THE STRUCTURE DETERMINATION OF SOME ORGANIC, INORGANIC AND ORGANOMETALLIC COMPOUNDS BY X-RAY DIFFRACTION

by

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ABSTRACT

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The structures of four compounds representing each of the organic (natural product), inorganic and organometallic classes of compounds have been determined by single-crystal X-ray diffraction, and the methods employed in solution of the structures have been discussed briefly. For all four structures, the intensity data were collected on a single-crystal diffractometer with Mo-K_α radiation and a scintillation counter.

The structure of the alkaloid, daphmacrine methiodide (acetone solvate), was determined from heavy-atom Patterson and Fourier syntheses, and refined by block-diagonal least-squares methods to a final R value of 0.089 for 1834 observed reflections. The absolute configuration was determined by the anomalous dispersion method. The molecule consists of two cage-structures which are linked by a chain of two carbon atoms, and the bond lengths and valency angles do not differ from normal values.

For both exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene—silver nitrate and silver nitrate itself, the silver ion was determined from Patterson syntheses to be lying in a pseudo-special position, so that the resulting electron-density maps exhibited pseudo-symmetry. A trial-and-error method based on detailed study of the shape of the Ag-Ag

Patterson peaks was adopted to find the exact location of the silver ions, and from the resulting electron-density maps the true light atom peaks could be discerned from their images. The refinement was carried out by full-matrix least-squares, and the final R for the complex of silver nitrate was 0.105 and for silver nitrate was 0.067.

The structure of the complex consists of thick layers perpendicular to the a crystallographic axis, and separated by ½ a. The silver ion is coordinated roughly tetrahedrally to the double bond of the hydrocarbon (in the exo-position, Ag...C = 2.4Å), and to three nitrate groups (Ag...O = 2.45 - 3.03Å). The layers are held together by van der Waals forces.

The silver nitrate structure consists of layers of silver ions parallel to the b crystallographic axis, and separated by ½ b, with the nitrate groups bridging the gap between layers. Previously observed inequalities in the N—O distances have been removed, all three bond lengths in the nitrate ion being 1.26(1)Å. The anisotropic thermal motion has been described.

The N,N-dimethyl(ferrocenylmethyl)ammonium tetrachlorozincate hydrate structure contains seven heavy atoms, and it was not possible to resolve the Patterson peaks because of the overlap. A direct sign-determining procedure was employed to locate the heavy atoms, and the light atoms were located from resulting electron-density maps. The structure was refined to a final R value of

0.068 for 2012 observed reflections. The mean bond distances are Fe-C = 2.04Å and C-C (cyclopentadienyl rings) = 1.43Å. Groups of four cations, two anions and two water molecules (two formula units), are linked around centres of symmetry by N-H...Cl (3.11Å), N-H...O (2.76Å) and O-H...Cl (3.05, 3.17Å) hydrogen bonds.

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PART I

GENERAL INTRODUCTION

Historical

The foundations of the science of crystallography were laid in the seventeenth century by Steno, Hooke, Huygens and other workers of that era, who proposed elementary theories of crystal structure based on the study of the external shapes of crystals. In 1784, Haüy discovered the fundamental law of rational indices, and even before Dalton's atomic theory, Haüy considered the crystal unit as 'molecules elementaires' or chemical atoms of definite and constant form. The idea of the crystal as a lattice structure was developed by Bravais who showed geometrically that only fourteen distinct types of space lattice are possible.

These important advances were made without tools for the examination of crystalline matter on an atomic scale, and such a tool did not become available until 1912 when von Laue demonstrated the three-dimensional lattice nature of crystals, and at the same time the wave nature of X-rays, by the first diffraction experiment. The elucidation of the first crystal structures, KCl, NaCl, KBr and KI by W.L. Bragg followed quickly, and for the first time the precise locations of atoms in crystals could be determined. This initial restriction to simple inorganic compounds of high symmetry passed with the subsequent refinement of the methods, and soon afterward more complex organic structures of low symmetry were also elucidated.

The advent of high speed digital computers brought about the development of powerful new methods and the capability of considering much more difficult problems, especially those of biological interest.

The principles and methods of structure analysis by X-ray diffraction have been discussed in detail in a number of reference books,[1-4] and are not reproduced here. However, the methods relevant to the present structures are reviewed briefly, as a definition of terms and a general knowledge of the methods used may be of use to one unfamiliar with the techniques.

Outline of the Principles of X-Ray Diffraction

One of the earliest observations made on natural crystals is that for a given crystalline structure, the angles between corresponding faces are constant. Hauy followed up this work by discovering the law of rational intercept ratios. A crystal face may be described in terms of the intercepts the face makes on a set of reference axes a, b, c. If these intercepts are a/h, b/k, c/ℓ, the face is said to have Miller indices (hkℓ). The fundamental law which Hauy discovered states that the ratios of the indices of any face are rational, and in general are the ratios of small whole numbers.

This law limits the symmetry a crystal may exhibit to 1,2,3,4,6 and the corresponding inversion elements $\bar{1},\bar{2},\bar{3},\bar{4},\bar{6}$. Only thirty-two distinct combinations (crystal classes) of these symmetry elements are possible, as shown by Hessel in 1830.

Bravais investigated crystal structure on a purely geometrical basis without regard for the fundamental particles, or the properties of crystals. He showed that only fourteen types of space lattice are possible, and the extension of this idea to crystal structures extended indefinitely in all directions brought about the consideration of further symmetry elements involving translations (mirror plane plus translation is a glide plane; rotational axis plus translation is a screw axis). The self-consistent

sets of all symmetry operations constitute the 230 space groups as shown by Fedorov, Schönflies and Barlow in the late nineteenth century.

Von Laue's famous experiment showed at once the wave nature of X-rays, and the lattice structure of crystals, but he was unable to interpret the results in terms of atomic positions. W. L. Bragg's success in solving the first crystal structures was based on his introduction of the concept of reflection of X-rays from planes within the crystal. By a simple geometric proof, it may be shown that reinforcement of X-rays of wavelength λ, reflected from parallel crystal planes at a distance d apart, occurs when their path difference equals a whole number of wavelengths, or $n\lambda = 2d \sin \theta$, which has become known as the Bragg Law, and is the basis for crystal structure analysis.

The problem is not this straightforward, however, since the scattering centres (atoms) do not lie on the crystal planes, but are distributed between the planes throughout the unit cell. This gives rise to a reduction of some of the intensities since waves scattered by atoms between planes are out of phase to varying degrees, depending on the exact position of the atoms between the planes. The crystallographer's task is the determination of the distribution of the scattering matter within the unit cell from the relative intensities of the X-ray reflections.

Since the electrons are responsible for the scattering of X-rays, the scattering power of a given atom, known as its scattering factor f_o, is dependent on the number of electrons in the atom (Z). The scattering factor varies with diffraction angle because of the finite size of the atom regarded as a scattering source. Thermal motion tends to spread the electron cloud over a larger volume and thus causes the scattering power to decrease more rapidly than for the ideal stationary model. This factor can be given by the expression

$$\exp\{-B \sin^2\theta/\lambda^2\},$$

where B is related to the mean-square amplitude of atomic vibration ($B = 8\pi^2\bar{u}^2$). (If the assumption of spherical symmetry for the vibrating electron cloud is abandoned, anisotropic thermal factors of the form

$$\exp\{-(b_{11}h^2 + b_{2\cdot2}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{13}h\ell)\}$$

may be used. These six b_{ij} parameters define the size and orientation of the ellipsoid of vibration.)

Consider a series of atoms scattering X-radiation, the wave scattered from each atom being characterised by an amplitude f_1, f_2, f_3... (depending on the scattering power of the atom), and a phase constant. The net amplitude resulting from a combination of these waves is known as the structure amplitude, symbolized by $|F|$. For the general plane $(hk\ell)$, the resultant is

$$F(hk\ell) = \Sigma f_j \exp\{2\pi i(hx_j+ky_j+\ell z_j)\},$$

summing over all the atoms in the unit cell, and where x_j, y_j and z_j are fractional coordinates of the atoms referred to unit cell axes a, b, c. This complex resultant, known as the structure factor, is characterised by an amplitude $|F|$ and a phase constant α, which may be evaluated by means of the expressions

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

$$\alpha(hk\ell) = \mathrm{Tan}^{-1}\ B/A$$

where

$$A = \Sigma f_j\ \mathrm{Cos}\ 2\pi(hx_j+ky_j+\ell z_j)$$

$$B = \Sigma f_j\ \mathrm{Sin}\ 2\pi(hx_j+ky_j+\ell z_j).$$

This expression may be simplified by the presence of symmetry. For example, if a centre of symmetry is chosen as origin, the possible phase angles are limited to 0 or π depending on whether the expression for A is positive or negative. The expression for B must be zero.

The significance of these equations is evident when it is realized that the square of the structure amplitude is proportional to the intensity of the X-ray reflection. If the appropriate corrections for the partial polarization by the reflecting of the X-rays, and for the geometry of the data recording method (Lorentz-polarization factor) are applied to the observed intensity, the observed structure factor F_o may be compared directly to the value calculated from the above expressions, F_c.

Since the electron-density in a crystal is periodic in three dimensions, it can be represented by a three-dimensional Fourier series as

$$\rho(xyz) = \frac{1}{V} \sum\sum\sum_{hk\ell} F(hk\ell)\exp\{-2\pi i(hx+ky+\ell z)\}$$

where V is the volume of the unit cell. It would seem therefore, that by observation of the intensities, the $F(hk\ell)$'s could be calculated, and the above series summed to give a representation of the entire crystal structure.

However, the structure factor is complex, and the measurement of intensity can give information only about the modulus, and not the phase. This is the fundamental difficulty in X-ray analysis, and is known as the phase problem. It is the task of the crystallographer to find means of overcoming this difficulty, and, having deduced the phases, to find the atomic positions corresponding to a chemically reasonable structure; and to test the structure by calculating structure factors based on the proposed positions and comparing them with the observed values.

Solution of the Phase Problem

If the Fourier series is summed with the phaseless quantities $|F|^2$ as coefficients, the resulting map has peaks which correspond to the interatomic vectors. This observation was made by A. L. Patterson in 1934, and today provides the basis for many structure analyses.

If there are N atoms in a cell, there are $N(N-1)/2$ distinct Patterson vectors contained in a cell of the same size, and with the inherently greater breadth of Patterson peaks compared with Fourier peaks, resolution may be poor. Thus, although the Patterson synthesis appears to provide an easy solution to the phase problem, its application to structures involving many atoms of the same weight is difficult.

The Patterson function may not possess the exact symmetry of the space group of the atomic distribution, reflecting the loss of information involved in using the phaseless $|F|^2$ quantities. To illustrate in a simple way the altered Patterson symmetry, consider two atoms A and B which give rise to two vectors AB and BA. These are equal in magnitude, but opposite in direction, so that the Patterson map has a centre of symmetry regardless of whether the original space group has one or not. In addition, all elements of symmetry involving translation are reduced to the corresponding non-translational ones

(ie. screw axes become rotational axes; glide planes become mirror planes).

Harker pointed out that useful information is contained in certain planes or lines of the three-dimensional Patterson function due to the presence of symmetry in the crystal. These Harker lines and planes arise because the vectors between corresponding atoms of molecules related by symmetry elements other than centres have one or two constant coordinates.

As an example, the space group Pm has a mirror plane perpendicular to the b axis so that for every atom at x, y, z there is another at x, $\bar{y}$, z. The vectors between these atoms all have coordinates 0, 2y, 0, so that they are concentrated on the Harker line which is the y axis of the Patterson function. For a molecule with a large number of atoms of equal weight, this often does not simplify the analysis.

However, if the structure under consideration has a 'heavy' atom, the vectors between it and its symmetry-related equivalents will stand out strongly against the poorly resolved background of light atom peaks. In this case the Patterson function provides information about part of the structure, that is, the position of the heavy atom. If this atom comprises the larger share of the structure factor, the component due to the lighter atoms being small, a first approximation to the phases may be obtained.

Expressed analytically:

If $F(hk\ell) = f_H \exp\{2\pi i(hx_H+ky_H+\ell z_H)\} + \Sigma f_L \exp\{2\pi i(hx_L+ky_L+\ell z_L)\}$

and $f_H >> f_L$

then $F(hk\ell) \simeq f_H \exp\{2\pi i(hx_H+ky_H+\ell z_H)\}$.

Using this first approximation to the phases, a Fourier series can be summed, and although it is only an approximate representation of the true electron-density distribution, it may reveal the position of some easily recognizable feature of the molecule. If this portion is then included, together with the heavy atom, in the phasing model, more accurate phases are obtained, and therefore a closer representation of the true electron-density distribution results. In this way, the entire structure may be deduced.

The fundamental difficulty of this method is in choosing an appropriate heavy atom derivative. On the one hand, the heavier the atom, the easier it is to find by the Patterson method, and the better a phasing model it is; while on the other hand, the more it dominates the structure, the less the $|F_o|$ and $|F_c|$ comparison is sensitive to the positions of the light atoms. Thus, the light atom positions are increasingly uncertain, and in the extreme, may not be found at all. For this reason the hydrogen atoms in a heavy atom derivative or organometallic compound are frequently not located. A convenient rule of

thumb used in selecting a heavy atom is $\Sigma Z_H^2/\Sigma Z_L^2 \simeq 1$, although fairly large deviations from it can be tolerated.

If the heavy atom is located on or very close to a symmetry element, it may contribute only to a certain class of reflection (e.g.h-even) while for the others (h-odd in this case) the heavy atom contributions are out of phase and cancel. Thus only the light atoms contribute to the odd reflections. A Fourier map computed from the heavy atom alone will exhibit additional, false symmetry, because the omission of the odd h reflections imposes the higher symmetry on the entire structure. Thus the light atoms may be accompanied by their mirror images, and to solve the structure, it is necessary to select a set of peaks which correspond to a chemically reasonable molecule, and whose positions give good agreement between F_o and F_c for the h-odd reflections.

For the case where the heavy atom is not exactly on a symmetry element, but somewhere near it, the heavy atom will contribute to a small part of the odd reflections. The Patterson map may not detect this slight displacement, but if a means can be found to estimate it, a Fourier series computed from the h-even reflections, and the h-odd reflections which are approximated by the heavy atom, may show the peaks corresponding to the true structure to be of higher electron-density than their unreal images. Careful selection of the higher density peaks which form

a reasonable model can then reveal the true structure.

Methods not employing the Patterson function, but examination of the intensity data alone are called direct methods, and are gaining importance with greater availability of high speed computers. Direct methods are based on the probability relationships deduced by Sayre which determine phases of one reflection in terms of other known phases. To evaluate the reliability of the phases so determined, it is convenient mathematically to define the normalized structure factor $E(hk\ell)$ such that

$$E^2(hk\ell) = |F(hk\ell)|^2/\varepsilon\Sigma\, f_i^2.$$

The symbol ε represents an integer which is generally 1, but varies for certain special sets of reflections depending on the symmetry of the space group in question. The distribution of $|E|$ values is independent of the size and shape of the unit cell, but dependent on the presence of a centre of symmetry. Thus these values provide a statistical test for centric and acentric distributions of intensities (compare Table 13).

The basis for the probability relationships for determining phases mentioned above is the relationship deduced by Sayre, who showed that for the centrosymmetric case

$$F(hk\ell) = \Phi(hk\ell) \sum_{h'k'\ell'} \Sigma F(h'k'\ell') \cdot F(h-h',k-k',\ell-\ell')$$

where $\Phi(hk\ell)$ is a simple scaling term. This implies that any structure factor $F(hk\ell)$ is determined by the products of all the pairs of structure factors whose indices add

to (hkℓ). For example, F(213) depends on the product of F(322) and F($\bar{1}\bar{1}$1), or F(612) and F($\bar{4}$01). This result appears to be of little value, since the signs are determined only in terms of others, none of which are known.

However, Sayre pointed out that for large F(hkℓ)'s the series must tend strongly in one direction (+ or -) and that this direction is indicated by agreement in sign among products of large F's. Thus for large reflections

$$S(F(hk\ell)) \sim S(F(h'k'\ell')) \cdot S(F(h-h',k-k',\ell-\ell')).$$

S means 'the sign of', and $\sim$ means 'is probably equal to'.

As shown by Cochran and Woolfson, the probability of the above relations being true in general is given by

$$P = \tfrac{1}{2}+\tfrac{1}{2}\mathrm{Tanh}\{\tfrac{\sigma_3}{\sigma_2^{3/2}}|E(hk\ell)\ E(h'k'\ell')\ E(h-h',k-k',\ell-\ell')|\}$$

where $\sigma_2 = \Sigma n_i^2$ and $\sigma_3 = \Sigma n_i^3$; n_i is the fraction of the total scattering power represented by the i^{th} atom (ie. $n_i = f_i/\Sigma f_j = 1/N$ if the atoms are all alike).

The application of Sayre's equation to the determination of phases has received much attention recently, and the usual method employed is called the symbolic addition method. This involves the selection of a small number of phases which can be assigned arbitrarily (since they represent a choice of origin which is arbitrary), and from these, and the subsequently determined ones, to deduce the signs of the others. If an impasse is reached, other

phases may be assigned symbols, and the remainder determined in terms of these symbols, which can then be varied and the consistency of the resulting sets of phases checked mathematically.

A consistency index has been defined

$$C = \frac{\langle |E(hk\ell)\Sigma E(h'k'\ell')\ E(h-h',k-k',\ell-\ell')| \rangle}{\langle |E(hk\ell)|\Sigma|E(h'k'\ell')||E(h-h',k-k',\ell-\ell')| \rangle}$$

the sums being taken over all pairs of (h'k'ℓ') and (h-h',k-k',ℓ-ℓ') whose sum is (hkℓ) and where < > means the average over all values of (hkℓ). If for each reflection all of the terms in the sum in Sayre's equation have the same sign as all other terms in that particular sum, C equals 1, and the solution is completely consistent. In general the true solution will be the one with the highest consistency index.

Having thus determined a set of phases for the E's, a Fourier series can be summed using the E's as coefficients, and from this the structure (or a partial structure) can be deduced. If the E-map is insufficiently resolved to give the position of the entire molecule, a partial structure may be used as a phasing model for further F_o Fourier syntheses.

Refinement of the Structure

Once a model of the structure has been proposed or elucidated from either Patterson or direct methods, some criterion for judging the correctness of the structure is necessary, as well as a means for improving the model as required. The most obvious method is direct comparison of the structure factors calculated from the postulated atomic positions with the observed values. The agreement between these quantities is usually described in terms of a 'residual' or 'discrepancy index' R, defined by

$$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|.$$

If a postulated model is correct, refinement will usually proceed to an R value of 0.10 or less.

Since the observed intensities are subject to errors of observation, the agreement between the F_o's and F_c's is not expected to be exact. According to Legendre's Principle, the most acceptable solution is the one which makes the sum of the squares of the errors ξ a minimum, and this occurs when the partial derivatives of $\Sigma\xi^2$ vanish. A set of 'normal equations' may be set up (n equations in n unknowns) and from them the best set of variables which satisfy Legendre's Principle can be determined by matrix algebra. This procedure is called the 'least-squares method'.

In crystal structure analysis the function minimized is

$$R' = \Sigma w(|F_o|-|F_c|)^2$$

where w is a weighting factor employed because some of the reflections may be measured more reliably than others. If such weights are used, the weighted R factor may be defined

$$R_w = \{\Sigma w||F_o|-|F_c||^2/\Sigma w|F_o|^2\}^{\frac{1}{2}},$$

and if the assigned weights are correct, R and R_w should be approximately the same.

Since each atom in the structure is fixed by four variables (x,y,z,B), large structures involve large matrices for solution of the normal equations, and a great deal of computation is required. It has been found that if a large number of equations is used, the off-diagonal terms of the normal equations are small, and may be neglected, to a first approximation. A better answer is obtained with the block-diagonal approximation at the cost of greater computing time, and if sufficient computing facilities are available, the full matrix may be used. None of these procedures will give the correct answer immediately, and usually a number of cycles of refinement is required to give the most acceptable fit of F_c's to the F_o's.

PART II

THE STRUCTURE DETERMINATION

OF

THE METHIODIDE DERIVATIVE OF DAPHMACRINE,

AN ALKALOID FROM DAPHNIPHYLLUM MACROPODUM

INTRODUCTION

The isolation and properties of daphmacrine ($C_{32}H_{49}O_4N$) have been described by Nakano and Saeki.[5] An X-ray crystal analysis of the methiodide derivative was undertaken to show the details of the molecular structure, including the absolute configuration, and to provide additional evidence for the novel framework of daphniphyllum alkaloids.

EXPERIMENTAL

Crystals of daphmacrine methiodide (acetone solvate) are colourless plates with (010) developed, and smaller {101} forms. Unit cell and space group data were determined from various rotation, Weissenberg and precession films.

Crystal Data.— $\lambda(Cu\text{-}K_\alpha) = 1.5418$; $\lambda(Mo\text{-}K_\alpha) = 0.7107$Å.
Daphmacrine methiodide acetone solvate (from acetone-ether), $C_{33}H_{52}O_4NI.(Me_2CO)$, M = 711.8, m.p. = 274-275°.
Orthorhombic, a = 14.23(2), b = 24.85(2), c = 10.02(1)Å .
U = 3543Å^3, D_m (flotation in aqueous KI) = 1.36 g.cm.$^{-3}$,
Z = 4, D_c = 1.33 g.cm.$^{-3}$
F(000) = 1496.
Absorption coefficients: $\mu(Cu\text{-}K_\alpha)$ = 76 cm.$^{-1}$; $\mu(Mo\text{-}K_\alpha)$ =9.6 cm.$^{-1}$
Absent reflections: h00, h odd; 0k0, k odd; 00ℓ,ℓ odd.
Space group $P2_12_12_1$ (D_2^4).

The intensities of all reflections with $2\theta(\text{Mo-K}_\alpha) \leq 40^\circ$ (minimum interplanar spacing, d = 1.04Å) were measured on a Datex-automated General Electric XRD 6 spectrogoniometer with a scintillation counter, approximately monochromatic Mo-K_α radiation (Zr filter and pulse-height analyser), and a θ-2θ scan. Background counts were made at the beginning and end of each scan. The crystal used was a plate with dimensions 0.1 mm. parallel to b and 0.3 mm. parallel to $\langle 101 \rangle$ and was mounted with a parallel to the ϕ axis of the goniostat. No absorption correction was made. Lorentz and polarization factors were applied, and the structure amplitudes were derived. Of 2047 reflections with $2\theta \leq 40^\circ$, 1834 (90%) were observed, and the 213 unobserved reflections were included in the structure refinement with $F_o = 0.6\ F(\text{min})$.

STRUCTURE ANALYSIS

The iodine position was determined from the three-dimensional Patterson function (0.041, 0.196, 0.167), and twenty-four atoms, mainly in the larger, nitrogen-containing cage, were located on a first three-dimensional electron-density map. Eleven additional atoms of the chain and the smaller, nitrogen-free cage were located on a second three-dimensional electron-density map on the basis of the phases computed from the positions of the first

twenty-five atoms. The positional and thermal parameters were refined by block-diagonal least-squares methods, with minimization of $\Sigma w(|F_o| - |F_c|)^2$, with $\sqrt{w} = 1$ when $|F_o| \leq F^*$, and $\sqrt{w} = F^*/|F_o|$ when $|F_o| > F^*$. F^* was initially taken as 30. For the 213 unobserved reflections, F_o was taken as 0.6 F(min) and $\sqrt{w} = 1.0$. The scattering factors of the International Tables for X-ray Crystallography[6] were used. After two cycles of isotropic refinement, a three-dimensional difference map revealed five further atoms, which were subsequently included in the refinement. Three of the atoms previously assigned as carbon were properly assigned as oxygen on the basis of their higher electron densities; only two positions are possible for the nitrogen atom of the larger cage (since it carries a methyl group), and one of these was assigned as nitrogen from chemical considerations.

After three further cycles of refinement, R was 0.18; $\sqrt{w}$ for the unobserved reflections was changed to 0.8, and the iodide ion was allowed anisotropic thermal parameters. After four more cycles of refinement, a second three-dimensional difference synthesis revealed the location of the final two atoms. The seven atoms located on the difference maps were those of the acetyl side chain and of the molecule of solvent of crystallization (acetone); the solvent atoms have high thermal parameters. At this point also, two other atoms were re-assigned as oxygens, and an

analysis of $w(F_o-F_c)^2$ suggested that F^* be changed to 40, and $\sqrt{w}$ for the unobserved reflections be changed to 0.6.

Four further cycles of refinement with all the atoms included and properly assigned resulted in an R value of 0.095. Four cycles with anisotropic thermal parameters for all 43 atoms completed the refinement, the maximum shift in the final cycle being 0.3σ, and the final R was 0.089 for 1834 reflections. Measured and calculated structure factors are listed in Table 1.

A final three-dimensional Fourier series was summed, and sections of the resulting electron-density distribution are shown in Figure 1, together with a drawing of the molecule. A final difference map showed no spurious detail, the maximum fluctions being ± 0.6 eÅ^{-3}, except at the iodide position, where fluctuations of ± 1.3 eÅ^{-3} were observed.

Table 1

Measured and calculated structure factors for daphmacrine methiodide. Unobserved reflections have $|F_o| = 0.6\ F(\min)$ and are indicated by a negative sign before F_o. With respect to the right-handed axial set used to describe the absolute configuration, the F_o values are those for reflections $\bar{h}\bar{k}\bar{\ell}$.

