetric unit have closely similar but not identical conformations; the small differences can be rationalised in terms of intermolecular packing effects. This can be seen in Figure 1.3.

In both molecules the Fe - S - Fe - S cycle is slightly puckered so that the ring is folded about a line through the iron atoms through 19.4° in molecule 1 and 16.8° in molecule 2. The mean length of the eight Fe - S bonds in the asymmetric unit is 2.261 Å, close to the mean lengths in $[EtSFe(CO)_3]_2$ (2.259 ± 0.007 Å) (Dahl et al., 1963), and in $[EtSFe(NO)_2]_2$ (2.27 ± 0.004 Å) (Thomas et al., 1958) and to three of the bonds in $(C_5H_5FeS)_4$ (2.256 ± 0.002 Å) (Schunn et al., 1966).

The incorporation of the octahedral iron and tetrahedral sulphur atoms in a four-membered ring has resulted in the internal angles at these atoms being reduced by about 10° from the values appropriate to undisturbed tetrahedral and octahedral geometry; thus the S - Fe - S angles have a mean value of 81.1° while the Fe - S - Fe angles have a mean value of 97.7°. The Fe ... Fe intramolecular distance, 3.42 Å in molecule 1 and 3.39 Å in molecule 2, is too long to accomodate a 'bent' bond of the type found in the compound



IV

$[EtSFe(CO)_3]_2$ (Dahl et al., 1963) but this kind of bond is, in any case, precluded here by consideration of the magnetic properties of (IV).

In each molecule the Fe - C - O bonds are, within experimental error, linear, parallel and therefore coplanar. The equations for the planes containing the O - C - Fe - Fe - C - O atoms in each molecule are given in Table 1.6 and Figure 1.5 shows this planar arrangement. The deviations of the atoms from this plane are, on average, 0.02 Å which is insignificant and the mean distance of the sulphur atoms from the corresponding planes is 1.46 Å in both molecules. The mean Fe - C and C - O distances of 1.693 Å and 1.133 Å respectively compare well with distances reported, for example, in $[C_5H_5Fe(CO)_2]_2$, (1.75 ± 0.03 Å and 1.12 ± 0.04 Å) (Mills, 1958). The orientation of the phenyl rings in both molecules is almost identical and can be seen clearly in Figure 1.5. The equations of the planes through the phenyl rings are listed in Table 1.6.

The mean sulphur - carbon bond length and Fe - S - C angle are 1.76 Å and 112.1° respectively, which compare well with those reported in similar compounds (see Table 1.7 which lists some average values for molecular parameters found in four similar compounds as well as those for di-μ-phenylthio-bis(cyclopentadienylcarbonyliron)). The mean distance of the iron atoms from the plane through the appropriate cyclopentadienyl ring is 1.71 Å, intermediate between the values found for ferrocene (1.66 ± 0.02 Å) (Dunitz et al.,

1956) and the somewhat larger values found for $[C_5H_5Fe(CO)_2]_2$ (1.75 ± 0.03 Å) (Mills, 1958) and $(C_5H_5FeS)_4$ (1.757 ± 0.005) (Schunn et al., 1966). The equations of the planes through the cyclopentadienyl rings are given in Table 1.6.

Disorder of cyclopentadienyl rings is not uncommon in ferrocene compounds at room temperature (Schunn et al., 1966). The intensity data used in our calculations were deliberately collected at -160° in an attempt to avoid such complications. However, there is evidence from a difference synthesis and from thermal parameters that even at this low temperature a cyclopentadienyl ring of molecule 2 is disordered.

The small differences in conformation of the two molecules in the asymmetric unit is due probably to the packing requirements in the unit cell whereas the configurational arrangement of both molecules is due to the intramolecular interactions within the molecules themselves, i.e., due to the steric requirements of the functional groups in the molecules.

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