Table 1

h	k	l	F_o	F_c
0	0	2	316.3	300.4
0	0	4	44.1	37.1
0	0	6	126.6	119.3
0	0	8	40.5	36.5
0	1	1	48.7	45.4
0	1	2	108.7	107.4
0	1	3	165.6	147.8
0	1	4	85.0	77.3
0	1	5	12.6	3.3
0	1	6	34.8	32.4
0	1	7	50.4	53.9
0	1	8	16.8	14.4
0	1	9	51.5	49.7
0	2	0	150.0	136.3
0	2	1	5.4	8.9
0	2	2	42.4	35.6
0	2	3	27.4	28.9
0	2	4	35.1	38.2
0	2	5	16.8	19.4
0	2	6	74.8	66.9
0	2	7	29.1	32.2
0	2	8	-5.6	7.1
0	2	9	-6.0	4.6
0	3	1	94.6	104.9
0	3	2	139.4	138.4
0	3	3	102.3	94.6
0	3	4	23.9	25.5
0	3	5	50.7	43.9
0	3	6	22.2	15.8
0	3	7	33.2	35.6
0	3	8	44.5	45.9
0	3	9	29.5	28.8
0	4	0	111.4	104.6
0	4	1	25.2	25.2
0	4	2	12.5	10.1
0	4	3	27.4	22.6
0	4	4	-3.9	2.5
0	4	5	94.7	96.4
0	4	6	14.7	15.6
0	4	7	46.9	46.6
0	4	8	28.1	27.5
0	4	9	-6.0	1.4
0	5	1	19.6	26.0
0	5	2	146.3	176.8
0	5	3	12.2	13.5
0	5	4	96.1	92.8
0	5	5	22.6	20.0
0	5	6	25.9	30.3
0	5	7	24.9	20.8
0	5	8	57.3	55.1
0	5	9	17.1	15.1
0	6	0	89.3	93.7
0	6	1	290.3	298.4
0	6	2	75.4	73.3
0	6	3	15.7	4.1
0	6	4	29.8	27.0
0	6	5	80.9	85.2
0	6	6	35.1	41.0
0	6	7	75.1	69.8
0	6	8	13.4	7.0
0	6	9	-6.1	4.4
0	7	1	47.9	48.1
0	7	2	74.8	76.7
0	7	3	100.7	110.2
0	7	4	76.1	71.8
0	7	5	48.2	47.3
0	7	6	21.6	21.8
0	7	7	-5.3	3.6
0	7	8	17.4	17.9
0	7	9	29.9	31.4
0	8	0	69.6	64.5
0	8	1	16.0	2.3
0	8	2	61.9	57.8
0	8	3	33.0	33.1
0	8	4	27.2	34.5
0	8	5	49.1	43.8
0	8	6	27.9	25.8
0	8	7	26.6	28.2
0	8	8	22.4	19.2
0	8	9	-6.2	2.5
0	9	1	68.0	70.4
0	9	2	35.2	37.8
0	9	3	74.0	87.8
0	9	4	16.3	18.5
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0	9	6	8.2	8.7
0	9	7	34.1	33.5
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0	9	9	43.1	41.4
0	10	0	60.0	61.9
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0	10	3	32.9	36.8
0	10	4	63.6	68.4
0	10	5	24.4	25.0
0	10	6	47.1	46.2
0	10	7	36.9	40.4
0	10	8	11.4	10.5
0	10	9	12.9	3.3
0	11	1	15.7	17.3
0	11	2	53.9	57.9
0	11	3	90.1	101.9
0	11	4	63.1	61.7
0	11	5	26.3	34.9
0	11	6	11.0	11.1
0	11	7	18.5	23.6
0	11	8	24.8	25.1
0	12	0	77.0	88.3
0	12	1	81.2	83.1
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0	12	3	8.9	9.5
0	12	4	46.7	49.1
0	12	5	41.0	47.1
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0	13	1	-4.1	7.9
0	13	2	67.6	65.5
0	13	3	59.1	53.0
0	13	4	43.1	50.6
0	13	5	-5.1	0.3
0	13	6	14.0	14.8
0	13	7	-5.8	9.1
0	13	8	19.1	17.8
0	14	0	-4.2	9.3
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0	14	5	51.3	51.5
0	14	6	-5.6	2.8
0	14	7	13.8	17.8
0	14	8	13.0	13.0
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0	15	7	12.8	8.0
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0	16	1	28.2	25.9
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0	16	5	18.2	19.4
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0	18	5	19.0	16.1
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0	19	3	33.6	30.6
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0	20	0	8.9	6.6
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0	22	0	18.1	9.6
0	22	1	20.6	17.8
0	22	2	-5.8	11.2
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0	23	1	-5.7	7.9
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0	24	0	18.0	16.7
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1	0	6	8.1	7.5
1	0	7	51.0	48.3
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1	0	9	20.8	22.3
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1	1	5	31.4	31.8
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1	2	4	90.1	83.0
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1	2	7	62.1	57.1
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1	2	9	12.9	9.6
1	3	0	54.4	60.8
1	3	1	72.0	77.9
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1	3	4	104.7	98.9
1	3	5	77.1	73.2
1	3	6	13.3	15.0
1	3	7	19.8	24.7
1	3	8	25.7	24.8
1	3	9	39.7	41.8
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1	4	2	85.7	97.2
1	4	3	17.2	14.1
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1	4	8	37.4	37.3
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1	5	2	65.5	62.2
1	5	3	138.8	140.6
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1	5	6	29.8	28.8
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1	5	9	30.3	31.7
1	6	0	126.6	130.4
1	6	1	97.8	97.6
1	6	2	42.6	37.0
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1	6	4	48.5	47.0
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1	6	6	83.2	78.5
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1	6	8	10.5	3.7
1	6	9	10.7	12.5
1	7	0	95.6	87.0
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1	7	2	68.4	79.2
1	7	3	72.4	82.6
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1	7	6	26.7	26.9
1	7	7	19.0	15.2
1	7	8	46.4	46.1
1	7	9	22.8	25.3
1	8	0	76.0	77.4
1	8	1	107.5	109.3
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1	8	3	33.0	33.5
1	8	4	51.9	53.5
1	8	5	73.1	76.6
1	8	6	18.9	23.6
1	8	7	47.0	49.1
1	8	8	14.5	12.3
1	8	9	13.1	10.4
1	9	0	52.3	45.2
1	9	1	46.9	44.9
1	9	2	117.5	127.3
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1	9	6	-5.1	4.0
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1	9	8	45.9	47.5
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1	10	0	57.6	50.4
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1	10	3	-4.1	7.8
1	10	4	11.0	8.4
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1	11	0	43.8	41.2
1	11	1	20.3	22.4
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1	11	7	13.2	9.1
1	11	8	14.5	10.0
1	12	0	101.5	90.5
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1	12	5	24.0	28.9
1	12	6	33.2	30.6
1	12	7	27.8	30.0
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1	13	0	65.2	61.3
1	13	1	33.1	33.2
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1	13	3	53.0	51.1
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1	13	5	21.7	27.1
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1	13	7	33.0	29.0
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1	14	0	69.3	64.4
1	14	1	26.9	29.2
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1	14	7	9.9	2.8
1	14	8	10.0	14.0
1	15	0	-4.3	13.3
1	15	1	51.6	46.5
1	15	2	8.0	13.5
1	15	3	65.3	64.9
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1	15	7	30.6	32.9
1	16	0	41.0	30.7
1	16	1	46.6	47.3
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1	17	0	28.0	29.6
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1	17	5	11.6	11.1
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1	17	7	11.1	10.6
1	18	0	30.3	26.5
1	18	1	49.5	47.4
1	18	2	17.1	13.7
1	18	3	24.7	22.0
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1	18	6	11.3	12.6
1	19	0	18.8	21.5
1	19	1	-5.1	16.5
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1	19	3	21.2	22.1
1	19	4	25.3	23.4
1	19	5	15.1	11.9
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1	20	0	17.1	12.0
1	20	1	46.2	38.8
1	20	2	15.3	19.6
1	20	3	11.2	10.8
1	20	4	-5.8	7.8
1	20	5	15.0	13.2
1	21	0	9.6	4.2
1	21	1	30.9	11.5
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1	21	3	23.6	21.8
1	21	4	22.0	20.1
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1	22	0	26.6	23.0
1	22	1	17.4	19.5
1	22	2	-5.8	2.8
1	22	3	12.5	9.9
1	22	4	-6.1	3.3
1	23	0	-5.6	3.5
1	23	1	-5.7	7.2
1	23	2	-5.9	9.0
1	23	3	20.5	16.6
1	24	0	29.4	20.8
1	24	1	13.9	11.8
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2	0	1	79.8	69.0
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2	0	3	43.4	39.6
2	0	4	20.7	15.5
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2	0	6	106.0	95.2
2	0	7	24.8	24.7
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2	1	0	124.7	119.0
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2	1	2	62.7	59.2
2	1	3	142.5	133.5
2	1	4	154.4	130.3
2	1	5	18.7	25.7
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2	2	0	27.7	7.3
2	2	1	144.5	137.6
2	2	2	71.7	56.2
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2	2	9	-6.1	9.9
2	3	0	103.1	114.5
2	3	1	144.4	146.5
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2	3	6	28.2	31.4
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2	4	0	13.6	14.0
2	4	1	112.6	114.6
2	4	2	75.7	71.0
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2	9	9	27.9	24.2
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2	21	2	20.5	18.7
2	21	3	24.4	19.2
2	21	4	13.9	4.2
2	22	0	-5.5	3.9
2	22	1	20.5	21.0
2	22	2	19.1	15.4
2	22	3	17.1	5.7
2	22	4	21.3	17.0
2	23	0	17.0	14.5
2	23	1	-5.8	7.5
2	23	2	13.6	7.1
2	23	3	-6.1	3.6
2	24	0	-5.8	3.1
2	24	1	13.5	5.8
3	0	1	142.5	128.8
3	0	2	205.3	178.9
3	0	3	-3.6	7.4
3	0	4	114.0	106.1
3	0	5	55.1	53.0
3	0	6	12.9	16.7
3	0	7	21.5	25.3
3	0	8	26.7	30.2
3	0	9	9.9	7.8
3	1	0	116.1	127.9
3	1	1	68.6	65.6
3	1	2	150.1	131.2
3	1	3	30.9	31.0
3	1	4	112.6	99.9
3	1	5	33.9	32.9
3	1	6	35.8	37.6
3	1	7	30.6	29.7
3	1	8	52.8	51.5
3	1	9	10.9	13.4
3	2	0	82.5	72.3
3	2	1	114.6	124.6
3	2	2	121.7	108.0
3	2	3	72.0	56.9
3	2	4	12.4	19.7
3	2	5	56.6	62.4
3	2	6	42.6	39.0
3	2	7	43.0	40.3
3	2	8	18.8	20.7
3	2	9	32.2	33.2
3	3	0	218.6	233.3
3	3	1	141.4	124.4
3	3	2	89.3	79.7
3	3	3	94.1	86.2
3	3	4	53.0	49.1
3	3	5	26.6	28.7
3	3	6	40.8	33.6
3	3	7	32.1	33.9
3	3	8	27.1	25.2
3	3	9	14.4	19.0
3	4	0	135.1	132.5
3	4	1	141.4	133.1
3	4	2	106.8	98.1
3	4	3	69.5	70.0
3	4	4	52.1	48.3
3	4	5	21.1	21.2
3	4	6	69.6	65.6
3	4	7	20.7	19.9
3	4	8	16.8	21.1
3	4	9	30.4	32.5
3	5	0	46.3	42.2
3	5	1	23.0	26.0
3	5	2	14.3	21.6
3	5	3	72.8	75.5
3	5	4	121.7	106.3
3	5	5	33.7	32.3
3	5	6	42.5	40.0
3	5	7	37.3	40.6
3	5	8	12.5	10.6
3	5	9	23.3	22.9
3	6	0	97.9	96.1
3	6	1	84.5	95.3
3	6	2	45.6	44.0
3	6	3	78.7	83.2
3	6	4	57.5	54.4
3	6	5	27.6	29.9
3	6	6	63.8	55.4
3	6	7	48.4	48.8
3	6	8	42.0	42.8
3	6	9	30.0	28.1
3	7	0	87.6	86.2
3	7	1	118.0	119.2
3	7	2	86.4	77.5
3	7	3	90.6	91.9
3	7	4	53.6	53.6
3	7	5	67.9	65.2
3	7	6	28.4	33.3
3	7	7	62.8	58.6
3	7	8	26.5	27.8
3	7	9	24.3	20.5
3	8	0	46.9	42.1
3	8	1	97.0	97.9
3	8	2	67.1	58.2
3	8	3	22.7	21.5
3	8	4	81.9	77.2

Table 1

continued

h	k	l	F_o	F_c
3	8	5	52.5	49.1
3	8	6	25.3	24.0
3	8	7	32.0	30.6
3	8	8	14.0	13.0
3	8	9	-6.3	0.7
3	9	0	61.3	52.7
3	9	1	87.6	92.7
3	9	2	66.3	66.1
3	9	3	32.5	27.2
3	9	4	34.3	37.7
3	9	5	35.6	38.2
3	9	6	-5.2	11.6
3	9	7	30.2	30.6
3	9	8	25.2	22.3
3	10	0	63.5	60.3
3	10	1	88.4	89.9
3	10	2	76.5	72.7
3	10	3	21.1	17.8
3	10	4	27.6	32.8
3	10	5	41.6	46.4
3	10	6	20.3	20.3
3	10	7	26.2	27.1
3	10	8	18.3	15.1
3	11	0	37.5	30.0
3	11	1	51.2	51.3
3	11	2	36.7	40.9
3	11	3	30.4	37.0
3	11	4	43.3	49.8
3	11	5	48.4	54.8
3	11	6	23.0	24.6
3	11	7	-5.7	9.9
3	11	8	31.8	31.8
3	12	0	-4.0	10.4
3	12	1	59.0	59.0
3	12	2	66.8	65.6
3	12	3	24.8	26.0
3	12	4	20.5	23.7
3	12	5	24.8	29.9
3	12	6	17.2	16.7
3	12	7	25.5	31.4
3	12	8	20.6	22.1
3	13	0	63.6	64.7
3	13	1	41.1	44.9
3	13	2	25.2	30.4
3	13	3	44.6	45.1
3	13	4	37.6	39.1
3	13	5	17.6	17.8
3	13	6	38.2	40.3
3	13	7	21.1	23.7
3	13	8	17.8	15.2
3	14	0	30.9	32.3
3	14	1	11.3	18.3
3	14	2	20.5	20.8
3	14	3	49.8	54.1
3	14	4	24.2	24.7
3	14	5	18.5	23.3
3	14	6	20.2	23.5
3	14	7	-6.0	1.6
3	15	0	31.8	29.0
3	15	1	37.1	40.5
3	15	2	17.2	18.3
3	15	3	26.1	32.6
3	15	4	11.3	12.4
3	15	5	20.3	19.0
3	15	6	17.8	19.5
3	15	7	13.9	11.4
3	16	0	31.8	30.0
3	16	1	18.9	26.0
3	16	2	39.0	38.2
3	16	3	28.7	26.7
3	16	4	34.6	36.2
3	16	5	20.6	23.4
3	16	6	29.2	33.9
3	16	7	26.3	26.2
3	17	0	-4.8	6.5
3	17	1	15.2	20.8
3	17	2	31.8	29.8
3	17	3	29.4	27.3
3	17	4	31.5	32.8
3	17	5	30.8	30.2
3	17	6	17.3	17.3
3	18	0	-4.9	3.3
3	18	1	14.6	26.0
3	18	2	36.0	31.7
3	18	3	9.2	6.6
3	18	4	24.0	20.7
3	18	5	20.5	17.8
3	18	6	18.8	18.4
3	19	0	-5.1	3.7
3	19	1	-5.2	22.9
3	19	2	16.0	14.6
3	19	3	-5.6	5.9
3	19	4	20.5	20.9
3	19	5	23.9	24.0
3	20	0	11.8	9.5
3	20	1	22.4	11.8
3	20	2	21.7	17.3
3	20	3	19.0	21.8
3	20	4	9.3	3.8
3	20	5	18.8	22.3
3	21	0	11.8	5.6
3	21	1	-5.5	9.9
3	21	2	13.2	12.5
3	21	3	16.8	15.2
3	21	4	-6.0	10.6
3	22	0	12.3	9.8
3	22	1	-5.7	11.1
3	22	2	12.4	8.7
3	22	3	12.1	8.5
3	23	0	10.5	9.6
3	23	1	10.7	9.6
3	23	2	14.4	8.5
4	23	1	-5.9	12.6
4	0	0	14.6	10.3
4	0	1	150.1	136.3
4	0	2	48.9	43.0
4	0	3	30.5	39.3
4	0	4	74.7	71.1
4	0	5	61.2	53.7
4	0	6	42.5	37.0
4	0	7	35.3	35.6
4	0	8	19.1	15.8
4	0	9	43.9	45.0
4	1	0	133.2	145.2
4	1	1	125.0	109.6
4	1	2	80.0	72.1
4	1	3	38.3	38.7
4	1	4	73.8	76.2
4	1	5	23.3	21.8
4	1	6	71.8	68.7
4	1	7	25.7	24.8
4	1	8	19.1	15.5
4	1	9	13.4	9.6
4	2	0	110.1	122.0
4	2	1	151.5	131.1
4	2	2	62.7	54.2
4	2	3	88.0	85.9
4	2	4	115.5	93.7
4	2	5	40.1	35.8
4	2	6	40.6	42.5
4	2	7	62.4	55.9
4	2	8	16.8	19.9
4	2	9	37.2	35.5
4	3	0	82.5	96.6
4	3	1	113.0	100.8
4	3	2	111.1	100.3
4	3	3	103.3	89.5
4	3	4	84.0	74.5
4	3	5	71.4	65.5
4	3	6	37.8	39.1
4	3	7	57.3	57.9
4	3	8	31.7	35.4
4	3	9	19.0	18.1
4	4	0	75.6	58.8
4	4	1	28.9	33.8
4	4	2	114.6	110.0
4	4	3	50.3	40.4
4	4	4	104.7	95.1
4	4	5	31.1	31.2
4	4	6	26.4	25.8
4	4	7	34.0	32.3
4	4	8	33.7	35.6
4	4	9	-6.2	4.5
4	5	0	20.6	25.6
4	5	1	107.5	105.3
4	5	2	66.7	60.5
4	5	3	39.0	35.6
4	5	4	50.4	43.4
4	5	5	60.4	58.4
4	5	6	11.8	18.0
4	5	7	49.5	50.8
4	5	8	22.7	22.8
4	5	9	13.0	3.0
4	6	0	-3.3	1.4
4	6	1	33.5	35.7
4	6	2	92.6	85.1
4	6	3	45.0	46.3
4	6	4	63.2	62.0
4	6	5	22.1	24.7
4	6	6	15.3	11.6
4	6	7	16.6	16.1
4	6	8	31.7	31.6
4	6	9	18.2	15.2
4	7	0	103.4	90.4
4	7	1	44.9	55.6
4	7	2	48.9	49.5
4	7	3	35.5	41.7
4	7	4	34.8	33.9
4	7	5	61.2	54.8
4	7	6	21.2	22.1
4	7	7	21.3	23.6
4	7	8	12.1	10.7
4	7	9	12.6	13.1
4	8	0	97.3	97.4
4	8	1	41.9	50.1
4	8	2	99.1	97.7
4	8	3	96.6	98.4
4	8	4	52.6	48.6
4	8	5	29.7	29.9
4	8	6	33.0	33.2
4	8	7	13.7	13.6
4	8	8	20.9	18.0
4	9	0	106.5	105.4
4	9	1	85.0	70.4
4	9	2	31.5	36.6
4	9	3	70.5	72.4
4	9	4	50.7	48.1
4	9	5	31.4	33.9
4	9	6	51.7	55.3
4	9	7	22.1	20.5
4	9	8	-6.0	8.9
4	10	0	-3.9	9.8
4	10	1	22.5	26.4
4	10	2	64.0	63.4
4	10	3	96.1	97.1
4	10	4	25.1	25.4
4	10	5	24.9	24.6
4	10	6	31.6	31.5
4	10	7	29.5	28.3
4	10	8	27.9	26.3
4	11	0	85.1	83.5
4	11	1	78.0	71.0
4	11	2	55.0	49.0
4	11	3	32.7	40.6
4	11	4	34.4	32.5
4	11	5	17.1	19.3
4	11	6	29.5	29.6
4	11	7	26.6	24.6
4	11	8	-6.1	8.4
4	12	0	-4.1	1.5
4	12	1	32.0	34.2
4	12	2	76.8	76.8
4	12	3	24.1	29.2
4	12	4	59.8	56.5
4	12	5	28.7	32.2
4	12	6	14.5	11.5
4	12	7	30.6	27.9
4	12	8	20.9	16.7
4	13	0	18.7	21.8
4	13	1	27.2	30.2
4	13	2	29.9	30.4
4	13	3	12.4	8.8
4	13	4	42.6	46.0
4	13	5	27.6	30.1
4	13	6	-5.7	8.0
4	13	7	14.4	12.5
4	14	0	-4.4	7.7
4	14	1	46.3	50.3
4	14	2	33.1	33.7
4	14	3	19.9	17.2
4	14	4	31.4	33.2
4	14	5	27.8	29.8
4	14	6	20.4	22.8
4	14	7	21.1	20.6
4	15	0	25.8	23.0
4	15	1	41.9	48.1
4	15	2	31.3	30.6
4	15	3	-5.1	3.3
4	15	4	25.4	26.1
4	15	5	41.7	45.4
4	15	6	23.6	24.2
4	15	7	26.8	25.6
4	16	0	21.6	22.4
4	16	1	16.3	25.2
4	16	2	43.8	41.4
4	16	3	21.7	22.2
4	16	4	13.9	10.9
4	16	5	19.9	20.0
4	16	6	11.9	15.4
4	17	0	29.7	28.8
4	17	1	9.7	12.1
4	17	2	27.6	31.7
4	17	3	9.1	5.7
4	17	4	13.0	13.6
4	17	5	27.3	24.1
4	17	6	32.9	30.8
4	18	0	-5.0	6.1
4	18	1	20.8	21.9
4	18	2	14.6	14.6
4	18	3	27.1	28.4
4	18	4	-5.7	2.6
4	18	5	25.4	31.5
4	18	6	-6.2	2.6
4	19	0	19.2	20.7
4	19	1	-5.3	16.2
4	19	2	10.9	6.8
4	19	3	12.4	6.1
4	19	4	12.9	9.6
4	19	5	14.6	13.7
4	20	0	55.7	50.8
4	20	1	-5.4	5.1
4	20	2	32.7	29.7
4	20	3	14.3	12.6
4	20	4	-6.0	5.0
4	21	0	32.4	29.8
4	21	1	20.4	15.6
4	21	2	13.8	11.2
4	21	3	11.6	10.1
4	21	4	12.6	8.0
4	22	0	20.9	20.8
4	22	1	10.7	13.3
4	22	2	21.5	17.4
4	22	3	12.8	8.6
4	23	0	-5.8	2.7
5	0	1	24.4	20.5
5	0	2	118.2	113.1
5	0	3	-4.1	3.6
5	0	4	134.6	119.8
5	0	5	23.5	19.0
5	0	6	13.3	14.7
5	0	7	-5.5	8.0
5	0	8	37.5	36.5
5	0	9	-6.3	3.1
5	1	0	70.5	65.3
5	1	1	105.5	88.8
5	1	2	89.0	78.3
5	1	3	63.7	49.7
5	1	4	74.3	62.6
5	1	5	90.1	86.4
5	1	6	44.3	46.4
5	1	7	44.0	44.4
5	1	8	-5.9	15.1
5	1	9	19.9	14.3
5	2	0	85.2	77.8
5	2	1	62.7	55.1
5	2	2	94.5	78.1
5	2	3	86.2	87.1
5	2	4	101.3	90.0
5	2	5	12.1	6.0
5	2	6	24.5	24.4
5	2	7	32.0	37.7
5	2	8	23.9	28.3
5	2	9	31.4	27.2
5	3	0	77.6	76.6
5	3	1	86.4	86.7
5	3	2	75.7	72.4
5	3	3	18.7	15.2
5	3	4	25.4	23.6
5	3	5	55.9	49.1
5	3	6	73.8	67.1
5	3	7	36.9	38.3
5	3	8	20.1	23.4
5	3	9	-6.3	7.7
5	4	0	76.6	74.6
5	4	1	55.4	56.0
5	4	2	58.7	55.2
5	4	3	133.9	127.1
5	4	4	33.5	28.9
5	4	5	68.3	66.1
5	4	6	26.6	23.2
5	4	7	33.5	35.8
5	4	8	24.1	23.1
5	4	9	34.9	36.6
5	5	0	70.7	70.3
5	5	1	45.3	50.7
5	5	2	40.6	50.4
5	5	3	23.8	20.4
5	5	4	57.1	60.5
5	5	5	15.0	18.9
5	5	6	86.3	79.4
5	5	7	26.6	24.0
5	5	8	-6.0	5.5
5	5	9	20.9	22.5
5	6	0	40.9	43.3
5	6	1	30.9	40.0
5	6	2	81.1	72.2
5	6	3	75.7	71.2
5	6	4	67.5	62.3
5	6	5	30.7	30.0
5	6	6	21.5	18.9
5	6	7	30.0	29.2
5	6	8	14.5	9.8
5	7	0	99.3	95.7
5	7	1	84.6	82.9
5	7	2	29.5	31.4
5	7	3	26.6	34.4
5	7	4	21.9	22.5
5	7	5	73.4	71.2
5	7	6	26.6	28.2
5	7	7	50.8	51.5
5	7	8	-6.0	4.6
5	8	0	20.9	16.7
5	8	1	18.3	12.1
5	8	2	88.9	82.3
5	8	3	16.7	19.1
5	8	4	57.6	55.0
5	8	5	17.7	17.7
5	8	6	10.3	10.7
5	8	7	24.2	21.8
5	8	8	27.7	29.2
5	9	0	71.8	65.1
5	9	1	92.1	94.7
5	9	2	39.6	37.0
5	9	3	14.5	11.4
5	9	4	21.7	21.7
5	9	5	52.4	54.6
5	9	6	-5.4	4.4
5	9	7	43.0	45.0
5	9	8	12.3	7.1
5	10	0	52.5	55.3
5	10	1	-4.3	6.4
5	10	2	72.8	73.3
5	10	3	7.6	11.8
5	10	4	59.7	58.1
5	10	5	16.1	14.8
5	10	6	-5.5	8.4
5	10	7	-5.8	5.6
5	10	8	44.8	43.1
5	11	0	46.5	42.8
5	11	1	36.8	39.5
5	11	2	36.0	33.6
5	11	3	11.8	10.0
5	11	4	33.3	35.9
5	11	5	51.7	52.9
5	11	6	22.0	20.6
5	11	7	27.7	23.2
5	11	8	20.3	18.3
5	12	0	-4.3	1.1
5	12	1	45.1	49.4
5	12	2	43.5	45.4
5	12	3	45.7	50.1
5	12	4	22.1	24.6
5	12	5	23.3	22.8
5	12	6	15.1	13.4
5	12	7	14.5	15.9
5	13	0	81.4	79.1
5	13	1	-4.6	7.3
5	13	2	26.2	27.4
5	13	3	25.2	23.7
5	13	4	29.0	30.2
5	13	5	25.3	27.3
5	13	6	53.7	55.2
5	13	7	-6.1	6.6
5	14	0	-4.6	11.1
5	14	1	35.5	35.9
5	14	2	8.4	9.4
5	14	3	76.0	75.8
5	14	4	15.9	11.9
5	14	5	18.0	17.0
5	14	6	10.6	8.9
5	14	7	-6.2	11.5
5	15	0	80.2	79.3
5	15	1	23.6	26.0
5	15	2	14.7	13.4
5	15	3	15.9	20.9
5	15	4	22.8	19.5
5	15	5	17.1	16.2
5	15	6	22.1	24.7
5	16	0	12.2	15.0
5	16	1	-5.0	10.2
5	16	2	20.4	20.5
5	16	3	38.9	38.3
5	16	4	18.7	16.3
5	16	5	-5.7	6.9
5	16	6	-6.0	9.3
5	17	0	25.4	24.3
5	17	1	-5.1	9.5
5	17	2	13.7	12.4
5	17	3	14.2	12.6
5	17	4	11.8	4.8
5	17	5	10.0	13.4
5	17	6	10.7	8.1
5	18	0	12.6	10.2
5	18	1	24.8	25.1
5	18	2	21.6	16.4
5	18	3	-5.6	2.2
5	18	4	23.7	19.6
5	18	5	16.6	16.9
5	19	0	12.7	15.2
5	19	1	36.6	35.6
5	19	2	18.2	17.8
5	19	3	-5.8	5.7
5	19	4	9.9	6.6
5	19	5	21.4	16.0
5	20	0	-5.4	6.2
5	20	1	21.9	18.7
5	20	2	25.1	19.7
5	20	3	27.0	27.3
5	20	4	20.6	16.3
5	21	0	26.0	25.3
5	21	1	19.0	21.8
5	21	2	17.2	14.4
5	21	3	-6.0	3.8
5	22	0	11.4	10.5
5	22	1	-5.8	11.4
5	22	2	-6.0	4.4
6	0	0	71.5	60.8
6	0	1	63.8	62.3
6	0	2	28.7	27.5
6	0	3	157.7	149.4
6	0	4	-4.6	3.0
6	0	5	38.4	36.5
6	0	6	13.8	10.4
6	0	7	25.9	27.0
6	0	8	10.9	9.4
6	1	0	93.4	101.4
6	1	1	66.7	53.9
6	1	2	95.5	90.0
6	1	3	20.5	18.5
6	1	4	28.5	33.2
6	1	5	31.0	33.3
6	1	6	62.7	58.2
6	1	7	20.0	18.1
6	1	8	15.9	14.7
6	2	0	-3.6	6.9
6	2	1	13.8	18.5
6	2	2	63.6	56.2
6	2	3	75.3	71.5
6	2	4	86.9	80.5
6	2	5	14.6	12.5
6	2	6	15.1	10.9
6	2	7	28.6	27.6
6	2	8	25.7	24.7
6	3	0	94.4	100.0
6	3	1	99.5	97.7
6	3	2	28.3	31.5
6	3	3	21.2	16.6
6	3	4	24.3	27.7
6	3	5	75.4	73.0
6	3	6	40.8	34.9
6	3	7	37.6	39.9
6	3	8	20.1	20.4
6	4	0	26.4	20.7
6	4	1	22.8	22.7
6	4	2	101.7	99.3
6	4	3	44.9	42.5
6	4	4	61.9	63.1
6	4	5	10.2	8.1
6	4	6	21.1	19.2
6	4	7	19.1	16.1
6	4	8	33.9	35.3
6	5	0	7.4	7.2
6	5	1	129.1	129.7
6	5	2	29.6	30.0
6	5	3	33.7	28.5
6	5	4	23.2	24.3
6	5	5	79.6	73.3
6	5	6	21.4	23.9
6	5	7	43.3	45.7
6	5	8	-6.1	4.6
6	6	0	15.7	10.6
6	6	1	25.2	28.3
6	6	2	89.6	89.6
6	6	3	39.4	36.1
6	6	4	75.1	73.0
6	6	5	24.1	25.0
6	6	6	-5.4	4.1
6	6	7	21.1	22.0
6	6	8	39.6	40.8
6	7	0	74.2	80.3
6	7	1	65.1	58.0
6	7	2	40.3	39.3
6	7	3	21.4	25.6
6	7	4	18.7	17.1
6	7	5	64.4	64.4
6	7	6	40.4	41.6
6	7	7	15.3	19.3
6	7	8	17.9	14.9
6	8	0	42.8	35.6
6	8	1	44.7	53.1
6	8	2	42.1	44.1
6	8	3	78.8	76.7
6	8	4	32.7	33.4
6	8	5	38.8	41.7
6	8	6	-5.5	2.0
6	8	7	39.0	39.2
6	8	8	32.1	32.3
6	9	0	76.0	83.1
6	9	1	32.6	35.5
6	9	2	25.6	28.2
6	9	3	13.2	11.8
6	9	4	32.3	31.9
6	9	5	20.5	19.8
6	9	6	72.1	64.4
6	9	7	17.5	15.6
6	9	8	14.4	9.1
6	10	0	-4.2	4.6
6	10	1	91.5	87.7
6	10	2	12.8	12.2
6	10	3	93.9	91.1
6	10	4	21.3	20.0
6	10	5	17.7	16.0
6	10	6	13.4	9.3
6	10	7	24.8	23.3
6	11	0	83.1	84.5
6	11	1	34.5	36.5
6	11	2	27.6	27.9
6	11	3	-4.9	11.3
6	11	4	-5.1	6.1
6	11	5	28.8	29.7
6	11	6	39.5	39.5
6	11	7	21.5	20.6
6	12	0	-4.5	0.5
6	12	1	21.8	19.2
6	12	2	31.7	29.0
6	12	3	31.4	30.6
6	12	4	39.1	41.0
6	12	5	-5.5	7.7
6	12	6	20.3	21.4
6	12	7	14.1	11.7
6	13	0	27.0	28.3
6	13	1	48.1	49.4
6	13	2	29.2	29.2
6	13	3	38.5	39.6
6	13	4	19.0	23.9
6	13	5	29.0	28.3
6	13	6	21.4	23.3
6	13	7	21.4	20.2
6	14	0	-4.7	4.6
6	14	1	13.8	10.9
6	14	2	48.4	51.6
6	14	3	16.5	13.8
6	14	4	39.3	39.6
6	14	5	10.5	13.9
6	14	6	15.6	10.2
6	15	0	24.8	27.2
6	15	1	38.6	39.0
6	15	2	-5.7	3.6
6	15	3	9.0	7.4
6	15	4	-5.5	2.9
6	15	5	30.4	29.5
6	15	6	15.6	11.4
6	16	0	-5.0	1.4
6	16	1	16.1	16.3
6	16	2	28.3	24.9
6	16	3	30.4	31.4
6	16	4	21.1	22.7
6	16	5	13.6	10.9
6	16	6	-6.2	9.0
6	17	0	61.0	53.8
6	17	1	31.7	35.5
6	17	2	22.9	22.6
6	17	3	19.0	17.8
6	17	4	16.7	13.6
6	17	5	20.6	21.3
6	18	0	-5.3	9.6
6	18	1	-5.4	11.0
6	18	2	-5.6	3.3
6	18	3	36.9	35.1
6	18	4	-5.9	7.8
6	18	5	10.8	6.8
6	19	0	20.1	19.6
6	19	1	-5.5	2.4
6	19	2	18.5	15.4
6	19	3	20.7	22.5
6	19	4	29.2	27.6
6	20	0	26.6	21.6
6	20	1	14.1	12.9
6	20	2	15.9	13.6
6	20	3	35.6	33.0
6	21	0	-5.7	9.9
6	21	1	-5.8	10.1
6	21	2	-6.0	6.2
6	22	0	-5.8	1.1
6	22	1	-5.9	5.8
7	0	1	23.9	6.0
7	0	2	95.4	80.3
7	0	3	-4.6	6.4
7	0	4	76.9	71.4
7	0	5	9.1	6.3
7	0	6	17.9	20.3
7	0	7	18.6	15.8
7	0	8	50.1	47.8
7	1	0	36.5	27.0
7	1	1	119.3	114.2
7	1	2	8.8	10.0
7	1	3	13.2	13.1
7	1	4	28.6	25.3
7	1	5	71.5	64.1
7	1	6	9.3	7.3
7	1	7	52.5	56.3
7	1	8	-6.2	5.6
7	2	0	8.3	4.2
7	2	1	65.5	63.4
7	2	2	82.7	76.1
7	2	3	44.2	49.5
7	2	4	44.9	46.1
7	2	5	17.7	18.2
7	2	6	10.6	7.7
7	2	7	18.7	17.6
7	2	8	31.3	30.2
7	3	0	74.8	69.8

Table 1

continued

h	k	l	F_o	F_c
7	3	1	72.9	60.6
7	3	2	25.1	26.7
7	3	3	25.8	27.0
7	3	4	52.9	51.3
7	3	5	35.5	32.7
7	3	6	42.8	44.4
7	3	7	19.9	20.9
7	3	8	16.2	12.8
7	4	0	60.4	64.2
7	4	1	67.8	64.6
7	4	2	39.4	42.4
7	4	3	95.4	91.1
7	4	4	23.9	22.6
7	4	5	36.2	32.0
7	4	6	14.1	14.5
7	4	7	23.3	22.8
7	4	8	12.7	2.5
7	5	0	114.6	125.5
7	5	1	27.2	24.3
7	5	2	53.7	50.7
7	5	3	20.2	17.0
7	5	4	46.8	46.4
7	5	5	15.9	18.7
7	5	6	71.9	65.1
7	5	7	19.1	23.4
7	5	8	18.3	14.6
7	6	0	24.1	28.2
7	6	1	50.4	52.2
7	6	2	41.8	45.0
7	6	3	116.0	112.8
7	6	4	41.8	39.3
7	6	5	21.9	21.3
7	6	6	23.6	17.9
7	6	7	18.8	22.3
7	6	8	14.7	15.6
7	7	0	90.7	97.5
7	7	1	40.4	46.9
7	7	2	22.2	18.7
7	7	3	32.5	32.5
7	7	4	34.5	32.1
7	7	5	31.8	27.2
7	7	6	51.1	52.4
7	7	7	19.5	15.1
7	7	8	21.6	19.7
7	8	0	10.6	10.9
7	8	1	32.7	36.4
7	8	2	45.6	48.5
7	8	3	53.5	60.8
7	8	4	58.1	51.3
7	8	5	14.6	15.8
7	8	6	28.1	30.7
7	8	7	19.4	17.5
7	9	0	8.0	8.1
7	9	1	73.4	79.6
7	9	2	28.4	31.1
7	9	3	26.4	27.9
7	9	4	19.3	14.6
7	9	5	47.4	47.5
7	9	6	12.4	12.8
7	9	7	29.1	30.1
7	10	0	57.9	52.7
7	10	1	16.0	15.4
7	10	2	59.0	55.3
7	10	3	28.0	30.5
7	10	4	48.9	47.3
7	10	5	24.5	24.0
7	10	6	-5.8	7.5
7	10	7	-6.1	5.4
7	11	0	72.7	73.2
7	11	1	50.8	54.8
7	11	2	33.7	33.2
7	11	3	23.0	23.2
7	11	4	13.7	8.7
7	11	5	42.7	46.4
7	11	6	26.2	25.7
7	11	7	14.2	9.9
7	12	0	26.8	22.2
7	12	1	20.6	21.2
7	12	2	50.5	52.6
7	12	3	41.0	44.8
7	12	4	31.0	26.8
7	12	5	14.3	14.2
7	12	6	-5.9	11.6
7	12	7	16.9	14.4
7	13	0	37.4	30.1
7	13	1	18.6	20.6
7	13	2	31.9	30.9
7	13	3	23.6	23.0
7	13	4	15.6	11.7
7	13	5	24.2	22.3
7	13	6	35.0	30.9
7	14	0	-4.9	4.8
7	14	1	12.7	14.3
7	14	2	21.1	16.8
7	14	3	38.0	38.4
7	14	4	-5.6	12.4
7	14	5	10.9	11.5
7	14	6	14.6	12.5
7	15	0	33.6	34.5
7	15	1	14.4	15.4
7	15	2	14.2	13.7
7	15	3	14.5	8.5
7	15	4	26.4	26.0
7	15	5	27.0	21.2
7	15	6	26.7	26.5
7	16	0	11.7	11.1
7	16	1	17.5	17.2
7	16	2	27.0	27.4
7	16	3	28.5	23.0
7	16	4	26.4	25.4
7	16	5	12.7	9.9
7	17	0	30.0	30.9
7	17	1	24.7	25.0
7	17	2	28.1	25.5
7	17	3	-5.8	2.2
7	17	4	27.7	22.6
7	17	5	22.2	22.6
7	18	0	10.4	14.7
7	18	1	12.3	12.6
7	18	2	35.8	33.1
7	18	3	-5.9	8.5
7	18	4	30.8	28.7
7	19	0	-5.5	6.1
7	19	1	22.8	20.1
7	19	2	-5.9	5.7
7	19	3	10.1	5.1
7	20	0	-5.7	6.0
7	20	1	-5.8	6.2
7	20	2	20.8	17.9
7	21	0	15.7	14.1
7	21	1	18.3	16.7
8	0	0	40.8	35.4
8	0	1	84.4	73.5
8	0	2	23.6	22.5
8	0	3	79.5	73.7
8	0	4	12.1	7.1
8	0	5	14.9	16.6
8	0	6	42.7	44.3
8	0	7	18.9	18.0
8	0	8	12.5	13.0
8	1	0	111.3	117.1
8	1	1	16.0	17.4
8	1	2	39.1	37.6
8	1	3	30.1	28.5
8	1	4	43.7	44.5
8	1	5	30.2	28.4
8	1	6	48.9	44.4
8	1	7	24.0	25.4
8	1	8	-6.3	4.8
8	2	0	18.6	15.7
8	2	1	66.5	62.1
8	2	2	76.4	67.6
8	2	3	73.1	69.5
8	2	4	53.6	49.0
8	2	5	47.4	47.3
8	2	6	22.1	22.0
8	2	7	20.8	20.7
8	2	8	23.1	21.6
8	3	0	39.7	37.8
8	3	1	52.2	53.8
8	3	2	35.8	41.3
8	3	3	14.4	15.1
8	3	4	31.5	33.4
8	3	5	46.7	45.3
8	3	6	37.0	38.0
8	3	7	36.2	35.5
8	3	8	18.8	17.2
8	4	0	8.0	0.9
8	4	1	56.6	48.5
8	4	2	54.4	54.4
8	4	3	26.1	27.6
8	4	4	62.6	55.7
8	4	5	31.8	32.6
8	4	6	-5.7	5.8
8	4	7	21.6	21.7
8	5	0	17.9	19.4
8	5	1	79.3	77.8
8	5	2	27.2	28.1
8	5	3	25.0	22.9
8	5	4	10.8	13.6
8	5	5	45.3	43.3
8	5	6	15.7	21.5
8	5	7	36.1	40.6
8	6	0	-4.4	3.7
8	6	1	29.7	32.4
8	6	2	43.1	41.6
8	6	3	41.4	41.2
8	6	4	27.1	26.0
8	6	5	37.4	35.3
8	6	6	24.7	24.6
8	6	7	24.4	24.9
8	7	0	40.6	47.3
8	7	1	46.5	50.0
8	7	2	44.6	45.9
8	7	3	42.7	47.4
8	7	4	36.4	35.5
8	7	5	35.3	34.7
8	7	6	34.6	36.9
8	7	7	14.9	12.6
8	8	0	29.7	28.3
8	8	1	40.9	45.8
8	8	2	29.3	29.5
8	8	3	51.5	53.7
8	8	4	38.4	37.1
8	8	5	25.7	26.6
8	8	6	15.4	15.9
8	8	7	15.0	16.4
8	9	0	58.8	55.2
8	9	1	28.7	26.9
8	9	2	22.0	21.5
8	9	3	29.7	31.7
8	9	4	46.2	47.7
8	9	5	25.3	22.2
8	9	6	31.5	32.4
8	9	7	21.8	19.8
8	10	0	27.0	29.4
8	10	1	18.1	15.2
8	10	2	25.7	28.6
8	10	3	54.5	58.6
8	10	4	12.6	16.8
8	10	5	25.5	26.0
8	10	6	15.1	3.9
8	10	7	16.1	13.3
8	11	0	55.7	53.7
8	11	1	11.0	13.7
8	11	2	24.9	25.0
8	11	3	20.9	21.5
8	11	4	30.7	30.6
8	11	5	22.6	22.0
8	11	6	34.0	33.9
8	12	0	26.5	21.3
8	12	1	10.1	13.1
8	12	2	45.6	47.4
8	12	3	37.6	41.2
8	12	4	38.5	41.7
8	12	5	11.3	8.9
8	12	6	12.0	12.1
8	13	0	31.8	30.0
8	13	1	34.3	37.9
8	13	2	35.4	34.7
8	13	3	12.4	10.2
8	13	4	29.4	28.6
8	13	5	42.5	43.3
8	13	6	21.8	16.9
8	14	0	-5.1	12.1
8	14	1	-5.2	4.2
8	14	2	50.4	53.6
8	14	3	10.5	4.1
8	14	4	31.6	32.3
8	14	5	24.6	25.8
8	15	0	-5.7	2.8
8	15	1	38.6	37.8
8	15	2	12.1	9.5
8	15	3	9.1	9.9
8	15	4	13.1	10.8
8	15	5	24.7	24.2
8	16	0	22.0	25.5
8	16	1	20.7	19.6
8	16	2	22.0	24.8
8	16	3	-5.8	4.1
8	16	4	21.1	18.8
8	17	0	24.0	22.9
8	17	1	12.4	14.5
8	17	2	9.2	11.6
8	17	3	12.5	7.3
8	17	4	-6.1	4.4
8	18	0	24.7	25.0
8	18	1	-5.7	11.6
8	18	2	-5.9	9.3
8	18	3	17.3	15.8
8	19	0	13.7	18.3
8	19	1	14.4	12.0
8	19	2	13.9	11.1
8	20	0	-5.8	1.9
9	0	1	56.4	48.9
9	0	2	28.6	28.6
9	0	3	13.9	16.7
9	0	4	34.6	32.2
9	0	5	65.9	57.7
9	0	6	20.6	18.4
9	0	7	-6.2	9.1
9	1	0	8.8	6.7
9	1	1	71.1	66.2
9	1	2	73.2	67.9
9	1	3	-5.2	1.9
9	1	4	26.4	29.8
9	1	5	42.9	42.8
9	1	6	-5.9	5.1
9	1	7	33.7	36.4
9	2	0	14.4	14.8
9	2	1	55.8	51.1
9	2	2	60.8	57.1
9	2	3	23.1	22.3
9	2	4	33.2	30.8
9	2	5	46.1	51.0
9	2	6	27.1	25.3
9	2	7	24.1	21.1
9	3	0	25.4	31.1
9	3	1	22.1	22.1
9	3	2	41.9	39.5
9	3	3	54.6	51.9
9	3	4	36.6	40.3
9	3	5	29.0	32.5
9	3	6	25.8	29.7
9	3	7	17.9	16.9
9	4	0	43.0	43.4
9	4	1	33.0	37.9
9	4	2	30.3	28.2
9	4	3	47.2	45.8
9	4	4	27.5	29.8
9	4	5	29.9	32.2
9	4	6	24.4	24.3
9	4	7	18.0	19.8
9	5	0	55.9	57.0
9	5	1	29.3	28.5
9	5	2	27.3	30.3
9	5	3	48.4	49.8
9	5	4	29.6	29.2
9	5	5	21.1	19.4
9	5	6	31.7	29.5
9	5	7	26.9	24.6
9	6	0	40.6	40.6
9	6	1	17.8	17.6
9	6	2	20.4	19.4
9	6	3	62.0	57.4
9	6	4	22.6	23.3
9	6	5	36.0	40.6
9	6	6	19.1	20.1
9	6	7	18.3	17.2
9	7	0	56.3	58.7
9	7	1	34.1	39.5
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9	7	4	41.4	39.1
9	7	5	11.3	11.4
9	7	6	34.2	34.7
9	7	7	12.6	15.0
9	8	0	23.0	29.3
9	8	1	39.2	40.6
9	8	2	50.0	51.2
9	8	3	22.2	20.2
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9	9	0	12.4	9.9
9	9	1	26.7	24.3
9	9	2	33.2	34.0
9	9	3	20.4	21.9
9	9	4	30.5	30.2
9	9	5	29.7	28.9
9	9	6	-6.1	13.2
9	10	0	7.8	2.9
9	10	1	21.0	24.6
9	10	2	46.6	47.6
9	10	3	25.6	27.0
9	10	4	31.2	29.3
9	10	5	20.2	20.7
9	10	6	16.7	17.1
9	11	0	41.0	47.2
9	11	1	32.8	33.5
9	11	2	36.9	38.4
9	11	3	20.5	22.9
9	11	4	32.8	33.0
9	11	5	21.8	20.6
9	11	6	-6.2	11.1
9	12	0	19.5	23.0
9	12	1	15.3	16.5
9	12	2	24.0	23.2
9	12	3	-5.6	9.4
9	12	4	34.6	34.2
9	12	5	15.6	2.6
9	13	0	50.5	48.4
9	13	1	26.9	29.0
9	13	2	21.3	19.4
9	13	3	24.8	22.0
9	13	4	19.9	19.4
9	13	5	17.0	14.0
9	14	0	52.0	42.5
9	14	1	15.0	14.0
9	14	2	22.5	23.6
9	14	3	15.3	16.0
9	14	4	17.9	16.1
9	14	5	-6.2	10.0
9	15	0	11.2	10.5
9	15	1	21.1	23.2
9	15	2	11.6	9.2
9	15	3	17.8	14.3
9	15	4	31.7	30.0
9	16	0	11.0	4.8
9	16	1	18.5	18.6
9	16	2	12.0	10.6
9	16	3	22.7	24.6
9	17	0	17.8	14.7
9	17	1	14.5	17.8
9	17	2	18.2	20.2
9	17	3	10.2	6.2
9	18	0	11.5	9.0
9	18	1	14.1	9.7
9	18	2	17.0	9.0
10	0	0	71.4	56.2
10	0	1	17.2	2.3
10	0	2	17.9	15.8
10	0	3	60.0	48.8
10	0	4	42.1	36.9
10	0	5	39.2	38.4
10	0	6	28.9	29.8
10	1	0	29.5	30.7
10	1	1	36.5	30.5
10	1	2	33.7	24.8
10	1	3	71.4	64.3
10	1	4	17.7	17.6
10	1	5	16.5	16.9
10	1	6	21.4	19.9
10	2	0	52.0	53.4
10	2	1	36.1	32.4
10	2	2	47.9	49.1
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10	3	1	37.5	41.9
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10	3	3	18.2	21.9
10	3	4	24.9	25.0
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10	3	6	13.9	3.1
10	4	0	9.4	4.5
10	4	1	53.8	55.1
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10	4	3	-5.4	10.8
10	4	4	21.6	19.0
10	4	5	41.4	38.8
10	4	6	-6.1	11.5
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10	5	4	41.2	39.0
10	5	5	33.5	32.7
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10	6	1	41.0	45.3
10	6	2	28.5	28.1
10	6	3	20.5	21.3
10	6	4	28.4	24.7
10	6	5	33.0	32.2
10	6	6	18.8	18.2
10	7	0	-4.4	4.3
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10	7	2	40.8	42.7
10	7	3	29.8	31.6
10	7	4	40.4	37.5
10	7	5	21.2	21.4
10	7	6	20.7	16.4
10	8	0	42.4	43.0
10	8	1	37.8	32.4
10	8	2	23.7	28.1
10	8	3	24.1	25.5
10	8	4	24.8	24.4
10	8	5	25.1	22.1
10	8	6	31.8	30.6
10	9	0	23.3	25.6
10	9	1	28.5	27.6
10	9	2	28.1	29.4
10	9	3	43.6	43.8
10	9	4	11.4	11.0
10	9	5	14.7	17.5
10	10	0	30.6	34.2
10	10	1	39.6	43.3
10	10	2	27.8	30.2
10	10	3	28.2	30.0
10	10	4	17.1	6.1
10	10	5	11.7	13.7
10	11	0	25.8	28.0
10	11	1	27.2	29.2
10	11	2	21.7	21.6
10	11	3	18.7	17.3
10	11	4	27.0	28.4
10	11	5	15.5	8.2
10	12	0	-5.3	11.1
10	12	1	45.6	48.4
10	12	2	12.3	9.1
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10	12	4	17.3	16.7
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10	13	3	-5.9	5.5
10	13	4	19.4	12.4
10	14	0	11.8	12.0
10	14	1	16.7	16.5
10	14	2	19.2	15.5
10	14	3	10.6	11.7
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10	15	0	14.5	13.0
10	15	1	13.6	16.4
10	15	2	21.5	19.6
10	15	3	11.2	10.2
10	16	0	9.5	7.4
10	16	1	11.7	15.0
10	16	2	18.5	17.6
10	17	0	21.6	16.1
10	17	1	13.9	12.7
11	0	1	63.8	58.9
11	0	2	-5.6	5.4
11	0	3	21.4	19.3
11	0	4	11.1	12.0
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11	0	6	-6.4	2.5
11	1	0	14.8	11.8
11	1	1	19.0	20.7
11	1	2	44.9	42.8
11	1	3	33.1	31.1
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11	1	5	-6.1	11.9
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11	4	5	-6.1	6.5
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11	5	4	-5.9	4.2
11	5	5	-6.1	6.5
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11	6	2	29.0	30.6
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11	6	4	28.7	29.8
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11	7	4	26.7	27.1
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11	9	3	-5.9	12.4
11	9	4	31.2	29.2
11	10	0	11.7	14.0
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11	10	2	18.6	17.1
11	10	3	10.0	11.6
11	10	4	-6.1	8.3
11	11	0	19.3	24.9
11	11	1	24.8	26.2
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11	11	3	13.2	9.4
11	11	4	21.2	19.0
11	12	0	16.5	17.9
11	12	1	9.2	11.8
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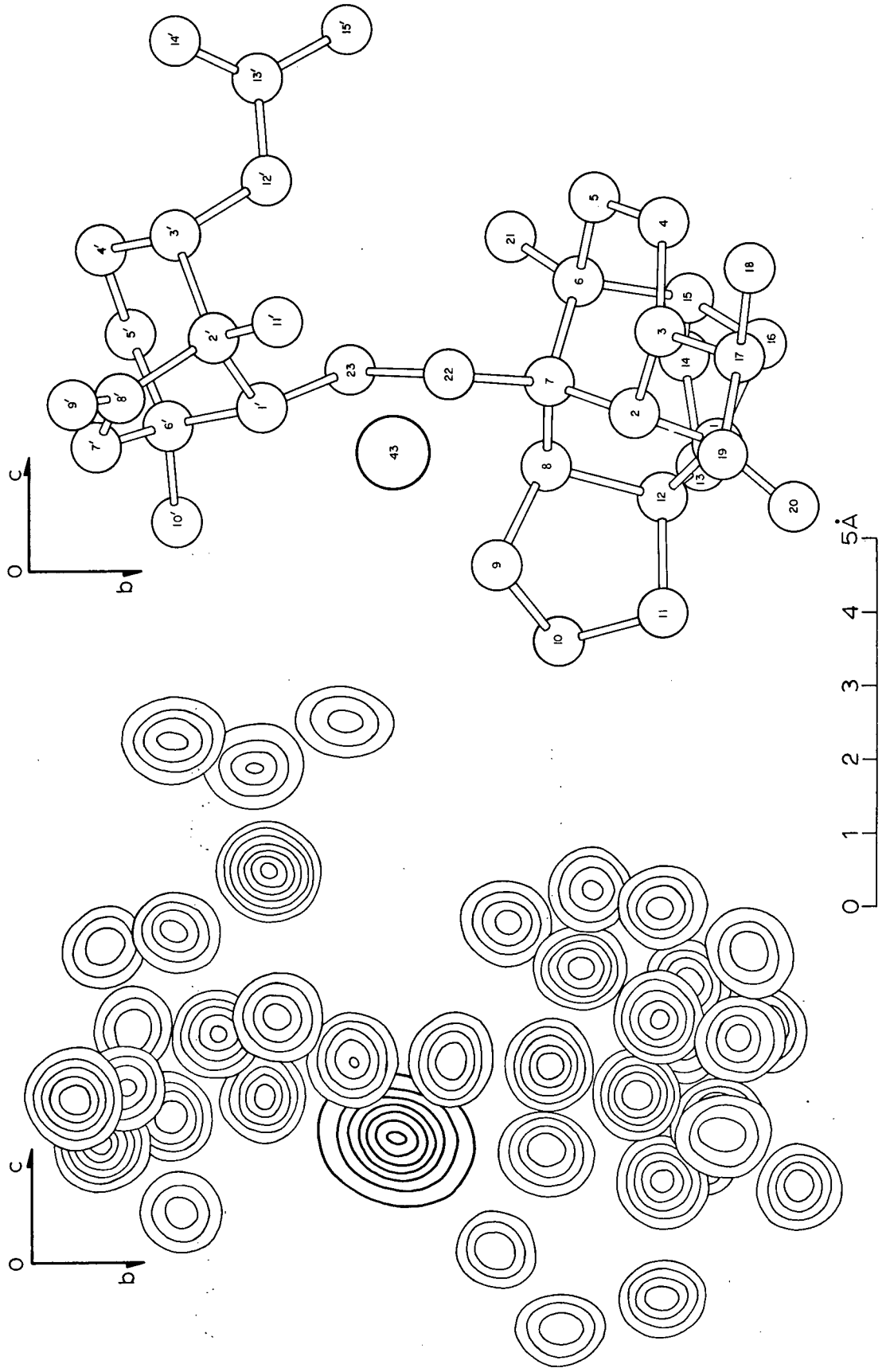
11	12	3	10.7	11.7
11	13	0	-5.6	2.7
11	13	1	-5.8	7.5
11	13	2	12.2	8.7
11	13	3	26.6	28.1
11	14	0	39.9	42.1
11	14	1	13.5	12.8
11	14	2	22.4	21.2
11	15	0	13.4	12.6
11	15	1	-5.9	7.2
12	0	0	40.9	34.0
12	0	1	22.8	23.9
12	0	2	15.0	8.3
12	0	3	34.8	33.5
12	0	4	28.8	26.2
12	0	5	-6.4	10.8
12	1	0	-5.3	6.0
12	1	1	26.1	21.1
12	1	2	13.9	11.3
12	1	3	46.0	45.1
12	1	4	13.4	8.5
12	1	5	24.2	16.8
12	2	0	39.6	41.9
12	2	1	31.7	28.9
12	2	2	22.0	20.4
12	2	3	14.3	7.8
12	2	4	19.3	17.6
12	2	5	27.0	24.7
12	3	0	16.6	14.3
12	3	1	16.8	12.6
12	3	2	45.4	48.4
12	3	3	32.6	31.3
12	3	4	33.4	30.1
12	4	0	22.7	26.4
12	4	1	45.3	51.0
12	4	2	10.2	10.3
12	4	3	13.7	14.2
12	4	4	17.3	13.5
12	5	0	-5.4	4.3
12	5	1	-5.7	7.3
12	5	2	43.9	45.2
12	5	3	17.7	13.4
12	5	4	33.3	33.4
12	6	0	10.3	8.2
12	6	1	19.4	25.7
12	6	2	11.3	11.2
12	6	3	10.5	6.9
12	6	4	15.2	15.2
12	7	0	-5.5	11.2
12	7	1	-5.7	8.0
12	7	2	22.3	22.6
12	7	3	30.3	29.4
12	7	4	18.2	17.4
12	8	0	42.6	46.4
12	8	1	13.4	13.2
12	8	2	15.6	13.5
12	8	3	13.3	12.3
12	9	0	17.6	13.5
12	9	1	14.1	15.6
12	9	2	13.7	13.2
12	9	3	40.0	39.8
12	10	0	55.4	53.1
12	10	1	17.0	14.0
12	10	2	19.5	21.7
12	10	3	-6.1	4.7
12	11	0	-5.7	3.7
12	11	1	17.2	16.9
12	11	2	24.3	20.9
12	12	0	10.1	9.4
12	12	1	13.4	13.4
13	0	1	66.7	57.2
13	0	2	10.3	3.0
13	0	3	10.3	15.5
13	1	0	-5.6	3.0
13	1	1	-6.0	6.8
13	1	2	44.8	44.7
13	1	3	21.7	21.5
13	2	0	41.0	42.2
13	2	1	31.1	30.5
13	2	2	20.8	15.7
13	2	3	10.9	4.7
13	3	0	-5.6	5.4
13	3	1	17.0	9.8
13	3	2	22.3	22.0
13	3	3	24.7	27.5
13	4	0	17.7	24.3
13	4	1	15.5	17.6
13	4	2	12.2	7.6
13	4	3	10.2	6.7
13	5	0	-5.6	1.0
13	5	1	17.4	17.1
13	5	2	14.0	7.9
13	5	3	35.0	36.5
13	6	0	29.2	32.2
13	6	1	20.2	23.3
13	6	2	-6.1	14.0
13	7	0	-5.7	1.4
13	7	1	18.7	22.7
13	7	2	21.3	20.9
13	8	0	16.7	15.7
13	8	1	32.5	32.0
13	9	0	15.1	18.5
14	0	0	16.8	15.6
14	1	0	23.1	29.7

Figure 1

(a) Superimposed sections of the three-dimensional electron-density distribution (contours at intervals of 2, 3, 4, ... $e\text{Å}^{-3}$ for carbon, oxygen and nitrogen, and 2, 20, 30, 40, ... $e\text{Å}^{-3}$ for iodine), and (b) a drawing of the molecule. The solvent (acetone) is omitted for clarity.


c
o
b
0 1 2 3 4 5Å
(a)
(b)

COORDINATES AND MOLECULAR DIMENSIONS

The final positional and isotropic thermal parameters are given in Table 2. In a structure of this complexity the detailed values of the anisotropic thermal parameters are probably of little significance, and they are not listed. The bond distances and valency angles are given in Table 3, and Figure 2 shows a packing diagram of the structure.

ABSOLUTE CONFIGURATION

To complete the analysis, the absolute configuration was determined by the anomalous dispersion method.[7] Fifteen pairs of reflections of varying intensity and $|F_c(hk\ell)|^2/|F_c(\bar{h}\bar{k}\bar{\ell})|^2$ ratio were chosen, and the intensities were measured with a scintillation counter and Cu-K_α radiation.

The results are given in Table 4, and indicate unambiguously that the parameters used to calculate the structure factors (those of Table 2 referred to a right-handed axial set) represent the true absolute configuration. All diagrams in this work show the correct absolute configuration. The molecular structure previously depicted (arbitrarily) in reports of daphmacrine[5,8] is the optical enantiomorph of the true configuration determined here.

Table 2

Final positional (fractional x 10^3) and isotropic ($Å^2$) thermal parameters. Mean standard deviations are $\sigma(x) = \sigma(y) = \sigma(z) = 0.001$ Å for I, 0.013 Å for N, 0.015 Å for O, 0.020 Å for C; $\sigma(B) = 0.05, 0.28, 0.34, 0.45$ for I^-, N, O, C.

Atom	x	y	z	B
N(1)	347	372	180	3.5
C(2)	414	327	219	3.3
C(3)	491	339	326	3.3
C(4)	456	342	472	4.7
C(5)	377	305	501	5.1
C(6)	299	298	391	3.0
C(7)	347	281	262	3.0
C(8)	275	280	144	3.0
C(9)	302	252	010	4.9
C(10)	250	286	-090	5.7
C(11)	278	342	-051	4.6
C(12)	265	341	104	3.5
C(13)	169	364	147	4.6
C(14)	149	352	294	5.6
C(15)	245	355	369	4.0
C(16)	306	396	311	4.3
C(17)	563	384	296	4.2
C(18)	633	389	411	5.8
C(19)	613	375	165	6.0
C(20)	389	414	096	4.1

..../continued

Table 2, continued

Atom	x	y	z	B
C(21)	226	258	451	4.6
C(22)	402	228	268	4.3
C(23)	343	174	272	3.8
C(1')	405	126	221	3.6
C(2')	480	100	310	3.6
C(3')	444	080	444	4.6
C(4')	360	040	426	5.2
C(5')	296	057	311	5.4
C(6')	345	075	195	3.8
O(7')	421	036	163	5.1
C(8')	495	050	232	4.8
O(9')	569	024	222	6.5
C(10')	285	082	066	6.7
C(11')	571	133	331	5.0
O(12')	416	128	523	4.0
C(13')	407	122	661	5.1
O(14')	418	077	706	8.1
C(15')	383	171	724	6.1
C(1")	817	039	339	10.5
C(2")	894	018	239	8.1
C(3")	992	039	263	11.4
O(4")	869	-008	145	7.8
I(43)	040.6	196.7	164.0	5.4

Table 3

Bond distances ($\sigma \simeq 0.03$ Å) and valency angles ($\sigma \simeq 1.6^{\circ}$)

Large cage:

C-C = 1.45-1.62 (21 bonds), mean = 1.54 Å

Angles at C: in 6-membered rings,
107.2-117.5 (13 angles), mean = 111.1°
in 5-membered rings,
101.9-106.0 (9 angles), mean = 103.2°
others (substituent groups and external angles),
105.3-120.2 (19 angles), mean = 112.6°

C-N = 1.48-1.59 (4 bonds), mean = 1.54 Å

Angles at N: 103.6 in 5-membered ring
107.2-114.4 (5 angles), mean = 110.6°

Small cage:

C-C = 1.43-1.57 (9 bonds), mean = 1.53 Å

Angles at C: 97.5 in γ-lactone
others in 6-membered ring
111.1-114.5 (5 angles), mean = 113.0°
others (substituent groups and external angles),
98.7-121.6 (14 angles), mean = 109.7°

Substituent groups:

Chain

C(7)-C(22) = 1.54	C(7)-C(22)-C(23) = 117.7
C(22)-C(23) = 1.57	C(22)-C(23)-C(1') = 109.9
C(23)-C(1') = 1.56	

γ-lactone

C(6')-O(7') = 1.49	C(6')-O(7')-C(8') = 107.9
O(7')-C(8') = 1.30	O(7')-C(8')-O(9') = 120.8
C(8')-O(9') = 1.23	O(7')-C(8')-C(2') = 112.5
	O(9')-C(8')-C(2') = 126.5

Acetoxy

C(3')-O(12') = 1.49	C(3')-O(12')-C(13') = 117.9
O(12')-C(13') = 1.39	O(12')-C(13')-O(14') = 116.9
C(13')-O(14') = 1.22	O(12')-C(13')-C(15') = 112.0
C(13')-C(15') = 1.40	O(14')-C(13')-C(15') = 130.9

..../continued

Table 3, continued

Solvent (acetone):

C(1")-C(2") = 1.58	C(1")-C(2")-C(3") = 115.6
C(2")-C(3") = 1.50	C(1")-C(2")-O(4") = 117.7
C(2")-O(4") = 1.20	C(3")-C(2")-O(4") = 126.1

Figure 2

Packing of the molecules in the unit cell (heavy lines indicate molecules in the upper part of the cell).

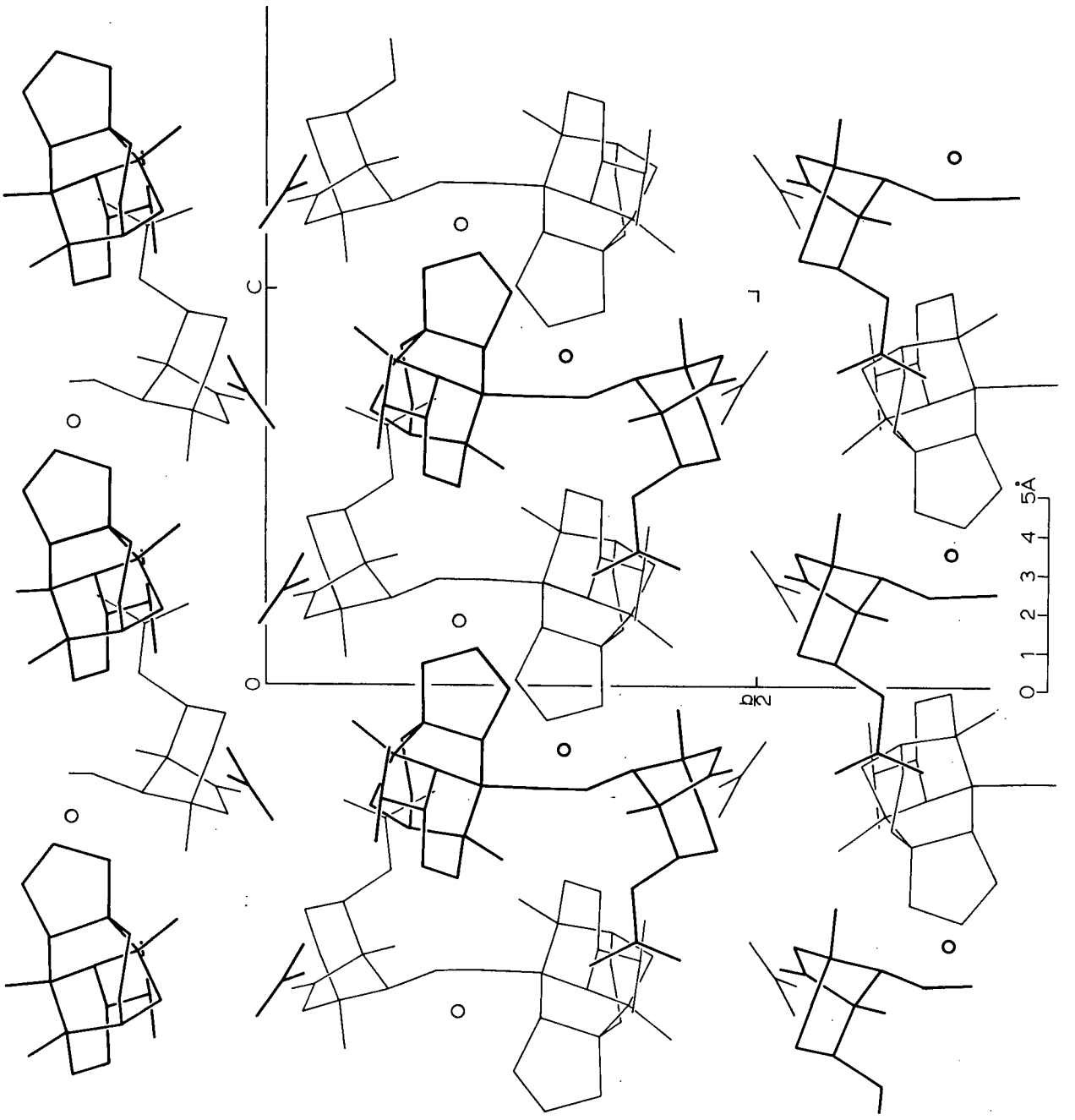

C
O
b
a
0 1 2 3 4 5Å

Table 4

Determination of the absolute configuration (Cu-K_α radiation)

h k ℓ	$\lvert F_c(hk\ell)\rvert$	$\lvert F_c(\bar{h}\bar{k}\bar{\ell})\rvert$	$\frac{\lvert F_c(hk\ell)\rvert^2}{\lvert F_c(\bar{h}\bar{k}\bar{\ell})\rvert^2}$	$\frac{I_o(hk\ell)}{I_o(\bar{h}\bar{k}\bar{\ell})}$
1 2 1	119.7	105.8	1.28	1.31
1 4 2	90.7	106.8	0.72	0.64
1 4 3	11.7	19.0	0.39	0.54
1 5 7	27.4	37.2	0.54	0.94
1 6 2	43.3	29.2	2.20	1.66
2 1 1	34.0	56.7	0.36	0.42
2 2 4	55.1	64.0	0.74	0.77
2 4 2	78.1	65.1	1.44	1.53
2 10 3	53.4	43.4	1.51	1.33
3 1 3	25.3	36.4	0.48	0.39
3 4 2	93.3	105.8	0.78	0.81
3 6 1	103.5	87.2	1.41	1.51
4 8 3	93.4	103.5	0.81	0.82
5 1 1	81.5	98.8	0.68	0.69
6 7 1	53.8	70.6	0.58	0.53

RESULTS AND DISCUSSION

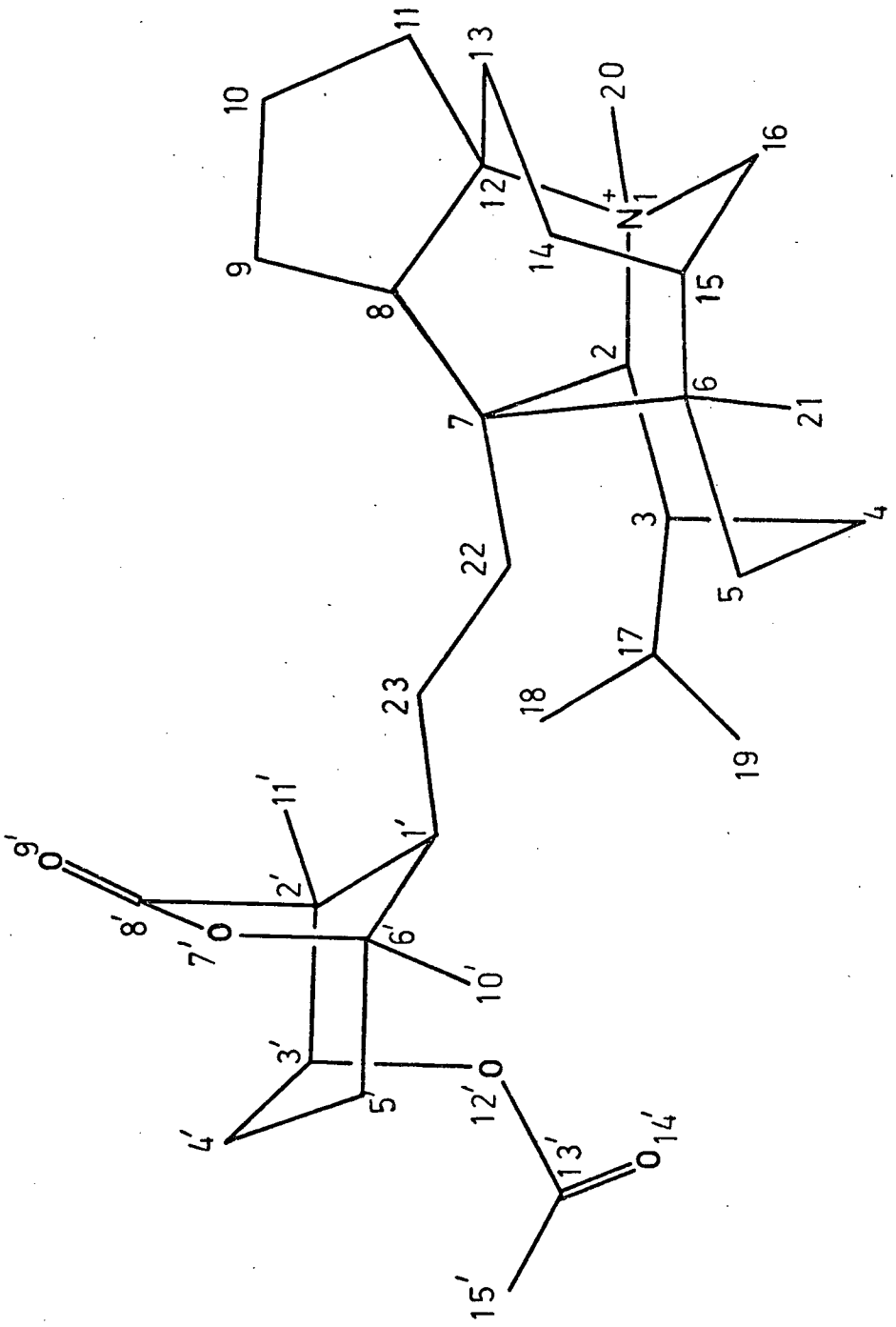
The crystal analysis has established the structure and absolute configuration of daphmacrine methiodide (acetone solvate). The compound consists of two cage structures which are linked by a flexible chain of two carbon atoms (Figures 1 and 3). The nitrogen-containing portion consists of two six-membered rings in the chair form, and one in the boat form, which are fused together with two five-membered rings, as has been reported for daphniphyllamine.[5,9,10] The smaller, nitrogen-free cage is formed of one six-membered ring in the chair form, bridged by carbon and oxygen atoms to form a five-membered lactone (γ-lactone), with methyl groups at each bridgehead. The C(6')-C(1')-C(2') angle (97.5°) is smaller than the other angles in the six-membered ring (111.1-114.5, mean of 5 angles 112.9°), presumably because of the bridging. Other bond lengths and angles generally appear to be normal, and considering the complex framework involved, are not significantly different from expected values. The position of the acetoxy group has been determined as shown in Figure 3, and the chain connecting the two cages contains two unsubstituted carbon atoms.

The acetone solvent molecule is in the same general region of the unit cell as the oxygen-containing cage (Figure 2), but is involved in only van der Waals

contacts. The shortest distances from acetone are to the acetyl group, the minimum O...O and C...O contacts being 3.54 and 3.21 Å respectively. The shortest intermolecular C...C distance is 3.53 Å.

Figure 3

Diagrammatic representation of the structure of daphmacrine methiodide.


I⁻
N
O

PART III

THE STRUCTURE DETERMINATION

OF

EXO-TRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE——SILVER NITRATE

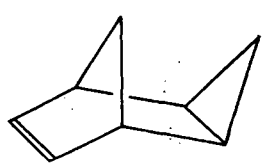
AND

A REFINEMENT OF THE SILVER NITRATE STRUCTURE

A. THE STRUCTURE OF EXO-TRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE——SILVER NITRATE.

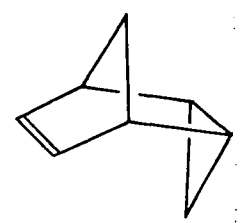
INTRODUCTION

A study of potential cyclopropyl——silver ion complex formation[11] had shown that silver nitrate forms a solid complex with exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (I), but not with the corresponding endo-isomer (II). The observed differences in the equilibrium constants for complex formation could be interpreted in terms of the inductive electron-withdrawing properties of the cyclopropyl group, and provided no evidence for cyclopropyl——silver ion interaction, although such interaction could not be discounted by the data obtained. An X-ray crystal structure analysis was undertaken to determine whether the silver ion is complexed to the cyclopropyl ring or the double bond, or to both, as has been reported for analogous platinum complexes (III)[12].



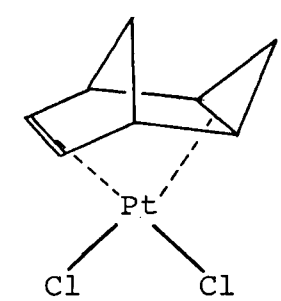
I

exo-(study compound)



II

endo-isomer



III

EXPERIMENTAL

Crystals of exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene——silver nitrate are colourless, but become white on exposure to light and air, and tend to cleave into irregular fragments elongated along the b crystallographic axis. The unit cell dimensions and space group were determined from rotation, Weissenberg and precession photographs. The density was not measured because of the instability of the complex.

Crystal Data.— λ(Cu-K_α) = 1.5418; λ(Mo-K_α) = 0.7107 Å.
Exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene——silver nitrate,
$C_8H_{10}AgNO_3$, M = 276.0.
Orthorhombic, a = 25.54(5), b = 6.28(1), c = 5.60(3) Å.
U = 898.2 $Å^3$, Z = 4, D_c = 2.04 $g.cm.^{-3}$
F(000) = 544.
Absorption coefficients: μ(Cu-K_α) = 182 $cm.^{-1}$; μ(Mo-K_α) = 22 $cm.^{-1}$
Absent reflections: h00, h odd; 0k0, k odd; 00ℓ, ℓ odd.
Space group $P2_12_12_1$ (D_2^4).

The crystals, although quite unstable on exposure to light and air, were found to remain for about a week in sealed capillary tubes without significant decomposition. Two crystals were therefore used in the analysis; one to determine the cell dimensions and space group from films, and the second to collect the intensity data on a diffractometer.

The intensities of all reflections with

$2\theta(\text{Mo-K}_\alpha) \leqslant 40^\circ$ (minimum interplanar spacing, d = 1.04 Å) were measured on a General Electric XRD 5 spectrogoniometer with a scintillation counter, approximately monochromatic Mo-K_α radiation (Zr filter and pulse-height analyser), and a θ-2θ scan. Background counts were made at the beginning and end of each scan. Two reflections measured periodically as a check showed essentially no change in intensity over the time required to collect the data. Some decomposition while mounting the crystal and sealing off the capillary is not precluded, however, and it was noted that the crystals became translucent during manipulation.

The crystal used for intensity measurement was an irregular cleavage fragment with approximate dimensions 0.25 × 0.80 × 0.15 mm., and was mounted with b parallel to the ϕ axis of the goniostat. No absorption correction was made. Lorentz and polarization factors were applied and the structure amplitudes derived. Of the 554 reflections with $2\theta \leqslant 40^\circ$, 322 (58%) had intensities greater than $3\sigma(I)$ above background, where $\sigma(I)$ is defined as

$$\sigma(I) = \{S + B + (0.05S)^2\}^{\frac{1}{2}}$$

where S = scan count and B = background count. The remaining 232 reflections were classified as unobserved and given zero weight in the refinement; they are included in the structure factor table with I(unobs) = σ(I(unobs)).

STRUCTURE ANALYSIS

Examination of the intensity data indicated that all planes (hkℓ) for which h is odd were weak, so that the silver ion was expected to be at or very close to a position which would confer false symmetry on the electron-density map based on the heavy atom alone. The three-dimensional Patterson function revealed this position to a first approximation to be on a screw axis (0.056, 0.25, 0.0), so that as expected from the observed intensity relationships, the resulting electron-density map exhibited pseudo-symmetry and could not be interpreted to give a reasonable hydrocarbon or nitrate structure. To compound this difficulty, no partial structure would refine by least-squares methods, the shifts to coordinates being large, and the temperature parameters ill-behaved (this occurred in spite of the partial structures being correct, as verified by the subsequent structure analysis).

A re-examination of the Patterson function, and an accurate plotting of the cross-section of the peaks then showed that there was some elongation of the peaks in the y and z directions, so that the silver ion appeared to be displaced slightly from the screw axis. The extent of this elongation was used to estimate new y and z parameters (0.259 and 0.02 respectively) and an electron-density map based on the phases computed from this silver position

showed clearly all the atoms except C(4) and C(7). These were subsequently located on a three-dimensional difference map as the highest peaks (but quite low electron-density) and included in the refinement. A least-squares calculation with all atoms assigned the appropriate scattering curves[6] for C, N, O and Ag^+, isotropic temperature factors equal to 4.0 $\AA^2$, and unit weights resulted in an R value of 0.15.

A comparison of the observed structure factors with films indicated that some of the reflections had been mis-indexed, probably due to the long a axial length (25.54 $\AA$), or inaccurately measured, particularly the weak odd h planes. Eighty-four reflections were re-evaluated on the basis of film measurements, sixty-one of these being odd h planes.

Two further cycles of full-matrix least-squares refinement with anisotropic thermal parameters for the silver ion, and a weighting scheme of the form $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o) = 59.56 - 2.56|F_o| + 0.037|F_o|^2$ resulted in a final R of 0.105, and a weighted R of 0.127. Calculated and observed structure factors are listed in Table 5.

The maximum ratio of parameter shift/estimated standard deviation (esd) in the final cycle was 0.23 and a final difference map showed maximum fluctuations of ± 1.3 $e\AA^{-3}$.

A final Fourier map was computed, and sections of the resulting electron-density distribution are shown in Figure 4, together with a drawing of the structure.

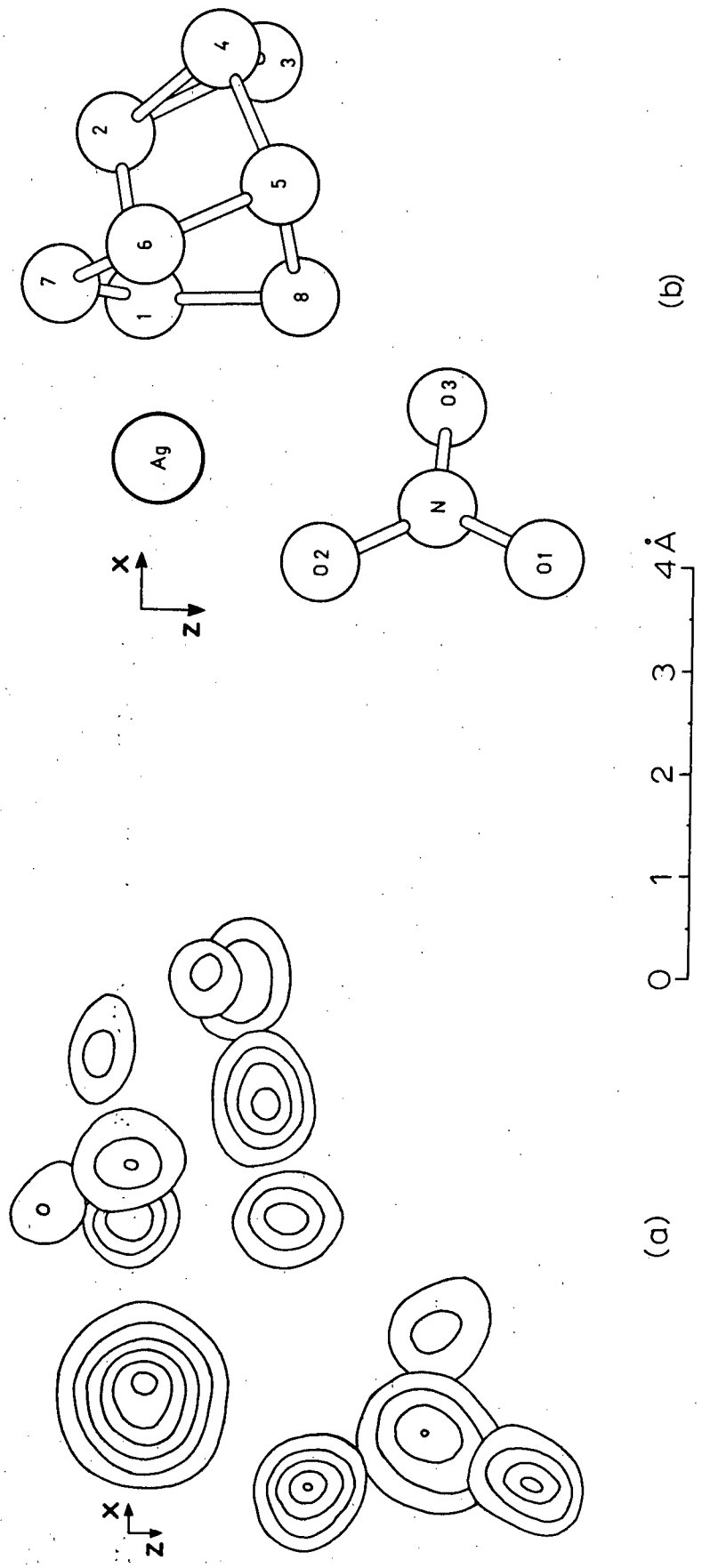
Table 5

Measured and calculated structure factors for exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene——silver nitrate. Unobserved reflections have I = σ(I) and are indicated by a negative sign before F_o.

h	k	l	F_o	F_c
2	0	0	136.84	173.79
4	0	0	-7.83	10.38
6	0	0	31.00	26.73
8	0	0	106.76	126.64
10	0	0	152.73	152.88
12	0	0	90.43	133.17
14	0	0	-17.05	12.12
16	0	0	36.36	36.15
18	0	0	53.84	50.71
20	0	0	35.66	35.15
22	0	0	-11.22	11.50
24	0	0	-11.98	2.57
1	0	1	58.86	47.85
2	0	1	126.83	138.55
3	0	1	40.48	27.71
4	0	1	66.00	62.18
5	0	1	30.49	27.99
6	0	1	84.16	85.17
7	0	1	24.06	21.34
8	0	1	41.93	49.46
9	0	1	17.92	13.55
10	0	1	-8.68	16.16
11	0	1	26.74	27.47
12	0	1	82.96	85.97
13	0	1	-8.76	2.19
14	0	1	136.90	129.52
15	0	1	-8.45	5.04
16	0	1	55.66	58.87
17	0	1	-14.98	9.53
18	0	1	-11.48	9.62
19	0	1	-12.95	19.84
20	0	1	23.47	24.55
21	0	1	-13.83	6.17
22	0	1	31.61	34.96
23	0	1	-12.05	4.03
24	0	1	27.38	32.33
0	0	2	144.47	142.84
1	0	2	96.49	96.05
2	0	2	117.71	130.89
3	0	2	28.52	28.47
4	0	2	-6.11	4.83
5	0	2	77.36	75.77
6	0	2	71.77	70.22
7	0	2	44.47	49.36
8	0	2	159.48	167.54
9	0	2	-6.66	3.25
10	0	2	127.04	122.36
11	0	2	4.37	16.42
12	0	2	56.01	53.73
13	0	2	41.46	37.21
14	0	2	-2.71	1.14
15	0	2	-17.31	11.13
16	0	2	49.72	44.13
17	0	2	-16.67	20.79
18	0	2	37.25	27.16
19	0	2	-12.16	4.76
20	0	2	47.37	48.50
21	0	2	-13.79	8.03
22	0	2	20.47	20.75
23	0	2	-12.68	10.53
1	0	3	25.74	27.73
2	0	3	66.43	62.64
3	0	3	37.96	46.59
4	0	3	83.11	75.93
5	0	3	-9.17	4.81
6	0	3	51.22	51.66
7	0	3	17.21	18.94
8	0	3	57.98	54.56
9	0	3	41.98	40.13
10	0	3	-12.53	9.12
11	0	3	41.77	42.04
12	0	3	25.04	27.23
13	0	3	-13.18	13.10
14	0	3	38.50	42.72
15	0	3	-11.61	13.43
16	0	3	23.75	24.45
17	0	3	-12.97	11.56
18	0	3	-12.36	9.14
19	0	3	24.61	21.76
20	0	3	-12.54	13.21
0	0	4	82.98	75.24
1	0	4	-6.91	14.57
2	0	4	44.22	39.79
3	0	4	64.14	54.27
4	0	4	-11.19	6.92
5	0	4	52.96	49.04
6	0	4	12.72	12.68
7	0	4	37.15	31.49
8	0	4	39.93	43.47
9	0	4	-11.76	13.46
10	0	4	44.75	46.09
11	0	4	-4.12	16.48
12	0	4	-12.76	10.86
13	0	4	26.27	29.66
14	0	4	-11.95	5.86
15	0	4	-12.31	27.22
16	0	4	-13.67	10.11
1	0	5	25.43	15.44
2	0	5	-12.56	16.57
3	0	5	-12.78	13.42
4	0	5	-12.04	12.95
5	0	5	-11.67	4.66
6	0	5	-12.14	13.67
7	0	5	-12.36	11.40
8	0	5	-12.34	5.76
9	0	5	26.94	31.42
1	1	0	37.72	46.67
2	1	0	65.56	61.74
3	1	0	25.24	28.30
4	1	0	178.66	166.72
5	1	0	118.22	126.19
6	1	0	119.23	115.65
7	1	0	69.83	67.31
8	1	0	68.20	71.77
9	1	0	-13.17	16.42
10	1	0	72.06	67.31
11	1	0	4.43	9.17
12	1	0	111.47	114.98
13	1	0	6.42	13.76
14	1	0	78.32	72.89
15	1	0	9.14	15.04
16	1	0	51.46	53.27
17	1	0	-10.45	4.32
18	1	0	10.23	24.72
19	1	0	-12.72	4.09
20	1	0	192.92	187.18
21	1	0	66.56	65.04
22	1	0	124.41	137.42
23	1	0	31.72	25.92
4	1	1	42.23	42.44
5	1	1	25.48	21.92
6	1	1	36.46	41.56
7	1	1	45.83	40.36
8	1	1	98.16	98.44
9	1	1	-13.48	20.28
10	1	1	106.29	128.45
11	1	1	21.09	24.16
12	1	1	61.30	61.60
13	1	1	-14.25	8.25
14	1	1	-9.34	6.27
15	1	1	-16.27	14.82
16	1	1	35.01	34.59
17	1	1	-11.27	15.07
18	1	1	54.34	50.64
19	1	1	-12.64	10.68
20	1	1	48.45	49.16
21	1	1	-12.33	5.97
22	1	1	-13.28	14.44
23	1	1	-12.90	9.86
24	1	1	-12.53	9.02
0	1	2	-4.99	24.57
1	1	2	51.30	50.68
2	1	2	87.46	92.39
3	1	2	48.43	38.10
4	1	2	128.38	127.78
5	1	2	22.62	24.54
6	1	2	157.95	76.66
7	1	2	26.41	25.29
8	1	2	41.13	48.32
9	1	2	57.75	49.44
10	1	2	-8.77	7.81
11	1	2	37.80	44.80
12	1	2	73.84	67.13
13	1	2	-13.24	16.96
14	1	2	66.75	58.64
15	1	2	15.29	19.92
16	1	2	29.51	37.05
17	1	2	21.64	25.48
18	1	2	10.28	17.10
19	1	2	-12.72	13.36
20	1	2	-12.24	14.66
21	1	2	-12.42	15.81
22	1	2	28.16	26.09
0	1	3	62.20	65.14
1	1	3	21.75	20.12
2	1	3	44.18	49.98
3	1	3	64.92	67.37
4	1	3	21.75	22.74
5	1	3	53.45	47.64
6	1	3	38.73	34.50
7	1	3	36.41	34.22
8	1	3	53.33	47.88
9	1	3	-12.78	12.91
10	1	3	46.89	43.62
11	1	3	-11.98	13.07
12	1	3	38.62	45.40
13	1	3	32.66	31.49
14	1	3	-12.18	14.23
15	1	3	31.38	32.24
16	1	3	21.49	20.13
17	1	3	-12.66	13.84
18	1	3	33.65	31.62
19	1	3	-12.16	1.46
20	1	3	35.14	32.58
0	1	4	-11.43	11.67
1	1	4	45.77	37.91
2	1	4	25.27	29.14
3	1	4	23.54	21.15
4	1	4	46.49	42.27
5	1	4	12.78	19.68
6	1	4	46.56	42.49
7	1	4	42.27	31.43
8	1	4	-12.37	20.69
9	1	4	39.74	33.44
10	1	4	-12.16	12.60
11	1	4	23.74	20.47
12	1	4	29.56	32.65
13	1	4	-12.05	13.64
14	1	4	19.17	21.43
15	1	4	-12.51	7.42
16	1	4	-12.78	12.47
0	1	5	-12.22	23.12
1	1	5	-13.15	15.43
2	1	5	-13.14	20.73
3	1	5	24.11	25.51
4	1	5	-13.04	5.59
5	1	5	27.43	31.43
6	1	5	-13.17	9.69
7	1	5	24.72	24.44
8	1	5	-13.18	16.69
9	1	5	-12.51	5.51
0	2	0	71.71	74.01
1	2	0	33.68	31.11
2	2	0	6.78	46.17
3	2	0	9.46	2.30
4	2	0	-7.52	1.85
5	2	0	56.01	49.67
6	2	0	62.77	57.42
7	2	0	50.24	52.13
8	2	0	124.54	118.68
9	2	0	-16.06	13.49
10	2	0	104.72	98.83
11	2	0	-13.36	9.06
12	2	0	50.29	47.63
13	2	0	-12.96	17.33
14	2	0	-5.96	6.91
15	2	0	-11.51	13.95
16	2	0	55.24	51.79
17	2	0	-3.98	23.68
18	2	0	56.10	48.81
19	2	0	-13.71	9.85
20	2	0	47.65	47.04
21	2	0	-13.99	3.50
22	2	0	20.77	23.64
23	2	0	-12.10	4.26
0	2	1	-0.26	3.66
1	2	1	21.96	20.28
2	2	1	127.81	130.91
3	2	1	8.52	21.63
4	2	1	123.17	124.86
5	2	1	33.78	34.09
6	2	1	115.64	125.55
7	2	1	24.63	21.41
8	2	1	71.67	72.50
9	2	1	9.50	12.70
10	2	1	-3.42	10.06
11	2	1	26.75	22.91
12	2	1	55.43	53.13
13	2	1	13.07	17.24
14	2	1	64.58	64.09
15	2	1	16.45	24.15
16	2	1	46.06	47.22
17	2	1	-11.42	11.59
18	2	1	-11.46	12.42
19	2	1	-11.42	12.57
20	2	1	-12.38	8.61
21	2	1	-11.96	13.48
22	2	1	23.94	27.07
23	2	1	-12.65	5.11
0	2	2	148.91	123.25
1	2	2	33.64	41.63
2	2	2	70.26	73.23
3	2	2	37.86	43.62
4	2	2	23.78	20.64
5	2	2	31.79	33.43
6	2	2	-10.56	17.13
7	2	2	31.86	32.69
8	2	2	69.21	65.37
9	2	2	27.24	23.89
10	2	2	67.67	63.28
11	2	2	8.61	7.54
12	2	2	29.06	29.72
13	2	2	24.43	21.62
14	2	2	-11.06	8.65
15	2	2	-11.95	21.52
16	2	2	27.17	35.51
17	2	2	-12.27	12.58
18	2	2	36.09	38.23
19	2	2	-12.44	7.24
20	2	2	24.63	21.43
21	2	2	-12.92	8.19
0	2	3	8.45	8.75
1	2	3	48.76	56.28
2	2	3	65.92	63.72
3	2	3	16.88	22.70
4	2	3	56.10	56.91
5	2	3	9.28	7.94
6	2	3	43.34	40.74
7	2	3	8.49	18.39
8	2	3	24.95	24.47
9	2	3	37.37	38.20
10	2	3	-11.58	14.91
11	2	3	32.14	31.83
12	2	3	40.42	40.64
13	2	3	-12.95	10.20
14	2	3	57.82	52.81
15	2	3	21.13	20.42
16	2	3	33.71	35.56
17	2	3	16.97	18.70
18	2	3	-13.37	12.49
19	2	3	-12.95	20.47
0	2	4	36.97	41.45
1	2	4	16.75	17.26
2	2	4	25.06	28.65
3	2	4	33.83	37.25
4	2	4	-4.93	12.43
5	2	4	32.10	32.79
6	2	4	25.38	19.36
7	2	4	24.98	21.33
8	2	4	25.76	25.18
9	2	4	-12.75	9.04
10	2	4	26.31	21.67
11	2	4	-13.06	15.49
12	2	4	25.97	19.57
13	2	4	25.72	26.28
14	2	4	-12.31	7.29
0	2	5	-11.42	2.49
1	2	5	32.91	30.23
2	2	5	26.12	21.29
3	2	5	25.50	22.72
4	2	5	19.91	21.87
5	2	5	-14.83	6.43
1	3	0	-9.91	3.38
2	3	0	53.84	48.33
3	3	0	8.36	15.64
4	3	0	111.66	98.79
5	3	0	16.85	24.03
6	3	0	61.24	59.80
7	3	0	4.37	2.69
8	3	0	29.27	35.25
9	3	0	26.69	29.21
10	3	0	-12.96	19.84
11	3	0	31.12	32.07
12	3	0	40.79	34.77
13	3	0	8.46	21.21
14	3	0	63.87	64.72
15	3	0	-12.79	11.43
16	3	0	27.45	28.26
17	3	0	-12.31	13.04
18	3	0	-11.65	11.64
19	3	0	-11.65	5.58
20	3	0	-12.52	14.64
21	3	0	-12.54	12.82
0	3	1	70.20	83.24
1	3	1	44.57	48.21
2	3	1	88.64	66.82
3	3	1	49.65	64.47
4	3	1	35.31	34.37
5	3	1	24.12	23.78
6	3	1	52.24	55.12
7	3	1	-11.47	24.45
8	3	1	75.74	71.21
9	3	1	-4.35	27.14
10	3	1	57.07	64.56
11	3	1	-3.67	27.46
12	3	1	34.18	30.23
13	3	1	12.71	25.26
14	3	1	-11.42	5.82
15	3	1	-10.96	11.36
16	3	1	-11.95	12.82
17	3	1	-10.97	12.79
18	3	1	31.51	37.28
19	3	1	-13.63	16.61
20	3	1	33.01	31.11
21	3	1	-12.03	6.61
0	3	2	19.06	13.69
1	3	2	26.25	10.58
2	3	2	28.53	24.74
3	3	2	28.01	25.61
4	3	2	54.06	55.64
5	3	2	26.12	34.15
6	3	2	63.96	55.33
7	3	2	22.35	22.67
8	3	2	29.46	31.56
9	3	2	21.42	17.80
10	3	2	-11.32	22.73
11	3	2	21.65	22.67
12	3	2	36.92	44.76
13	3	2	-12.10	13.41
14	3	2	33.52	38.37
15	3	2	-12.75	8.34
16	3	2	30.15	34.72
17	3	2	-12.47	9.65
18	3	2	-12.23	14.69
19	3	2	-12.25	15.28
0	3	3	56.81	53.97
1	3	3	25.77	17.06
2	3	3	59.31	55.65
3	3	3	36.27	32.05
4	3	3	-12.21	22.72
5	3	3	31.47	29.87
6	3	3	-11.99	24.15
7	3	3	34.22	35.26
8	3	3	32.55	32.62
9	3	3	24.68	24.32
10	3	3	35.55	37.98
11	3	3	-13.04	12.74
12	3	3	-12.16	18.62
13	3	3	-12.78	16.31
14	3	3	-12.17	11.67
15	3	3	-12.16	15.84
16	3	3	-12.17	15.91
0	3	4	-12.24	7.49
1	3	4	29.20	28.55
2	3	4	-12.42	14.15
3	3	4	-11.73	14.28
4	3	4	31.00	35.27
5	3	4	-12.56	12.34
6	3	4	-11.82	26.27
7	3	4	-12.58	17.65
8	3	4	-12.44	14.62
9	3	4	-13.76	25.61
10	3	4	-11.55	7.61
11	3	4	-13.57	22.03
0	4	0	54.18	55.80
1	4	0	53.45	51.64
2	4	0	63.47	65.15
3	4	0	29.25	28.58
4	4	0	29.45	28.45
5	4	0	21.72	3.67
6	4	0	-14.95	11.45
7	4	0	-16.86	4.07
8	4	0	44.41	53.67
9	4	0	-15.56	27.19
10	4	0	51.41	55.06
11	4	0	-14.76	10.99
12	4	0	32.01	27.62
13	4	0	-12.48	15.62
14	4	0	-11.64	17.98
15	4	0	-10.62	9.84
16	4	0	-12.60	14.53
17	4	0	-11.78	20.13
18	4	0	29.83	26.80
0	4	1	8.24	6.20
1	4	1	-16.55	16.47
2	4	1	37.57	35.57
3	4	1	25.63	45.84
4	4	1	45.73	55.44
5	4	1	-3.22	21.84
6	4	1	57.40	40.71
7	4	1	-11.62	13.15
8	4	1	-12.47	14.93
9	4	1	-3.38	18.21
10	4	1	22.97	27.56
11	4	1	-12.11	12.29
12	4	1	27.23	25.51
13	4	1	-12.09	18.47
14	4	1	37.91	33.84
15	4	1	-11.97	24.81
16	4	1	24.73	26.24
17	4	1	-12.81	6.59
18	4	1	-11.46	5.80
0	4	2	51.55	52.33
1	4	2	-11.63	16.63
2	4	2	43.60	36.69
3	4	2	-11.24	18.17
4	4	2	20.13	19.43
5	4	2	23.08	20.60
6	4	2	20.66	21.13
7	4	2	27.97	25.60
8	4	2	46.06	40.15
9	4	2	-13.06	13.16
10	4	2	38.88	38.65
11	4	2	-13.30	18.66
12	4	2	26.93	32.61
13	4	2	-11.84	15.85
14	4	2	-12.58	10.93
15	4	2	-13.13	14.73
16	4	2	-13.45	13.93
0	4	3	-11.47	4.50
1	4	3	26.41	22.22
2	4	3	24.46	22.55
3	4	3	27.90	25.69
4	4	3	25.88	27.83
5	4	3	29.14	21.76
6	4	3	37.84	37.24
7	4	3	25.50	20.88
8	4	3	-12.92	6.54
9	4	3	-12.36	15.20
10	4	3	-12.42	12.70
11	4	3	-12.78	13.34
12	4	3	-12.78	17.61
0	4	4	-13.70	20.64
1	4	4	-12.57	12.73
2	4	4	-13.47	16.66
3	4	4	-13.19	14.95
4	4	4	-13.17	13.74
1	5	0	-11.66	7.82
2	5	0	-12.56	20.69
3	5	0	-8.51	21.72
4	5	0	26.20	28.80
6	5	0	-17.27	3.93
6	5	0	16.62	25.98
7	5	0	16.98	21.54
8	5	0	-13.77	9.47
9	5	0	-11.56	7.96
10	5	0	-12.71	7.63
11	5	0	-11.42	8.14
12	5	0	-12.74	22.19
13	5	0	-11.87	19.34
14	5	0	28.76	28.47
0	5	1	35.82	39.72
1	5	1	-11.92	17.69
2	5	1	44.97	34.88
3	5	1	-11.34	14.04
4	5	1	-12.12	12.23
5	5	1	-11.16	3.48
6	5	1	-11.63	17.76
7	5	1	22.10	20.52
8	5	1	23.53	24.63
9	5	1	-12.47	18.03
10	5	1	25.44	23.20
11	5	1	-12.85	11.93
12	5	1	-12.41	17.45
13	5	1	-12.31	5.19
0	5	2	-11.71	9.91
1	5	2	-12.15	15.45
2	5	2	-11.64	17.48
3	5	2	-11.95	15.73
4	5	2	34.15	37.32
5	5	2	40.44	36.25
6	5	2	35.04	24.92
7	5	2	24.42	19.74
8	5	2	-13.61	13.64
9	5	2	-12.45	11.22
10	5	2	-12.26	7.40
11	5	2	-12.42	13.42
0	5	3	-12.54	13.62
1	5	3	-12.44	9.88
2	5	3	24.52	16.17
3	5	3	-12.34	12.89
4	5	3	-12.06	7.77
0	6	0	-12.95	17.42
1	6	0	-11.75	11.24
2	6	0	-11.73	12.47
3	6	0	-12.14	7.16
4	6	0	-11.67	7.91
0	6	1	-12.72	22.14
1	6	1	-12.05	12.65

Figure 4

(a) Superimposed sections of the three-dimensional electron-density distribution (contours at 2, 3, 4,... $e\text{Å}^{-3}$ for carbon, oxygen and nitrogen, and 2, 10, 20, 30,... $e\text{Å}^{-3}$ for silver), and (b) a drawing of the structure of the complex.


1
2
3
4
5
6
7
8
Ag
X
Z
O3
N
O2
O1
(b)
0
1
2
3
4Å
O
O
X
Z
(a)

COORDINATES AND MOLECULAR DIMENSIONS

The final positional and thermal parameters, together with their standard deviations, are listed in Table 6. Table 7 lists the bond lengths and angles, and Figure 5 shows a view of the structure along the b crystallographic axis. Although some bond lengths appear abnormal, they do not differ from the expected values by more than 3σ, and it would appear that any differences are due to inaccurate data.

Table 6

Final positional (fractional × 10^4) and isotropic ($Å^2$) thermal parameters, with standard deviations in parentheses.

Atom	x	y	z	B
C(1)	1207(21)	-1799(076)	0053(092)	4.26(125)
C(2)	1823(19)	-2171(111)	-0205(094)	4.96(139)
C(3)	2131(35)	-3624(131)	1799(151)	6.40(209)
C(4)	2114(34)	-0936(116)	1290(148)	5.59(210)
C(5)	1654(19)	0535(077)	2422(088)	2.34(100)
C(6)	1430(20)	1470(085)	0175(100)	3.69(116)
C(7)	1190(28)	0220(127)	-1039(141)	6.53(202)
C(8)	1189(21)	-1183(100)	2743(100)	3.81(129)
O(1)	0208(19)	5632(085)	6743(087)	6.75(131)
O(2)	0209(17)	5334(077)	3170(072)	5.24(104)
O(3)	0817(23)	3789(086)	5413(100)	8.27(136)
N	0420(14)	4948(063)	5231(074)	3.34(086)
Ag^+	0532(02)	2687(009)	0316(006)	4.69(014)

The anisotropic thermal factor for Ag^+ is

$\exp\{-(19h^2 + 345k^2 + 334\ell^2 + 8hk + 17k\ell - 15h\ell) \times 10^{-4}\}$.

Table 7

Bond distances ($\sigma \simeq 0.09$ Å for C-C; 0.05 for others) and valency angles ($\sigma \simeq 5^{\circ}$) for $C_8H_{10}AgNO_3$.

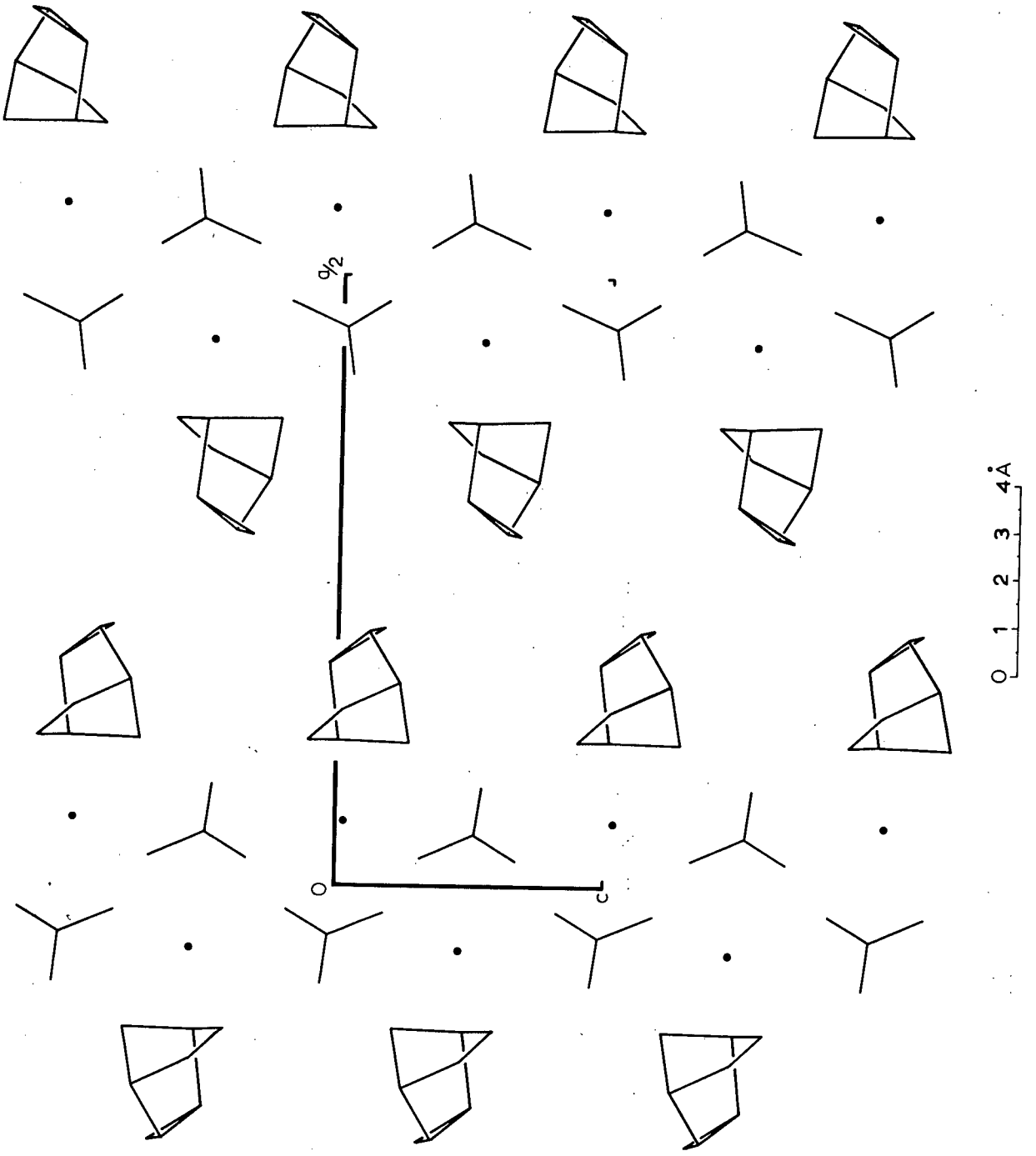
C(1)-C(2) = 1.60	C(2)-C(1)-C(7) = 97
C(1)-C(7) = 1.41	C(2)-C(1)-C(8) = 99
C(1)-C(8) = 1.56	C(7)-C(1)-C(8) = 101
C(2)-C(3) = 1.65	C(1)-C(2)-C(3) = 119
C(2)-C(4) = 1.36	C(1)-C(2)-C(4) = 113
C(3)-C(4) = 1.71	C(3)-C(2)-C(4) = 69
C(4)-C(5) = 1.62	C(2)-C(3)-C(4) = 48
C(5)-C(8) = 1.61	C(2)-C(4)-C(3) = 64
C(5)-C(6) = 1.50	C(3)-C(4)-C(5) = 121
C(6)=C(7) = 1.21	C(2)-C(4)-C(5) = 100
N-O(1) = 1.09	C(4)-C(5)-C(8) = 101
N-O(2) = 1.30	C(4)-C(5)-C(6) = 100
N-O(3) = 1.25	C(6)-C(5)-C(8) = 94
	C(5)-C(6)-C(7) = 114
	C(1)-C(7)-C(6) = 109
Ag-C(6) = 2.42	C(1)-C(8)-C(5) = 92
Ag-C(7) = 2.41	O(1)- N -O(2) = 114
Ag-O(2) = 2.45	O(1)- N -O(3) = 124
Ag-O(3) = 3.03	O(2)- N -O(3) = 121
$Ag\text{-}O(1)^{I} = 2.85$	
$Ag\text{-}O(3)^{I} = 2.92$	
$Ag\text{-}O(1)^{II} = 2.56$	
$Ag\text{-}O(2)^{II} = 2.55$	

I x, y, -1 + z

II -x, -½ + y, ½ - z

Figure 5

A view of the structure along the b crystallographic axis.


a/2
O
c
0 1 2 3 4Å

RESULTS AND DISCUSSION

The crystal analysis has established the structure of the silver nitrate complex (Figure 4). The silver ion occupies the exo- position and is therefore quite distant from the three-membered ring, so that no silver ion—— cyclopropyl interaction is possible. This is in agreement with the conclusion that such interaction is not required to explain the relative equilibrium constants for complex formation[11].

As in other complexes of this type (cf. ref 13), the nitrate groups are linked by coordination to the silver ions to build up layers, in this case parallel to (100). The layers are centred around 0 and ½a (Figure 5), with the hydrocarbon molecules between, and with only van der Waals forces between the hydrocarbon molecules (the closest interlayer contact is C...C at 3.6 Å). The silver ion approaches three nitrate groups in the layer, so that close contact is made with two oxygen atoms of one nitrate group (Ag...O = 2.55 and 2.56 Å); a second nitrate group is more distant (Ag...O = 2.85 and 2.92 Å); and the third nitrate group shares its oxygen atoms unequally (Ag...O = 2.45 and 3.03 Å). Thus the silver ion appears to be coordinated to each nitrate group as a whole rather than to individual oxygen atoms, similar to other compounds of this type[13-15]. On this basis the silver ion coordination can be described as distorted tetrahedral (to three

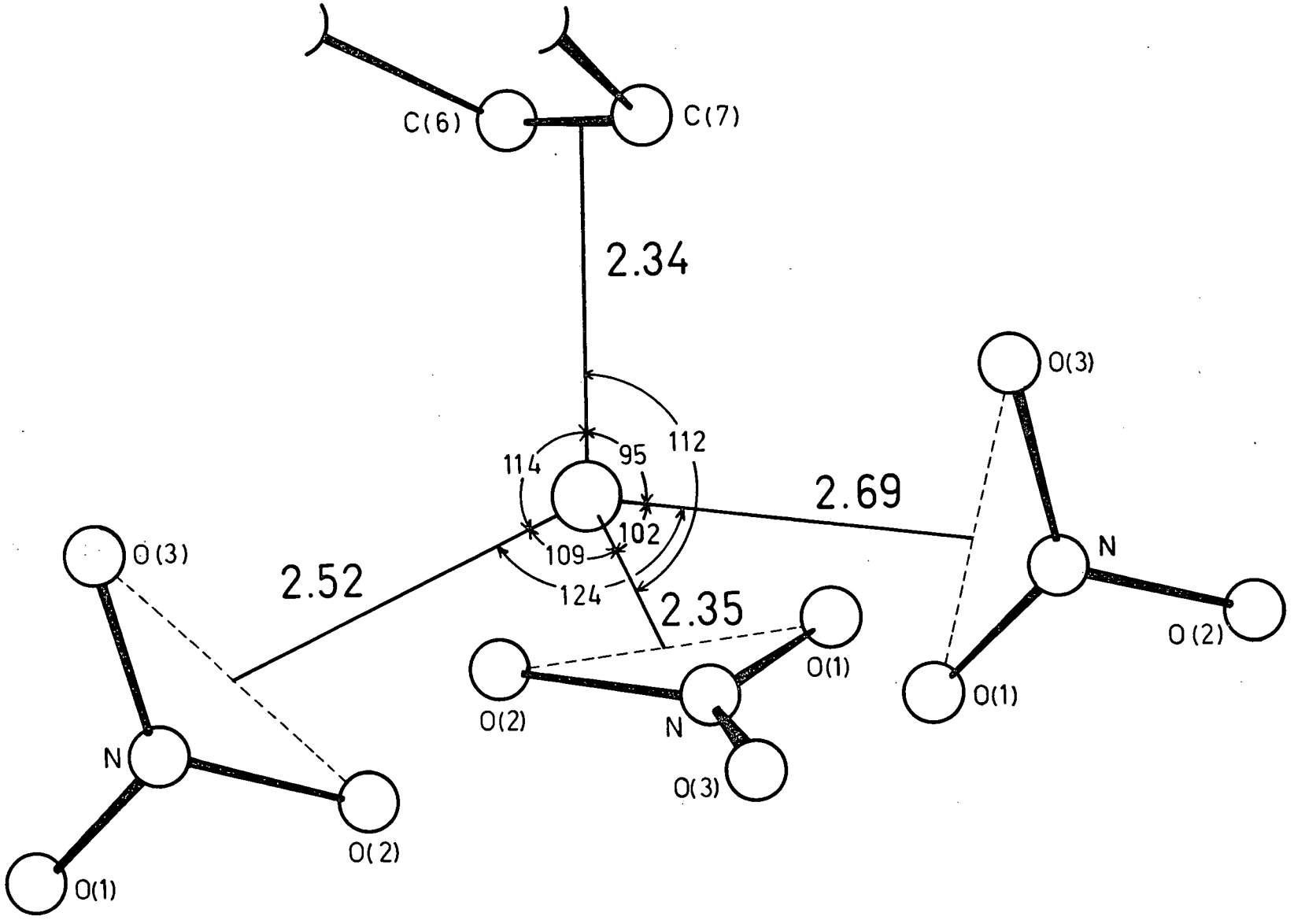
nitrate groups and one double bond), and Figure 6 shows the lengths and angles involved if the mid-points of the O...O vectors and the C=C double bond are taken as apices of the tetrahedron. This type of distorted tetrahedral coordination has been reported for germacratriene[14] and geijerene[16] silver nitrate complexes.

Within the somewhat limited accuracy of the refinement, the bond lengths and angles do not differ significantly from the expected values[17] (average $C(sp^3)$-$C(sp^3)$ = 1.59, $C(sp^3)$-$C(sp^2)$ = 1.46, $C(sp^2)$-$C(sp^2)$ = 1.21 Å). The nitrate group is planar (average O-N-O angle is 120°), and the average N-O distance of 1.21 Å is comparable to values determined for other silver nitrate complexes,[13-16, 18-20] and for silver nitrate (see next section). No attempt should be made to correlate N-O and corresponding Ag...O distances as has been done for $AgCN \cdot 2AgNO_3$,[21] since the low accuracy precludes any comparison of individual values. In a case where the accuracy is low, this correlation is not always justified. For example, the apparent distortion of the nitrate group in silver nitrate reported previously[22] has led others to make this correlation[15], but the present refinement of the silver nitrate structure has shown that there is in fact no significant distortion, so the comparison is not valid.

The silver ion contacts the two carbon atoms of the double bond at Ag...C distances of 2.41 and 2.42 Å

Figure 6

Coordination around the silver ion in the complex.


C(6)
C(7)
2.34
O(3)
112
95
114
2.69
102
109
124
2.52
2.35
O(3)
N
O(2)
O(1)
O(2)
N
O(1)
O(3)
O(1)
N
O(2)

(Ag—mid-point of C=C = 2.34 Å), and the interaction is similar to that in other silver-olefin complexes to which reference has been made. The silver ion is equidistant from the two carbon atoms, although in other complexes this is not always the case (see Table 8). Maximum overlap of the metal orbitals with the π-orbital of the alkene would be expected[23] when the Ag, C(6), C(7) and the C(1), C(5), C(6), C(7) planes are at 90° to each other. This angle was found to be 114°, somewhat larger than the corresponding value for similar compounds, but as shown in Table 8, large deviations from 90° have been reported. It appears that trans-double bonds afford the greatest ability to meet the requirement for maximum overlap, and cis-double bonds show deviations from it depending at least partially on the amount of steric hindrance involved. It should be noted that the greatest deviation from 90° reported previously, 112°, is for norbornadiene, which is closely related to the present compound, so that the angles may be expected to be similar.

Table 8

Angles between the Ag, C=C plane and the C, C=C, C plane, and Ag-C(olefin) distances for some related compounds.

Compound	Angle(°)	C=C type	Ag-C(Å)	Reference
$C_7H_8(AgNO_3)_2$ (Norbornadiene)	112	cis	2.31, 2.41	19
$C_8H_8AgNO_3$ (Cyclooctatetraene)	93	cis	2.78, 2.84	18
	100	cis	2.46, 2.51	
$C_9H_{12}(AgNO_3)_3$ (Cyclononatriene)	107	cis	2.38, 2.41	20
$(C_{10}H_{10})_3AgBF_4$ (Bullvalene)	91	cis	2.69, 2.84	23
	92	cis	2.66, 2.78	
	103	cis	2.45, 2.58	
	104	cis	2.48, 2.55	
$C_{12}H_{18}(AgNO_3)_2$ (Geijerene)	105	cis	2.30, 2.33	16
	84	terminal	2.39, 2.59	
	82	terminal	2.54, 2.54	
$C_{15}H_{24}AgNO_3$ (Germacratriene)	86	trans	2.48, 2.57	14
	90	trans	2.52, 2.54	
$C_{15}H_{24}(AgNO_3)_2$ (Humulene)	85	trans	2.35, 2.43	13
	87	trans	2.33, 2.42	
$C_8H_{10}AgNO_3$ (Study compound)	114	cis	2.41, 2.42	

B. A REFINEMENT OF THE SILVER NITRATE STRUCTURE.

INTRODUCTION

During the course of refinement of the complex of silver nitrate ($C_8H_{10}AgNO_3$) described previously, attempts were made to compare the coordination in the complex with that in silver nitrate. A structure analysis had been carried out[22], and showed silver nitrate to have a structure unique in the AXO_3 class of compounds, and quite irregular silver ion coordination. Unfortunately the accuracy of the analysis was no better than for the unstable complex (σ,bond distances 0.05-0.08 Å), because of the use of visual photographic data, the limited number of reflections measured and the use of Cu-K_α radiation, for which the absorption is high. It was considered useful to collect more extensive data by the single-crystal diffractometer method, with an attempt to minimize the errors due to absorption by using Mo-K_α radiation.

EXPERIMENTAL

Crystals of silver nitrate are colourless plates with well-developed {001} faces. The space group was determined from precession photographs and diffractometer data, and accurate unit cell parameters were determined by application of the extrapolation method of Farquhar and Lipson[24] to a back-reflection Weissenberg photograph

obtained with Cu-K_α radiation. The values obtained agree well with those reported previously,[22,25] and the parameters of the U.S. National Bureau of Standards[25] are used throughout.

Crystal Data.—— λ(Cu-K_α, K_{α_1}, K_{α_2}) = 1.5418, 1.54051, 1.54433; λ(Mo-K_α) = 0.7107 Å.

Silver nitrate, $AgNO_3$, M = 169.9.

Orthorhombic, a = 6.995, b = 7.328, c = 10.118 Å, U = 518.6 Å^3, D_m = 4.35 g.cm.$^{-3}$, Z = 8, D_c = 4.35 g.cm.$^{-3}$

F(000) = 624.

Absorption coefficients: μ(Cu-K_α) = 617 cm.$^{-1}$, μ(Mo-K_α) = 73 cm.$^{-1}$

Absent reflections: 0kℓ, k odd; h0ℓ, ℓ odd; hk0, h odd.

Space group Pbca (D_{2h}^{15}).

The intensities of all reflections with 2θ(Mo-K_α) $\leqslant$ 54° (minimum interplanar spacing, d = 0.83 Å) were measured on a Datex-automated General Electric XRD 6 spectrogoniometer with a scintillation counter, approximately monochromatic Mo-K_α radiation (Zr filter and pulse-height analyser), and a θ-2θ scan of 2° per minute in 2θ. Background counts of 20 seconds were made at the beginning and end of each scan. The crystal used for data collection was cut to a roughly square cross-section of 0.2 mm., and length 0.6 mm., and was mounted with a (needle axis) parallel to the ϕ axis of the goniostat. No absorption correction was made. Lorentz and polarization factors were applied,

and the structure amplitudes derived. On the basis of comparison with the intensities of systematically absent reflections, 410 (76%) of the 538 independent reflections were classified as observed. The remaining 128 were assigned their measured value, but were given zero weight in the refinement.

STRUCTURE ANALYSIS

Because reflections $hk\ell$, $k + \ell$ odd are weak, the silver ion was expected to lie on or near to a position which causes the appearance of false symmetry in the electron-density map based on the silver ion alone. The three-dimensional Patterson function showed an apparent silver ion position at 0.125, 0.0, 0.125, but slight elongation of the peaks in the y direction indicated that the y parameter could be changed to 0.01. This change resulted in enhancement of some of the resulting Fourier peaks at the expense of others, so that the true nitrate group could be discerned from its false image. A cycle of full-matrix least-squares refinement with the light atoms assigned the scattering curve for oxygen[6], initial isotropic thermal parameters equal to 4.0 Å^2, and with unit weights, resulted in an R value of 0.15. Two further cycles with weights based on the counting statistics, and with the nitrogen assigned its usual scattering curve reduced R to

0.13, and two cycles with anisotropic temperature factors further reduced R to 0.082.

Examination of the structure factors indicated that the 211, 004, 020, 024, 040 and 102 reflections were reduced due to extinction. These were excluded from the refinement, and the two anisotropic cycles were repeated, resulting in an R value of 0.064, and R_w of 0.094. Two further cycles of full-matrix least-squares refinement with a weighting scheme of the form $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o) = 32.66 - 1.09|F_o| + 0.0088|F_o|^2 + 0.00008|F_o|^3$ gave a final R of 0.067 and R_w of 0.068 for the remaining 404 reflections.

The maximum ratio of parameter shift/esd in the final cycle was equal to 1.0. A final difference map showed maximum fluctuations of ± 2.2 eA^{-3}, except at the silver ion position, where a trough of -4.4 eA^{-3} was observed. Final measured and calculated structure factors are listed in Table 9.

Table 9

Measured and calculated structure factors for silver nitrate. Unobserved reflections are assigned their measured value, but are given zero weight in the refinement, and are indicated by a negative sign before F_o.

Table 9

h	k	l	F_o	F_c
0	0	2	17.60	16.29
0	0	4	61.28	61.49
0	0	8	129.66	151.22
0	0	10	28.14	25.37
0	0	12	65.38	65.66
0	2	1	76.92	76.86
0	2	2	33.30	29.39
0	2	3	49.50	48.50
0	2	5	47.81	45.71
0	2	6	14.04	13.64
0	2	7	37.35	36.89
0	2	8	132.85	134.99
0	2	9	11.15	10.70
0	2	10	34.39	33.35
0	2	11	-7.07	2.09
0	2	12	67.80	70.39
0	4	1	24.75	27.29
0	4	2	34.51	33.33
0	4	3	54.46	52.92
0	4	4	158.76	182.48
0	4	5	10.99	10.55
0	4	6	49.62	48.37
0	4	7	24.18	24.16
0	4	8	101.31	106.65
0	4	9	37.15	36.15
0	4	10	31.51	32.13
0	4	11	25.56	26.20
0	6	0	135.57	157.12
0	6	1	45.04	47.31
0	6	2	-6.64	3.86
0	6	3	23.37	24.27
0	6	4	108.13	112.51
0	6	5	46.00	46.21
0	6	6	23.18	21.20
0	6	7	20.05	19.78
0	6	8	74.22	73.17
0	6	9	20.51	17.73
0	8	0	65.20	68.57
0	8	1	27.82	29.20
0	8	2	-7.95	8.56
0	8	3	34.64	35.74
0	8	4	70.14	71.23
0	8	5	23.01	22.08
0	8	6	-5.82	3.47
1	0	4	21.86	20.71
1	0	6	97.83	108.81
1	0	8	49.48	49.51
1	0	10	75.53	78.54
1	0	12	19.11	19.05
1	1	1	94.90	106.85
1	1	2	41.69	35.63
1	1	3	120.36	140.76
1	1	4	43.23	38.97
1	1	5	88.27	92.94
1	1	6	-2.95	2.53
1	1	7	88.96	92.59
1	1	8	12.71	15.03
1	1	9	42.48	42.91
1	1	10	24.61	24.97
1	1	11	52.83	53.90
1	1	12	-5.18	0.41
1	2	1	47.36	37.01
1	2	2	140.39	172.24
1	2	3	21.11	20.23
1	2	4	34.71	31.03
1	2	5	-5.86	4.83
1	2	6	114.77	121.23
1	2	7	9.48	9.36
1	2	8	18.60	16.98
1	2	9	-4.02	2.85
1	2	10	55.81	55.07
1	2	11	11.22	8.57
1	2	12	21.25	21.35
1	3	1	137.22	166.81
1	3	2	40.47	37.62
1	3	3	113.09	117.24
1	3	4	24.01	24.82
1	3	5	64.22	62.27
1	3	6	14.73	14.45
1	3	7	77.19	77.49
1	3	8	-6.08	2.97
1	3	9	34.72	32.11
1	3	10	8.64	4.92
1	3	11	35.96	35.24
1	4	1	38.59	39.21
1	4	2	126.16	138.12
1	4	3	-2.40	1.78
1	4	4	9.56	8.18
1	4	5	13.61	9.43
1	4	6	95.69	96.56
1	4	7	13.10	11.40
1	4	8	13.64	13.13
1	4	9	14.59	12.61
1	4	10	46.99	46.58
1	4	11	9.55	5.42
1	5	1	56.39	53.87
1	5	2	39.13	38.96
1	5	3	70.16	68.60
1	5	4	8.82	8.73
1	5	5	70.02	67.41
1	5	6	34.45	33.17
1	5	7	53.17	49.72
1	5	8	12.42	12.62
1	5	9	32.11	31.29
1	5	10	14.86	11.68
1	6	1	18.16	18.55
1	6	2	76.82	80.72
1	6	3	18.36	19.72
1	6	4	12.05	11.45
1	6	5	27.09	24.43
1	6	6	54.99	54.35
1	6	7	-4.59	6.93
1	6	8	21.90	23.02
1	6	9	16.37	14.05
1	7	1	39.86	40.85
1	7	2	27.64	29.16
1	7	3	47.43	48.59
1	7	4	9.85	8.51
1	7	5	25.98	26.01
1	7	6	19.40	18.26
1	7	7	38.96	38.92
1	7	8	-7.00	0.09
1	8	1	10.90	10.37
1	8	2	41.40	42.20
1	8	3	14.15	14.62
1	8	4	13.35	13.35
1	8	5	11.87	10.55
1	8	6	37.48	37.80
1	9	1	24.56	22.54
1	9	2	19.11	17.88
2	0	0	34.48	44.60
2	0	2	12.51	11.76
2	0	4	55.72	53.84
2	0	6	-6.82	5.62
2	0	8	36.45	38.07
2	0	10	15.57	13.54
2	0	12	14.51	13.61
2	1	0	93.64	99.29
2	1	2	47.73	42.05
2	1	3	150.33	178.75
2	1	4	-3.74	4.71
2	1	5	144.19	172.70
2	1	6	0.3	0.25
2	1	7	46.27	49.87
2	1	8	9.68	8.49
2	1	9	81.76	86.33
2	1	10	9.64	8.17
2	1	11	33.81	32.65
2	1	12	-4.00	3.47
2	2	0	97.28	111.07
2	2	1	12.29	6.93
2	2	2	25.58	22.95
2	2	3	13.96	11.41
2	2	4	60.39	57.04
2	2	5	-4.33	3.52
2	2	6	33.64	31.81
2	2	7	10.52	10.10
2	2	8	15.74	14.67
2	2	9	-7.42	6.38
2	2	10	12.56	12.54
2	2	11	-5.86	3.20
2	2	12	-4.73	4.99
2	3	0	34.41	42.04
2	3	1	147.32	155.92
2	3	2	-1.99	0.72
2	3	3	120.13	124.77
2	3	4	51.71	49.72
2	3	6	16.11	14.52
2	3	7	50.56	49.26
2	3	8	21.97	23.05
2	3	9	97.79	103.23
2	3	10	-6.79	4.67
2	3	11	36.12	35.72
2	4	0	32.46	32.30
2	4	1	32.14	30.42
2	4	2	-1.51	0.78
2	4	3	-5.74	6.06
2	4	4	35.21	32.44
2	4	5	21.56	20.85
2	4	6	-0.09	5.52
2	4	7	-4.20	3.69
2	4	8	20.64	20.78
2	4	9	-1.04	0.92
2	4	10	11.72	10.58
2	4	11	-5.69	1.42
2	5	0	24.68	25.69
2	5	1	99.83	105.12
2	5	2	14.47	13.66
2	5	3	75.64	73.58
2	5	4	39.21	38.13
2	5	5	101.42	104.10
2	5	6	-7.38	5.14
2	5	7	53.21	51.85
2	5	8	28.18	26.42
2	5	9	55.88	56.31
2	5	10	-7.26	2.17
2	6	0	20.91	21.79
2	6	1	-4.31	9.63
2	6	2	-1.60	3.79
2	6	3	10.44	10.20
2	6	4	19.47	18.14
2	6	5	-4.89	1.04
2	6	6	-7.21	7.03
2	6	7	11.12	10.07
2	6	8	12.00	10.17
2	6	9	9.62	8.84
2	7	0	45.10	47.33
2	7	1	63.58	67.37
2	7	2	9.53	9.05
2	7	3	59.94	60.54
2	7	4	25.43	28.06
2	7	5	56.20	55.23
2	7	6	-5.50	2.20
2	7	7	30.27	34.33
2	7	8	10.97	10.10
2	8	1	10.69	10.81
2	8	2	-7.06	2.01
2	8	3	-6.64	3.88
2	8	4	13.57	10.08
2	8	5	9.99	8.08
2	8	7	131.36	153.04
3	0	4	-3.23	2.41
3	0	6	90.47	94.27
3	0	8	27.11	27.90
3	0	10	65.71	68.51
3	1	1	122.38	116.51
3	1	2	26.77	27.26
3	1	3	140.36	148.86
3	1	4	25.42	22.88
3	1	5	71.86	71.19
3	1	6	8.19	7.82
3	1	7	99.36	99.41
3	1	8	17.94	19.82
3	1	9	30.64	29.35
3	1	10	-3.26	3.96
3	1	11	55.20	56.08
3	2	1	17.57	13.86
3	2	2	149.37	149.38
3	2	3	27.47	24.29
3	2	4	19.90	18.62
3	2	5	11.97	12.59
3	2	6	99.18	101.16
3	2	7	12.57	11.93
3	2	8	-4.04	1.25
3	2	9	-4.14	4.71
3	2	10	43.62	43.50
3	2	11	10.43	8.46
3	3	1	114.21	120.98
3	3	2	-6.47	6.82
3	3	3	91.72	86.10
3	3	4	9.18	6.85
3	3	5	74.43	74.80
3	3	6	22.44	22.31
3	3	7	78.41	78.15
3	3	8	-3.58	2.32
3	3	9	37.20	37.17
3	3	10	18.75	16.59
3	3	11	47.17	48.19
3	4	1	48.69	47.16
3	4	2	104.78	107.86
3	4	3	16.18	13.91
3	4	4	-6.97	3.95
3	4	5	12.56	13.66
3	4	6	77.09	76.10
3	4	7	16.81	13.73
3	4	8	-4.69	0.20
3	4	9	14.69	13.67
3	4	10	40.37	38.87
3	5	1	72.44	72.45
3	5	2	34.71	38.93
3	5	3	94.41	94.17
3	5	4	-2.37	1.79
3	5	5	65.47	63.75
3	5	6	29.77	27.45
3	5	7	56.20	57.56
3	5	8	7.64	8.47
3	5	9	17.40	15.21
3	6	1	22.49	22.73
3	6	2	54.51	59.41
3	6	3	26.49	24.75
3	6	4	4.69	4.34
3	6	5	49.74	51.06
3	6	6	40.71	39.12
3	6	7	10.46	10.35
3	6	8	12.01	12.27
3	7	1	32.23	33.23
3	7	2	37.60	31.44
3	7	4	38.45	39.16
3	7	4	-6.56	1.84
3	7	5	28.14	25.19
3	7	6	20.15	18.46
3	7	7	43.19	43.66
3	8	1	15.79	15.34
3	8	2	28.02	26.89
3	8	3	17.47	17.27
3	8	4	15.61	7.99
4	0	0	153.66	145.96
4	0	2	35.54	35.03
4	0	4	118.69	127.19
4	0	6	5.79	0.74
4	0	8	91.66	96.85
4	0	10	15.86	9.98
4	1	0	15.13	12.43
4	1	1	43.71	39.64
4	1	3	24.37	24.79
4	1	4	-7.25	4.91
4	1	5	35.39	37.93
4	1	6	-0.49	4.63
4	1	7	-4.74	4.42
4	1	8	-6.75	4.92
4	1	9	27.95	27.77
4	1	10	-5.27	2.96
4	1	11	-7.42	3.99
4	2	0	127.68	148.61
4	2	1	14.05	7.93
4	2	2	35.55	30.48
4	2	3	29.60	21.83
4	2	4	134.46	136.55
4	2	5	4.49	6.73
4	2	6	29.67	24.19
4	2	7	36.53	36.77
4	2	8	72.87	72.35
4	2	9	-6.34	7.28
4	2	10	15.41	17.37
4	3	0	13.11	13.26
4	3	1	37.72	36.20
4	3	2	-1.56	1.87
4	3	3	15.72	15.91
4	3	4	-5.68	1.95
4	3	5	36.59	36.04
4	3	6	-1.98	4.86
4	3	7	-6.47	3.99
4	3	8	-5.69	0.30
4	3	9	19.18	19.26
4	3	10	-5.16	0.02
4	4	0	85.99	91.82
4	4	1	25.69	26.60
4	4	2	12.80	9.54
4	4	3	15.74	16.94
4	4	4	91.23	88.73
4	4	5	14.34	12.39
4	4	6	20.66	18.54
4	4	7	-4.56	3.29
4	4	8	66.67	66.58
4	4	9	13.56	14.88
4	5	0	-6.67	2.47
4	5	1	14.09	20.23
4	5	2	-3.45	0.62
4	5	3	23.48	16.26
4	5	4	-5.56	4.80
4	5	5	25.29	21.61
4	5	6	-6.65	0.20
4	5	7	-4.68	3.10
4	5	8	-6.65	4.88
4	6	0	41.84	46.32
4	6	1	-7.66	4.30
4	6	2	-6.66	4.34
4	6	3	15.26	9.01
4	6	4	64.45	63.33
4	6	5	16.90	12.60
4	6	6	-4.72	9.25
4	6	7	14.71	14.10
4	7	0	-6.67	3.65
4	7	1	15.48	17.14
4	7	2	-4.82	2.35
4	7	3	-5.96	7.72
4	7	4	-7.36	5.12
4	7	5	16.78	17.36
4	8	0	44.44	48.14
4	8	1	20.16	19.40
4	8	2	-7.86	7.45
5	0	2	148.05	141.21
5	0	4	28.67	29.27
5	0	6	86.46	89.06
5	0	8	32.04	34.68
5	0	10	56.89	57.01
5	1	1	43.60	40.59
5	1	2	14.47	13.16
5	1	3	53.56	51.23
5	1	4	10.65	9.23
5	1	5	36.08	35.97
5	1	6	-7.61	7.89
5	1	7	32.18	31.55
5	1	8	15.24	15.62
5	1	9	23.76	22.54
5	1	10	-7.16	3.23
5	2	1	-6.13	6.16
5	2	2	129.67	125.81
5	2	3	18.78	17.72
5	2	4	13.41	13.65
5	2	5	-2.77	3.57
5	2	6	94.06	97.03
5	2	7	11.13	9.76
5	2	8	20.00	20.61
5	2	9	-6.12	3.25
5	2	10	49.48	50.20
5	3	1	54.57	53.77
5	3	2	17.03	1.25
5	3	3	22.73	21.45
5	3	4	-2.70	3.04
5	3	5	42.28	39.11
5	3	6	12.29	11.59
5	3	7	23.36	23.19
5	3	8	-6.03	4.74
5	3	9	28.43	28.44
5	4	1	24.86	26.12
5	4	2	163.20	166.29
5	4	3	12.57	12.13
5	4	4	12.47	13.92
5	4	5	20.62	17.94
5	4	6	73.41	71.84
5	4	7	15.71	15.17
5	4	8	12.67	13.73
5	5	1	27.56	26.41
5	5	2	21.63	21.10
5	5	3	39.26	39.78
5	5	4	-5.68	3.40
5	5	5	27.85	25.20
5	5	6	17.41	15.60
5	5	7	17.93	17.98
5	6	1	24.75	24.61
5	6	2	54.97	60.74
5	6	3	22.45	23.29
5	6	4	-9.34	9.35
5	6	5	19.66	18.52
5	6	6	45.65	44.74
5	7	1	13.27	12.88
5	7	2	18.01	17.59
5	7	3	12.62	9.65
5	7	4	-4.61	2.15
6	0	0	31.14	32.91
6	0	2	16.27	15.42
6	0	4	26.53	27.08
6	0	6	20.31	21.66
6	0	8	10.64	8.91
6	1	0	17.76	19.15
6	1	1	15.71	16.79
6	1	2	17.49	16.64
6	1	3	67.04	63.84
6	1	4	-8.05	5.16
6	1	5	57.87	58.98
6	1	6	-9.07	9.38
6	1	7	45.16	45.54
6	1	8	9.58	8.97
6	1	9	34.36	35.01
6	2	0	17.42	22.12
6	2	1	-7.14	4.79
6	2	2	-7.09	9.49
6	2	3	-1.35	0.41
6	2	4	17.43	16.61
6	2	5	-6.69	1.42
6	2	6	11.83	9.77
6	2	7	-5.47	5.45
6	2	8	15.39	16.86
6	3	0	23.01	23.91
6	3	1	55.84	55.23
6	3	2	-5.49	2.45
6	3	3	43.22	42.40
6	3	4	14.34	16.27
6	3	5	55.74	57.77
6	3	6	-5.56	3.72
6	3	7	23.20	20.35
6	3	8	-6.20	6.35
6	4	0	14.99	22.41
6	4	1	-9.28	7.14
6	4	2	-7.06	7.75
6	4	3	-6.67	1.73
6	4	4	11.29	20.23
6	4	5	-5.35	2.47
6	4	6	14.20	13.77
6	4	7	-5.33	5.52
6	5	0	-7.98	6.41
6	5	1	37.90	35.16
6	5	2	-8.22	3.84
6	5	3	33.82	41.39
6	5	4	14.43	15.14
6	5	5	40.72	38.93
6	6	0	-7.66	1.74
6	6	2	15.35	16.55
6	6	4	-6.34	3.59
6	6	6	-6.19	5.32
6	7	1	-6.31	0.79
6	7	3	13.21	14.45
6	7	5	15.53	15.64
7	0	4	-5.76	0.91
7	0	6	-5.97	5.81
7	1	1	44.75	44.24
7	1	2	-8.68	4.99
7	1	3	52.39	53.47
7	1	4	-5.42	2.86
7	1	5	39.65	41.47
7	1	6	-5.51	1.15
7	1	7	42.96	46.57
7	2	1	9.17	7.41
7	2	2	13.25	12.13
7	2	3	-7.59	6.44
7	2	4	-6.96	7.69
7	2	5	-5.98	2.22
7	2	6	20.43	19.53
7	2	7	-6.75	0.32
7	3	1	44.71	41.75
7	3	2	11.98	10.59
7	3	3	49.71	50.21
7	3	4	-6.84	4.74
7	3	5	29.79	28.35
7	3	6	-9.66	7.34
7	4	1	-7.51	8.16
7	4	2	20.72	18.68
7	4	3	-6.13	4.81
7	4	4	-7.48	4.60
7	4	5	-7.95	4.66
7	5	1	28.48	30.62
7	5	3	18.35	16.35
7	5	5	17.56	17.30
8	0	0	65.50	69.93
8	0	2	-6.02	3.41
8	0	4	60.14	51.11
8	1	0	-4.75	2.37
8	1	1	14.41	18.95
8	1	2	-6.73	4.35
8	1	3	11.96	10.23
8	1	4	-6.96	1.84
8	1	5	17.38	18.47
8	2	0	42.62	42.78
8	2	1	14.10	11.09
8	2	2	-4.98	2.44
8	2	3	12.98	10.39
8	2	4	44.86	43.44
8	3	0	-6.20	1.13
8	3	1	10.15	13.11
8	3	2	-5.72	2.49
8	3	3	-10.08	8.98

Table 9, continued

The following reflections were excluded from the refinement for suspected extinction. F_c values were determined from the last cycle in which they were included.

h k ℓ	F_o	F_c
0 0 4	188	320
0 2 0	153	282
0 2 4	208	290
0 4 0	171	230
1 0 2	121	171
2 1 1	165	238

COORDINATES AND MOLECULAR DIMENSIONS

The final positional and anisotropic thermal parameters, with their standard deviations, are listed in Table 10. Interatomic distances and angles are listed in Table 11, together with those determined previously[22], for comparison. Figure 7 is a view of the structure along the b crystallographic axis, and Figure 8 shows the thermal vibration ellipsoids projected in the plane of the nitrate group.

Table 10

Final positional (fractional × 10^4) and anisotropic thermal ($\AA^2 \times 10^2$) parameters for silver nitrate, with standard deviations in parentheses.

Atom	x	y	z
Ag	3650(1)	4902(1)	1298(1)
N	3749(14)	3608(12)	4074(9)
O(1)	3841(13)	3164(11)	5264(8)
O(2)	4860(14)	2930(12)	3243(8)
O(3)	2580(12)	4757(11)	3711(8)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	mean $\sigma(U)$
Ag	4.59	3.49	3.09	-0.23	-0.81	0.54	0.05
N	2.64	2.29	2.27	-0.38	-0.25	-0.25	0.4
O(1)	4.73	3.47	2.04	-0.97	0.18	0.23	0.4
O(2)	4.04	3.92	3.06	1.10	1.75	0.41	0.4
O(3)	2.87	3.45	4.51	1.01	-0.43	-0.26	0.4

Table 11

Interatomic distances (Å, $\sigma \simeq 0.01$ Å) and valency angles (degrees, $\sigma \simeq 1^{\circ}$) for silver nitrate, with previously determined values for comparison.

		ref. 22			ref. 22
N-O(1)	= 1.25	1.19±0.06	O(1)-N-O(2)	= 121	118±5.6
N-O(2)	= 1.25	1.32±0.06	O(1)-N-O(3)	= 120	117±5.6
N-O(3)	= 1.23	1.23±0.06	O(2)-N-O(3)	= 119	125±6.0

Ag...O and Ag...N contacts

		ref. 22
Ag...O(1)^{I}	= 2.48	2.51±0.05
Ag...O(1)^{II}	= 2.48	2.54±0.05
Ag...O(2)^{III}	= 2.50	2.48±0.05
Ag...O(3)	= 2.56	2.53±0.05
Ag...O(2)	= 2.58	2.59±0.05
Ag...O(3)^{IV}	= 2.75	2.73±0.04
Ag...O(3)^{I}	= 2.77	2.80±0.05
Ag...O(2)^{V}	= 3.05	2.99±0.05
Ag...N	= 2.97	2.98±0.06
Ag...N^{I}	= 3.01	2.99±0.06
Ag...N^{III}	= 3.29	3.32±0.06

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

Figure 7

The silver nitrate structure, viewed along the b crystallographic axis. Heavy lines are nearer the viewer; the distorted octahedron of nitrate groups is indicated.

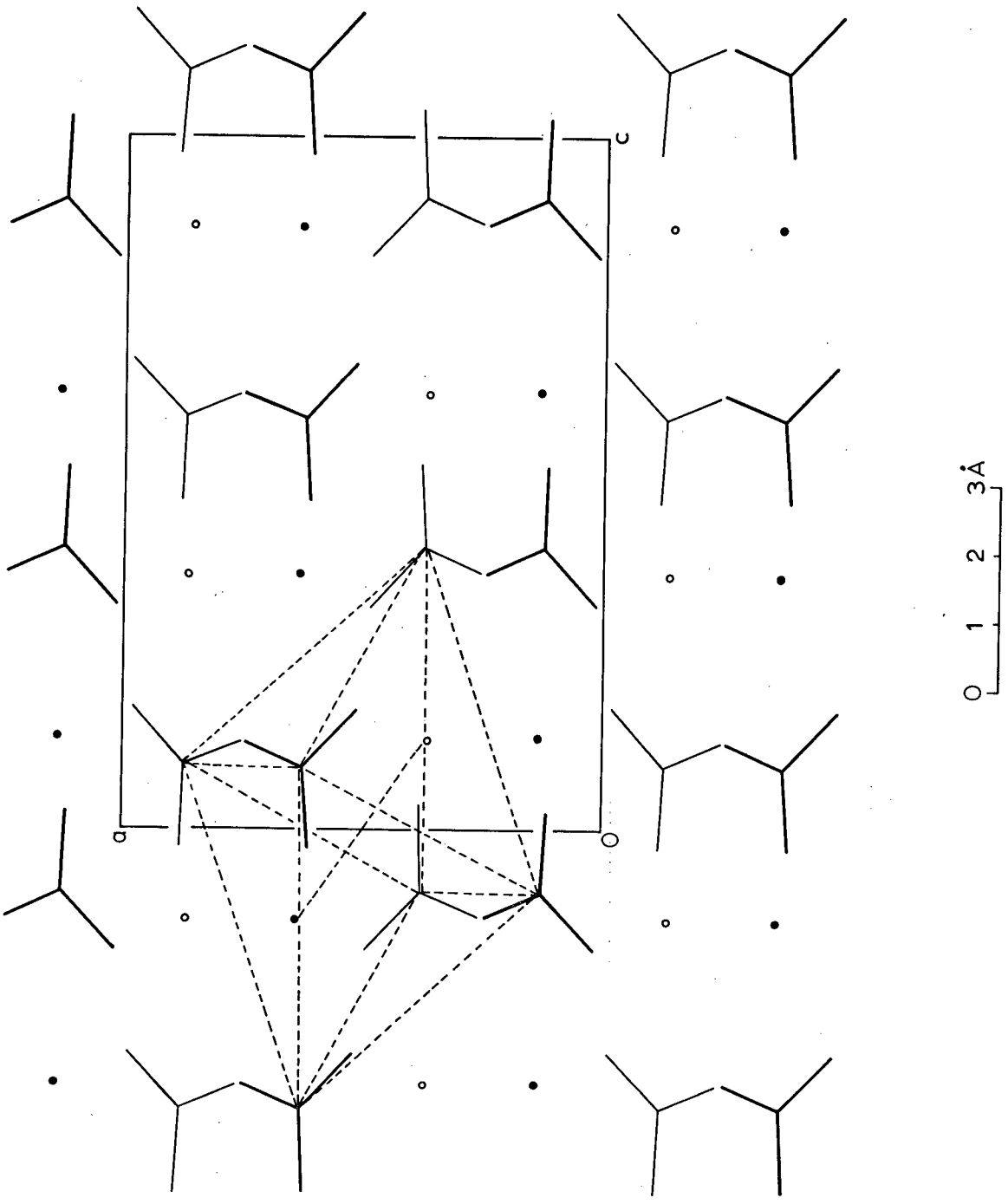
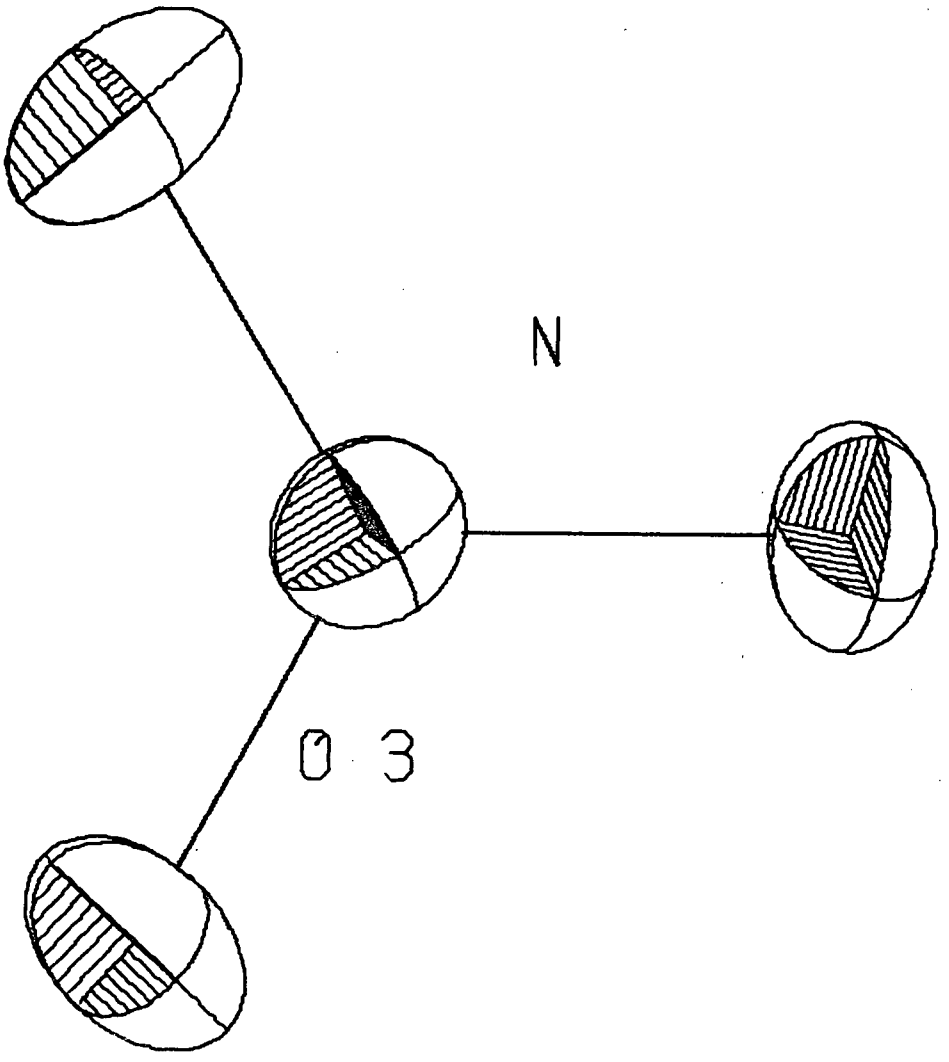
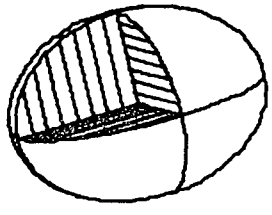

c
a
0 1 2 3Å

Figure 8

The thermal vibration ellipsoids viewed perpendicular to the plane of the nitrate group.



AG



RESULTS AND DISCUSSION

The crystal analysis has verified the structure of silver nitrate, as previously determined[22], and has provided more accurate interatomic distances and angles (Table 11), as well as a detailed analysis of the anisotropic thermal motion.

The average N-O distance in the nitrate group is 1.24(1) Å, and the average O-N-O angle is 120°. As shown in Table 11, the individual values do not differ significantly from the averages, so the slight asymmetry of the nitrate environment does not cause any significant distortion of the nitrate ion from D_{3h} symmetry. After correction for rotational oscillation errors[26], the mean N-O distance is 1.26(1) Å, slightly longer than that reported for sodium nitrate[27], 1.218(4) Å, but comparable to the values reported for several silver nitrate—olefin complexes discussed previously. The average N-O length reported earlier[22], 1.25 Å, is in good agreement, but the variation in length (1.19-1.32 Å), although not significant in terms of their estimated standard deviations, suggests a distortion of the nitrate group which in fact, does not exist, as shown by the present analysis.

The thermal vibration ellipsoids are shown in Figure 8, and Table 12 lists the lengths and directions of the principal axes with respect to axis $\vec{1}$ along the N-O(1) bond, axis $\vec{2}$ perpendicular to the NO_3^- plane, and axis $\vec{3}$

Table 12

Principal components of the thermal vibration ellipsoids and their orientations with respect to axis $\vec{1}$ along the N-O(1) bond, axis $\vec{2}$ perpendicular to the NO_3^- plane and axis $\vec{3}$ equal to $\vec{1} \times \vec{2}$.

Atom	Component	U (Å)	Angle with respect to Axis $\vec{1}$	Axis $\vec{2}$	Axis $\vec{3}$
Ag	1	0.160	17.6	91.3	72.5
	2	0.189	85.9	162.1	107.4
	3	0.225	72.9	72.1	154.9
N	1	0.134	65.0	152.4	101.0
	2	0.159	155.0	114.7	93.6
	3	0.170	91.3	78.5	168.4
O(1)	1	0.140	11.4	83.5	99.3
	2	0.174	86.0	164.5	104.9
	3	0.230	100.7	76.0	162.3
O(2)	1	0.130	49.6	80.1	137.9
	2	0.183	130.7	112.1	131.1
	3	0.245	113.1	24.4	97.6
O(3)	1	0.145	105.8	83.3	162.8
	2	0.197	114.0	27.7	77.0
	3	0.220	29.3	63.3	101.1

equal to $\vec{1} \times \vec{2}$. The nitrogen atom has its smallest component of motion perpendicular to this plane, and approximately equal components in the plane. The smallest vibration of all three oxygen atoms is directed along the N-O bonds, and the largest motion is roughly in the plane of the nitrate group.

The structure is composed of silver ions co-ordinated to nitrate ions to form a three-dimensional network so that the silver ions, which lie essentially in layers parallel to (010) separated by ½b, are linked by coordination to the nitrate groups which bridge the gap between layers. Ag...O and Ag...N distances are listed in Table 11 with the values determined previously[22], for comparison. The eight Ag...O lengths listed do not form any easily recognizable geometric coordination around the silver ion, and the silver environment is best described as irregular.

As noted in the earlier report[22], there are groups of six nitrate ions in an irregular octahedral arrangement around centres of symmetry. These form a large cavity (Figure 7) which is occupied by two silver ions 3.238(2) Å apart, related by the centre of symmetry. No nitrate group is uniquely associated with any one silver ion, but all contacts are shared; of the eight nearest oxygen neighbours, three are very close to the silver layers (O(3)), and the other five (O(1) and (O(2)), lie between layers to bridge the gap and form the three-dimensional network.

PART IV

THE STRUCTURE DETERMINATION

OF

N,N-DIMETHYL(FERROCENYLMETHYL)AMMONIUM TETRACHLOROZINCATE

INTRODUCTION

The isolation of N,N-dimethyl(ferrocenylmethyl)ammonium tetrachlorozincate, an intermediary complex in the $ZnCl_2$-HCl catalysed self-condensation of N,N-dimethylaminomethylferrocene, has been reported[28]. Although the ammonium structure was indicated by the strong infrared absorption near 3.7μ for the solution, infrared data on KBr pellets for the crystalline compound appeared to be inconsistent with N-protonation in the solid state, and suggested the possibility of coordinate covalent N→Zn bonding[28]. The crystal structure analysis was undertaken to resolve this problem, and to obtain information about the orientation of the rings in the ferrocene portion of the structure.

EXPERIMENTAL

Crystals of N,N-dimethyl(ferrocenylmethyl)ammonium tetrachlorozincate hydrate, $[C_5H_5FeC_5H_4 \cdot CH_2 \cdot NHMe_2]_2^+ \cdot ZnCl_4^{-2} \cdot H_2O$, are thin orange-brown plates elongated along c with {100} developed. The unit cell parameters and space group were determined from rotation and Weissenberg photographs, the unit cell parameters being refined by a least-squares procedure applied to the 2θ values of 30 reflections measured on a single-crystal diffractometer with Mo-K_α radiation.

Crystal Data.— $\lambda(Cu\text{-}K_\alpha) = 1.5418$; $\lambda(Mo\text{-}K_\alpha) = 0.7107$ Å.
N,N-dimethyl(ferrocenylmethyl)ammonium tetrachlorozincate hydrate, $[C_{13}H_{18}NFe]_2ZnCl_4 \cdot H_2O$, M = 713.5.
Monoclinic, a = 18.076(6), b = 14.038(5), c = 12.246(5) Å, $\beta = 95.70(1)^\circ$, U = 3092.1 Å^3, D_m (flotation in bromoform-benzene) = 1.522 g.cm.$^{-3}$, Z = 4, D_c = 1.532 g.cm.$^{-3}$
F(000) = 1464.
Absorption coefficients: $\mu(Cu\text{-}K_\alpha) = 118$ cm.$^{-1}$; $\mu(Mo\text{-}K_\alpha) = 21$ cm.$^{-1}$
Absent reflections: h0ℓ, ℓ odd; 0k0, k odd.
Space group $P2_1/c$ (C_{2h}^5).

The intensities of all reflections with $2\theta(Mo\text{-}K_\alpha) \leqslant 40^\circ$ (minimum interplanar spacing, d = 1.04 Å) were measured on a Datex-automated General Electric XRD 6 spectrogoniometer with a scintillation counter, approximately monochromatic $Mo\text{-}K_\alpha$ radiation (Zr filter and pulse-height analyser), and a θ-2θ scan of 2° per minute in 2θ. Background counts were made at the beginning and end of each scan. The crystal used was a thin plate with dimensions 0.1 × 0.4 × 0.6 mm., and was mounted with c parallel to the ϕ axis of the goniostat. No absorption correction was made. Lorentz and polarization factors were applied, and the structure amplitudes derived. Of the 2991 independent reflections 2012 (67%) had intensities greater than $3\sigma(I)$ above background, where $\sigma(I)$ is defined by

$$\sigma(I) = \{S + B + (0.05S)^2\}^{\frac{1}{2}}$$

where S = scan count and B = background count. The

remaining 979 reflections were classified as unobserved.

STRUCTURE ANALYSIS

The data were placed on an absolute scale using Wilson's method[29], and values of |E| were calculated with the program of Hall[30]. The |E| statistics obtained are compared with the theoretical values[31] for centrosymmetric and non-centrosymmetric structures in Table 13.

The structure was solved by a direct sign-determining procedure[32], which uses a reiterative application of Sayre relationships[33]. The origin-determining reflections and symbols (Table 14) were selected from those reflections of highest |E| which enter into the greatest number of Sayre relationships and which were of suitable parity groups. Permutations of the signs of the symbols 'a', 'b', 'c' and 'd' led to 16 starting sets. Planes having |E| values greater than 1.7 were used and twelve passes through the list were performed for each starting set, with newly determined signs not used to estimate additional signs until the next pass. This procedure yielded two possible solutions with consistency index of 0.83 (next highest 0.60), and the E-map computed with the signs of one of these showed the two Fe positions and the $ZnCl_4^{-2}$ group. Compared with the fully refined structure, 280 of the 296 predicted signs were correct. The E-map computed from the other set with consistency index 0.83 did not show recognizable structural features.

Table 13

|E| statistics for N,N-dimethyl(ferrocenylmethyl)ammonium tetrachlorozincate hydrate.

	Experimental	Theoretical	
		Centro.	Non-centro.
$<\|E\|>$	0.785	0.798	0.886
$<\|E^2\|>$	1.008	1.000	1.000
$<\|E^2 - 1\|>$	0.995	0.968	0.736
$\|E\| \geq 3.0$ (%)	0.37	0.30	0.01
$\|E\| \geq 2.0$ (%)	4.28	5.00	1.80
$\|E\| \geq 1.0$ (%)	32.83	32.00	37.00

Table 14

Base set of reflections for sign-determination.

h	k	ℓ	E	sign/symbol	determined sign
1	2	1	4.64	+	origin
$\bar{1}0$	2	1	3.23	+	
4	5	9	3.77	+	
$\bar{2}$	2	1	2.61	a	+
$\bar{1}$	0	2	3.02	b	-
1	4	4	2.93	c	-
$\bar{5}$	2	5	2.33	d	-

A structure factor calculation based on the heavy-atom coordinates from the E-map, with the Wilson scale, scattering factors from the International Tables[6] and isotropic thermal parameters B of 3.0 $\AA^2$ for all seven atoms gave an R value of 0.40. A difference map based on the heavy-atom positions was computed, from which twenty-two light atoms were located. With these included in the phasing model, subsequent difference maps revealed the positions of the remaining non-hydrogen atoms. With all light atoms assigned the scattering curve for carbon, and isotropic thermal parameters of 4.0 $\AA^2$, the R value was 0.35.

The nitrogen and oxygen atoms were assigned their appropriate scattering curves, and three cycles of full-matrix least-squares refinement with the Fe, Zn and Cl atoms allowed anisotropic thermal parameters, and unit weights for observed, zero weights for unobserved reflections, reduced R to 0.082. Two cycles of block-diagonal least-squares with all atoms assigned anisotropic thermal parameters further reduced R to 0.068, but the anisotropic thermal parameters for the light atoms are not considered accurate, and are not listed. In the final cycles the data were weighted so that $\sqrt{w} = 1$ when $|F_o| \leq 45$, and $\sqrt{w} = 45/|F_o|$ when $|F_o| > 45$. For the 979 unobserved reflections, $\sqrt{w}$ was taken as 0.80. Final measured and calculated structure factors are listed in Table 15.

A final difference electron-density map showed spurious fluctuations as high as ±1 $e\text{Å}^{-3}$, and hydrogen atoms could not be located reliably.

Table 15

Measured and calculated structure factors for N,N-dimethyl(ferrocenylmethyl)ammonium tetrachlorozincate hydrate. Unobserved reflections are assigned their measured value, but weighted as described in the text, and are indicated by a negative sign before F_o.

Table 15

h	k	l	F	F
2	0	0	46.94	[illegible]
3	0	0	63.95	74.17
5	0	0	0.0	6.75
6	0	0	0.0	2.73
7	0	0	70.97	55.51
8	0	0	233.11	252.63
9	0	0	117.09	125.14
10	0	0	50.67	50.89
11	0	0	84.44	86.96
12	0	0	146.56	144.20
13	0	0	-30.22	29.47
14	0	0	-24.24	22.07
15	0	0	36.47	36.27
16	0	0	55.69	52.30
17	0	0	39.14	33.26
2	1	0	82.13	77.46
3	1	0	21.70	13.95
4	1	0	-2.11	5.67
5	1	0	46.78	45.71
6	1	0	0.0	0.06
7	1	0	17.47	21.51
8	1	0	31.06	35.21
9	1	0	27.01	29.46
10	1	0	42.82	45.04
11	1	0	46.10	44.30
12	1	0	24.85	22.95
13	1	0	16.32	13.79
14	1	0	22.91	24.80
15	1	0	-5.99	3.34
16	1	0	-5.79	1.95
17	1	0	-9.94	5.10
0	2	0	192.31	192.06
1	2	0	58.25	55.39
2	2	0	48.23	43.05
3	2	0	12.37	9.52
4	2	0	159.39	164.98
5	2	0	163.81	155.05
6	2	0	-7.00	9.49
7	2	0	63.37	51.19
8	2	0	105.58	102.56
9	2	0	52.71	55.67
10	2	0	14.33	13.50
11	2	0	62.61	5.10
12	2	0	48.98	57.40
13	2	0	43.09	41.10
14	2	0	21.67	[illegible]
15	2	0	-11.15	12.21
16	2	0	26.93	21.29
17	2	0	22.06	13.90
1	3	0	58.19	55.46
2	3	0	174.67	165.26
3	3	0	-12.04	11.19
4	3	0	55.37	53.11
5	3	0	-0.93	1.37
6	3	0	85.34	81.08
7	3	0	61.55	57.27
8	3	0	67.45	66.42
9	3	0	44.22	44.74
10	3	0	66.73	66.06
11	3	0	46.19	46.74
12	3	0	43.55	43.56
13	3	0	0.0	9.59
14	3	0	35.57	33.17
15	3	0	-3.94	5.42
16	3	0	20.25	17.40
17	3	0	-4.91	[illegible]
0	4	0	374.82	374.14
1	4	0	47.54	36.16
2	4	0	-4.54	1.11
3	4	0	20.66	13.42
4	4	0	81.44	84.22
5	4	0	75.72	81.10
6	4	0	54.72	51.95
7	4	0	53.14	53.42
8	4	0	115.46	114.25
9	4	0	35.65	34.51
10	4	0	-7.02	1.57
11	4	0	62.69	63.07
12	4	0	74.45	63.62
13	4	0	18.43	16.47
14	4	0	31.58	32.74
15	4	0	26.47	24.07
16	4	0	35.08	29.52
1	5	0	44.09	38.50
2	5	0	69.50	65.74
3	5	0	50.04	46.42
4	5	0	31.69	31.92
5	5	0	65.15	64.06
6	5	0	102.43	95.72
7	5	0	68.03	65.66
8	5	0	14.59	13.32
9	5	0	14.95	11.77
10	5	0	-6.03	3.14
11	5	0	-12.60	10.95
12	5	0	-14.37	15.95
13	5	0	-6.95	[illegible]
14	5	0	16.65	12.36
15	5	0	34.67	22.21
16	5	0	24.55	23.80
0	6	0	174.31	122.26
1	6	0	31.40	29.83
2	6	0	25.01	22.64
3	6	0	27.45	25.55
4	6	0	207.78	196.62
5	6	0	84.45	84.87
6	6	0	44.37	44.47
7	6	0	48.30	44.69
8	6	0	143.52	134.84
9	6	0	32.99	33.82
10	6	0	0.0	2.32
11	6	0	-2.50	7.93
12	6	0	62.19	57.87
13	6	0	39.65	37.48
14	6	0	-15.35	15.52
15	6	0	25.71	25.32
1	7	0	-6.59	9.57
2	7	0	50.84	45.62
3	7	0	24.44	24.55
4	7	0	24.90	21.72
5	7	0	-9.18	2.10
6	7	0	23.51	23.57
7	7	0	25.05	24.41
8	7	0	37.29	39.61
9	7	0	-11.69	12.52
10	7	0	-9.83	7.29
11	7	0	36.11	34.53
12	7	0	-13.86	9.42
13	7	0	0.0	1.70
14	7	0	-3.04	7.15
15	7	0	20.47	20.74
0	8	0	42.43	43.45
1	8	0	105.47	99.73
2	8	0	30.45	27.31
3	8	0	104.28	99.55
4	8	0	37.60	33.56
5	8	0	117.59	117.70
6	8	0	63.15	59.85
7	8	0	54.81	50.36
8	8	0	0.0	0.84
9	8	0	58.46	55.69
10	8	0	23.08	22.84
11	8	0	47.46	42.50
12	8	0	0.0	1.44
13	8	0	48.04	42.96
14	8	0	35.29	37.46
1	9	0	-10.10	3.74
2	9	0	15.44	12.39
3	9	0	0.0	4.30
4	9	0	25.41	22.96
5	9	0	29.75	28.57
6	9	0	41.13	40.00
7	9	0	-8.26	1.37
8	9	0	-10.54	12.26
9	9	0	0.0	4.25
10	9	0	-3.91	5.49
11	9	0	-14.02	9.69
12	9	0	0.0	4.95
13	9	0	-13.45	5.35
0	10	0	-15.07	22.68
1	10	0	64.90	65.11
2	10	0	-2.17	5.10
3	10	0	63.29	64.26
4	10	0	50.46	51.92
5	10	0	17.09	17.14
6	10	0	0.0	2.94
7	10	0	20.59	21.92
8	10	0	36.97	36.96
9	10	0	46.14	45.05
10	10	0	26.42	27.21
11	10	0	25.75	25.21
1	11	0	37.23	34.79
2	11	0	28.53	31.43
3	11	0	35.91	35.36
4	11	0	-4.97	[illegible]
5	11	0	18.78	19.80
6	11	0	17.69	11.27
7	11	0	14.17	11.21
8	11	0	0.0	5.42
9	11	0	0.0	2.72
10	11	0	18.43	17.03
0	12	0	[illegible]	4.35
1	12	0	16.64	16.95
2	12	0	-9.01	2.71
3	12	0	15.07	23.35
4	12	0	-11.54	7.12
5	12	0	18.73	19.77
6	12	0	-12.75	11.12
7	12	0	-14.54	14.72
8	12	0	0.0	3.86
1	13	0	27.67	24.35
2	13	0	29.55	31.10
3	13	0	25.14	27.57
4	13	0	-4.40	5.61
5	13	0	-8.68	6.83
-17	1	1	-11.55	9.86
-16	1	1	-12.09	[illegible]
-15	1	1	19.37	16.75
-14	1	1	-14.23	13.76
-13	1	1	36.66	37.35
-12	1	1	29.65	27.27
-11	1	1	111.40	111.75
-10	1	1	34.32	30.47
-9	1	1	53.55	55.06
-8	1	1	41.57	44.63
-7	1	1	121.32	125.34
-6	1	1	31.31	31.12
-5	1	1	34.58	36.78
-4	1	1	40.44	31.17
-3	1	1	169.14	173.67
-2	1	1	108.73	110.32
-1	1	1	97.17	91.65
0	1	1	13.84	11.67
2	1	1	97.63	106.43
3	1	1	79.57	95.75
4	1	1	47.49	[illegible]
5	1	1	12.76	19.50
6	1	1	75.59	77.72
7	1	1	35.09	47.45
8	1	1	41.27	39.41
9	1	1	13.37	17.79
10	1	1	107.74	109.65
11	1	1	46.11	43.12
12	1	1	-8.79	4.69
13	1	1	-8.50	6.29
14	1	1	26.76	27.05
15	1	1	41.25	[illegible]
16	1	1	-5.34	9.02
17	1	1	16.09	8.83
-17	2	1	15.65	14.56
-16	2	1	-5.34	2.46
-15	2	1	16.37	16.24
-14	2	1	57.65	50.17
-13	2	1	44.12	[illegible]
-12	2	1	78.74	3.75
-11	2	1	53.08	57.62
-10	2	1	168.70	173.47
-9	2	1	-5.47	5.62
-8	2	1	19.68	14.75
-7	2	1	46.87	53.98
-6	2	1	149.77	147.13
-5	2	1	101.56	93.52
-4	2	1	167.45	157.02
-3	2	1	179.51	158.39
-2	2	1	253.52	245.15
-1	2	1	111.23	72.46
0	2	1	60.59	63.19
2	2	1	209.01	219.37
3	2	1	-2.87	6.18
4	2	1	77.01	85.07
5	2	1	35.77	32.05
6	2	1	176.15	174.78
7	2	1	65.29	66.45
8	2	1	25.72	27.58
9	2	1	118.56	127.57
10	2	1	50.47	63.26
11	2	1	21.03	22.75
12	2	1	38.06	39.55
13	2	1	56.76	57.27
14	2	1	53.84	50.58
15	2	1	37.18	35.61
16	2	1	25.76	25.39
17	2	1	43.47	43.09
-17	3	1	0.0	1.00
-16	3	1	40.89	37.23
-15	3	1	36.41	37.28
-14	3	1	15.27	11.99
-13	3	1	21.96	7.89
-12	3	1	29.47	33.09
-11	3	1	-6.70	2.54
-10	3	1	21.35	20.77
-9	3	1	28.13	29.42
-8	3	1	0.0	2.30
-7	3	1	24.35	27.71
-6	3	1	62.57	77.76
-5	3	1	52.86	45.59
-4	3	1	-7.20	6.02
-3	3	1	54.15	52.78
-2	3	1	41.67	35.42
-1	3	1	14.09	18.75
0	3	1	16.32	11.77
1	3	1	42.62	41.01
2	3	1	173.26	160.34
3	3	1	32.77	31.18
4	3	1	15.22	16.37
5	3	1	-6.14	14.50
6	3	1	79.70	74.10
7	3	1	25.80	25.97
8	3	1	-12.02	13.54
9	3	1	-8.20	9.14
10	3	1	-7.43	0.85
11	3	1	-12.56	17.38
12	3	1	0.0	0.04
13	3	1	-5.81	3.07
14	3	1	28.19	28.89
15	3	1	15.70	9.02
16	3	1	-12.54	4.31
-16	4	1	-8.17	9.70
-15	4	1	16.13	13.31
-14	4	1	51.66	52.37
-13	4	1	24.72	22.36
-12	4	1	0.0	6.92
-11	4	1	-12.75	12.45
-10	4	1	64.01	65.11
-9	4	1	33.81	32.91
-8	4	1	32.49	31.63
-7	4	1	17.32	15.16
-6	4	1	72.21	70.01
-5	4	1	84.25	84.93
-4	4	1	53.32	56.35
-3	4	1	-2.97	0.17
-2	4	1	198.56	186.25
-1	4	1	134.72	121.45
0	4	1	-5.40	5.05
1	4	1	12.78	1.14
2	4	1	119.43	115.98
3	4	1	155.44	147.24
4	4	1	31.83	[illegible]
5	4	1	85.44	81.02
6	4	1	21.45	23.54
7	4	1	49.72	49.67
8	4	1	53.51	53.12
9	4	1	64.67	61.34
10	4	1	28.26	28.80
11	4	1	42.44	42.27
12	4	1	-12.97	13.22
13	4	1	43.35	44.56
14	4	1	-5.44	[illegible]
15	4	1	17.74	14.77
16	4	1	-3.27	3.41
-16	5	1	-4.86	3.15
-15	5	1	19.83	18.79
-14	5	1	0.0	1.38
-13	5	1	18.09	17.71
-12	5	1	22.44	19.17
-11	5	1	47.59	43.45
-10	5	1	-8.05	6.91
-9	5	1	60.25	55.55
-8	5	1	19.64	14.40
-7	5	1	73.17	69.55
-6	5	1	0.0	7.56
-5	5	1	46.33	37.31
-4	5	1	12.83	17.35
-3	5	1	87.64	81.98
-2	5	1	43.25	39.65
-1	5	1	49.41	52.80
0	5	1	12.86	[illegible]
1	5	1	48.57	53.50
2	5	1	53.41	52.13
3	5	1	40.90	41.92
4	5	1	15.72	14.75
5	5	1	26.05	[illegible]
6	5	1	29.75	27.17
7	5	1	-4.31	[illegible]
8	5	1	41.63	36.60
9	5	1	0.0	2.91
10	5	1	36.32	37.41
11	5	1	24.45	21.17
12	5	1	-4.75	[illegible]
13	5	1	-4.05	13.36
14	5	1	-9.64	11.63
15	5	1	-6.13	7.22
16	5	1	-2.67	3.92
-15	6	1	21.09	22.27
-14	6	1	-3.47	5.82
-13	6	1	65.13	63.42
-12	6	1	-12.55	12.24
-11	6	1	36.56	31.77
-10	6	1	39.59	35.67
-9	6	1	71.17	73.30
-8	6	1	39.44	36.15
-7	6	1	42.42	47.47
-6	6	1	25.24	21.64
-5	6	1	183.46	179.10
-4	6	1	136.07	141.24
-3	6	1	112.67	[illegible]
-2	6	1	41.56	37.82
-1	6	1	121.29	117.62
0	6	1	50.73	56.70
1	6	1	111.91	109.96
2	6	1	39.37	37.39
3	6	1	82.77	85.50
4	6	1	139.15	140.84
5	6	1	16.52	15.56
6	6	1	55.55	61.75
7	6	1	15.51	17.11
8	6	1	100.76	102.75
9	6	1	53.47	57.66
10	6	1	25.47	26.14
11	6	1	15.04	16.26
12	6	1	74.74	72.43
13	6	1	0.0	5.39
14	6	1	45.06	41.99
15	6	1	0.0	1.16
-15	7	1	41.80	41.35
-14	7	1	34.66	32.44
-13	7	1	17.17	15.41
-12	7	1	30.58	29.59
-11	7	1	24.64	23.50
-10	7	1	0.0	6.42
-9	7	1	-7.53	6.72
-8	7	1	30.84	32.64
-7	7	1	75.95	69.63
-6	7	1	73.05	71.60
-5	7	1	64.64	65.52
-4	7	1	27.24	26.20
-3	7	1	120.40	119.65
-2	7	1	52.91	53.46
-1	7	1	25.21	27.54
0	7	1	27.96	24.11
1	7	1	69.80	71.84
2	7	1	90.19	92.58
3	7	1	85.14	82.64
4	7	1	-13.01	11.66
5	7	1	96.47	93.22
6	7	1	79.69	74.89
7	7	1	61.65	59.23
8	7	1	-6.17	2.61
9	7	1	51.45	52.19
10	7	1	26.01	24.44
11	7	1	21.30	21.72
12	7	1	16.22	12.77
13	7	1	26.09	23.39
14	7	1	26.29	25.39
-14	8	1	27.73	26.05
-13	8	1	-10.31	7.84
-12	8	1	-4.61	9.87
-11	8	1	-9.81	3.19
-10	8	1	23.22	22.17
-9	8	1	35.47	35.26
-8	8	1	31.07	37.19
-7	8	1	48.27	44.16
-6	8	1	44.77	47.31
-5	8	1	-9.03	7.21
-4	8	1	25.10	23.11
-3	8	1	50.70	54.87
-2	8	1	100.91	99.79
-1	8	1	15.81	19.44
0	8	1	90.59	92.76
1	8	1	-4.22	7.67
2	8	1	75.81	75.61
3	8	1	15.35	14.47
4	8	1	50.28	51.52
5	8	1	-26.93	31.05
6	8	1	50.94	51.59
7	8	1	-14.05	15.92
8	8	1	45.85	46.91
9	8	1	23.28	21.62
10	8	1	43.45	44.04
11	8	1	21.05	19.50
12	8	1	33.71	34.33
13	8	1	-14.14	15.36
14	8	1	16.69	16.87
-13	9	1	18.85	21.06
-12	9	1	23.17	21.79
-11	9	1	0.0	3.54
-10	9	1	51.33	51.34
-9	9	1	26.55	28.29
-8	9	1	32.17	33.28
-7	9	1	17.24	13.63
-6	9	1	43.67	47.93
-5	9	1	-6.97	9.38
-4	9	1	23.18	23.52
-3	9	1	36.67	26.73
-2	9	1	55.50	47.55
-1	9	1	18.73	16.97
0	9	1	-15.61	15.81
1	9	1	50.93	[illegible]
2	9	1	41.40	41.74
3	9	1	25.09	27.44
4	9	1	-5.07	1.02
5	9	1	36.73	40.75
6	9	1	42.53	42.59
7	9	1	28.91	30.16
8	9	1	-6.42	2.55
9	9	1	37.49	35.03
10	9	1	17.12	16.52
11	9	1	25.54	23.21
12	9	1	20.95	21.45
-12	10	1	-7.63	4.37
-11	10	1	25.32	23.49
-10	10	1	0.0	2.64
-9	10	1	32.36	29.57
-8	10	1	35.91	37.05
-7	10	1	21.13	[illegible]
-6	10	1	23.93	24.75
-5	10	1	70.77	71.60
-4	10	1	54.61	57.52
-3	10	1	31.54	31.00
-2	10	1	0.0	[illegible]
-1	10	1	51.59	57.23
0	10	1	24.97	24.20
1	10	1	50.34	53.12
2	10	1	15.53	15.41
3	10	1	35.64	36.87
4	10	1	65.42	[illegible]
5	10	1	-15.42	14.19
6	10	1	-5.61	1.64
7	10	1	21.31	21.05
8	10	1	29.97	[illegible]
9	10	1	27.96	27.69
10	10	1	-20.37	[illegible]
11	10	1	22.75	19.10
-10	11	1	-14.54	11.04
-9	11	1	-5.00	5.37
-8	11	1	-7.12	4.74
-7	11	1	0.0	1.80
-6	11	1	-15.21	5.87
-5	11	1	28.33	28.18
-4	11	1	0.0	4.30
-3	11	1	15.42	11.55
-2	11	1	0.0	4.07
-1	11	1	-6.94	3.76
0	11	1	0.0	7.20
1	11	1	16.22	17.35
2	11	1	17.29	14.57
3	11	1	25.60	19.20
4	11	1	-5.56	5.20
5	11	1	-11.74	7.37
6	11	1	-12.56	15.54
7	11	1	-4.55	[illegible]
8	11	1	-14.37	10.66
9	11	1	-11.79	11.03
10	11	1	0.0	2.44
-8	12	1	33.63	32.71
-7	12	1	37.63	39.50
-5	12	1	49.21	41.17
-4	12	1	18.74	22.24
-3	12	1	25.41	[illegible]
-2	12	1	31.46	34.71
-1	12	1	64.09	72.20
0	12	1	-54.15	74.60
1	12	1	-11.42	13.34
2	12	1	25.49	26.67
3	12	1	45.59	40.44
4	12	1	61.22	65.20
5	12	1	20.97	19.61
6	12	1	-14.60	17.12
7	12	1	29.77	28.59
8	12	1	51.96	51.71
-5	13	1	0.0	1.66
-4	13	1	-14.41	12.62
-3	13	1	18.62	16.31
-2	13	1	21.55	23.60
-1	13	1	-9.16	7.11
0	13	1	-4.77	4.49
1	13	1	20.56	15.82
2	13	1	30.13	17.74
3	13	1	0.0	11.29
4	13	1	-5.19	4.92
5	13	1	-9.43	15.56
-17	0	2	53.16	49.78
-16	0	2	21.87	25.67
-15	0	2	-4.33	3.76
-14	0	2	-11.94	13.96
-13	0	2	106.27	107.94
-12	0	2	44.71	45.74
-11	0	2	-5.74	11.39
-10	0	2	-2.55	13.63
-9	0	2	217.20	244.82
-8	0	2	55.33	46.50
-7	0	2	0.0	5.63
-6	0	2	40.76	34.72
-5	0	2	117.38	132.04
-4	0	2	136.25	148.14
-3	0	2	24.97	25.00
-2	0	2	79.55	76.97
-1	0	2	332.26	407.65
0	0	2	39.73	33.61
1	0	2	8.33	17.12
2	0	2	134.75	157.21
3	0	2	195.85	230.48
4	0	2	-10.73	7.12
5	0	2	45.72	55.66
6	0	2	31.41	34.27
7	0	2	163.42	173.96
9	0	2	60.67	56.62
10	0	2	99.54	113.67
11	0	2	79.33	83.13
12	0	2	30.37	27.60
13	0	2	-12.26	12.67
14	0	2	27.17	30.44
15	0	2	56.29	56.45
16	0	2	28.92	26.40
-17	1	2	31.86	29.01
-16	1	2	-4.56	1.77
-15	1	2	14.69	14.40
-14	1	2	15.17	13.51
-13	1	2	43.43	44.73
-12	1	2	-13.30	13.76
-11	1	2	39.25	39.57
-10	1	2	56.26	60.56
-9	1	2	34.56	38.48
-8	1	2	12.48	14.86
-7	1	2	32.15	31.49
-6	1	2	-3.40	5.00
-5	1	2	96.91	101.28
-4	1	2	69.79	67.50
-3	1	2	17.89	22.34
-2	1	2	178.56	153.39
-1	1	2	40.95	29.54
0	1	2	72.36	57.19
1	1	2	85.70	92.30
2	1	2	89.91	91.34
3	1	2	126.08	138.37
4	1	2	70.11	76.00
5	1	2	31.92	34.35
6	1	2	0.0	3.93
7	1	2	-7.90	9.21
8	1	2	-11.01	11.69
9	1	2	19.38	22.67
10	1	2	21.77	22.65
11	1	2	29.37	26.57
12	1	2	-1.15	2.97
13	1	2	25.34	22.40
14	1	2	14.26	15.12
15	1	2	-12.46	11.79
16	1	2	0.0	4.67
-17	2	2	16.98	19.72
-16	2	2	0.0	4.79
-15	2	2	-12.46	7.91
-14	2	2	0.0	1.19
-13	2	2	35.72	35.41
-12	2	2	-11.25	12.12
-11	2	2	14.21	15.15
-10	2	2	-6.71	6.62
-9	2	2	78.16	70.61
-8	2	2	-8.47	4.55
-7	2	2	44.17	47.56
-6	2	2	27.19	26.70
-5	2	2	102.22	97.11
-4	2	2	-2.27	4.96
-3	2	2	45.54	44.13
-2	2	2	31.17	26.02
-1	2	2	132.79	171.58
0	2	2	43.56	39.94
1	2	2	30.49	35.73
2	2	2	46.39	43.10
3	2	2	63.56	62.67
4	2	2	114.34	120.26
5	2	2	33.04	25.61
6	2	2	15.08	15.93
7	2	2	17.31	25.41
8	2	2	45.31	40.50
9	2	2	-4.03	7.01
10	2	2	0.0	1.14
11	2	2	18.53	16.72
12	2	2	37.43	32.27
13	2	2	-12.19	16.30
14	2	2	-9.30	9.73
15	2	2	-5.53	6.30
16	2	2	-14.59	11.67
-17	3	2	12.12	22.15
-16	3	2	0.0	2.70
-15	3	2	-10.91	12.59
-14	3	2	-8.67	3.12
-13	3	2	52.41	53.06
-12	3	2	-12.58	6.51
-11	3	2	62.07	64.65
-10	3	2	37.43	42.91
-9	3	2	62.56	61.43
-8	3	2	-10.91	9.43
-7	3	2	65.42	69.15
-6	3	2	-8.39	11.65
-5	3	2	55.59	66.52
-4	3	2	72.42	64.57
-3	3	2	71.12	61.97
-2	3	2	82.25	92.49
-1	3	2	-3.32	9.14
0	3	2	70.37	63.47
1	3	2	134.11	132.90
2	3	2	24.96	15.31
3	3	2	47.19	50.43
4	3	2	38.56	46.19
5	3	2	85.51	72.27
6	3	2	21.94	27.60
7	3	2	-7.77	7.58
8	3	2	54.81	43.18
9	3	2	0.0	4.69
10	3	2	27.57	4.11
11	3	2	28.79	31.54
12	3	2	-11.43	11.25
13	3	2	25.31	23.64
14	3	2	-6.81	5.56
15	3	2	-10.75	11.17
16	3	2	0.0	2.77
-16	4	2	21.67	2.77
-15	4	2	-4.54	2.46
-14	4	2	-10.65	9.27
-13	4	2	43.40	47.39
-12	4	2	25.11	24.06
-11	4	2	-5.59	4.92
-9	4	2	134.62	117.57
-8	4	2	44.47	35.47
-7	4	2	-11.15	10.67
-6	4	2	51.51	47.54
-5	4	2	95.84	95.32
-4	4	2	125.63	115.73
-3	4	2	33.06	36.17
-2	4	2	95.65	93.82
-1	4	2	158.53	151.36
0	4	2	39.65	32.75
1	4	2	71.22	63.09
2	4	2	64.52	74.22
3	4	2	61.76	65.79
4	4	2	44.74	47.60
5	4	2	52.98	51.17
6	4	2	73.79	71.41
7	4	2	109.75	107.44
9	4	2	-5.44	4.77
10	4	2	117.85	127.17
11	4	2	54.69	54.03
12	4	2	-7.19	7.37
13	4	2	41.24	41.19
14	4	2	33.61	31.67
15	4	2	45.49	43.50
16	4	2	-4.25	6.37
-16	5	2	-14.49	13.16
-15	5	2	42.75	37.69
-14	5	2	26.02	24.46
-13	5	2	-2.60	5.46
-12	5	2	26.49	27.19
-11	5	2	-11.54	15.75
-10	5	2	19.60	13.81
-9	5	2	19.63	20.82
-8	5	2	61.11	53.15
-7	5	2	32.35	35.78
-6	5	2	44.20	47.70
-5	5	2	38.36	36.47
-4	5	2	34.64	33.73
-2	5	2	0.0	4.24
-1	5	2	36.53	32.49
0	5	2	45.48	40.42
1	5	2	-0.43	5.67
2	5	2	36.53	35.11
3	5	2	45.86	52.12
4	5	2	28.45	34.14
5	5	2	35.43	34.20
6	5	2	114.49	125.62
7	5	2	24.53	20.78
8	5	2	17.71	19.54
9	5	2	33.52	32.35
10	5	2	30.45	29.15
11	5	2	19.79	1.17
12	5	2	-11.55	7.95
13	5	2	-8.16	17.71
14	5	2	31.55	30.71
15	5	2	25.88	30.84
-15	6	2	-7.65	8.50

Table 15

continued:-

h	k	l	F_o	F_c
-14	6	2	-6.43	5.95
-13	6	2	31.50	28.11
-12	6	2	-3.22	6.07
-11	6	2	-11.43	10.37
-10	6	2	-11.71	10.42
-9	6	2	59.92	59.65
-8	6	2	-5.53	9.95
-7	6	2	26.32	25.10
-6	6	2	0.0	9.34
-5	6	2	140.02	139.76
-4	6	2	14.52	13.73
-3	6	2	-5.02	9.27
-2	6	2	40.96	35.43
-1	6	2	131.58	122.27
0	6	2	38.22	38.60
1	6	2	-11.22	17.29
2	6	2	37.81	36.56
3	6	2	102.14	97.66
4	6	2	25.75	29.74
5	6	2	39.56	35.18
6	6	2	66.30	64.52
7	6	2	92.68	95.23
8	6	2	-9.56	2.75
9	6	2	18.27	14.80
10	6	2	40.71	41.64
11	6	2	42.58	41.68
12	6	2	21.30	29.02
13	6	2	0.0	2.61
14	6	2	38.01	37.59
15	6	2	22.60	19.06
-15	7	2	0.0	1.59
-14	7	2	0.0	1.16
-13	7	2	26.90	29.06
-12	7	2	35.50	36.10
-11	7	2	-12.35	12.70
-10	7	2	-7.13	2.84
-9	7	2	50.36	47.58
-8	7	2	49.34	49.73
-7	7	2	-6.87	5.77
-6	7	2	0.0	3.95
-5	7	2	68.57	65.29
-4	7	2	14.57	17.16
-3	7	2	32.90	33.07
-2	7	2	0.0	2.95
-1	7	2	39.95	42.54
0	7	2	20.75	2.26
1	7	2	38.08	36.80
2	7	2	29.16	29.55
3	7	2	54.26	51.70
4	7	2	24.31	22.03
5	7	2	33.52	29.06
6	7	2	-3.92	1.74
7	7	2	41.13	39.76
8	7	2	33.85	33.77
9	7	2	14.79	11.85
10	7	2	26.42	26.20
11	7	2	20.69	19.82
12	7	2	-3.34	1.37
13	7	2	-9.07	6.80
14	7	2	-11.19	3.73
-14	8	2	20.44	21.95
-13	8	2	-4.72	6.24
-12	8	2	36.28	39.44
-11	8	2	-13.21	14.71
-10	8	2	28.19	27.41
-9	8	2	47.63	51.24
-8	8	2	41.34	37.81
-7	8	2	25.29	26.99
-6	8	2	55.32	56.71
-5	8	2	-13.06	14.64
-4	8	2	97.54	95.67
-3	8	2	-13.99	4.03
-2	8	2	75.33	83.60
-1	8	2	54.59	55.80
0	8	2	63.89	58.31
1	8	2	28.65	24.54
2	8	2	43.97	55.75
3	8	2	35.33	32.43
4	8	2	65.92	63.52
5	8	2	65.29	67.03
6	8	2	52.97	54.91
7	8	2	-10.84	6.45
8	8	2	25.59	26.86
9	8	2	-12.43	15.80
10	8	2	51.49	53.16
11	8	2	-11.29	3.18
12	8	2	26.39	25.37
13	8	2	36.53	34.87
-13	9	2	-6.29	3.11
-12	9	2	-5.03	3.49
-11	9	2	-7.81	1.47
-10	9	2	20.42	17.56
-9	9	2	31.45	34.17
-8	9	2	26.35	5.16
-7	9	2	-9.37	17.52
-6	9	2	-12.01	17.73
-5	9	2	22.06	22.70
-4	9	2	0.0	1.06
-3	9	2	-4.64	4.56
-2	9	2	18.32	15.29
-1	9	2	45.72	47.27
0	9	2	21.33	27.44
1	9	2	-12.01	7.37
2	9	2	-14.01	14.33
3	9	2	-3.61	2.47
4	9	2	-13.46	4.67
5	9	2	-10.29	7.11
6	9	2	25.24	27.37
9	9	2	22.01	19.14
10	9	2	-14.91	15.55
11	9	2	-12.47	9.55
12	9	2	-6.04	7.16
-11	10	2	-4.21	6.71
-10	10	2	33.02	34.01
-9	10	2	25.07	26.03
-8	10	2	25.03	26.81
-7	10	2	-3.29	3.66
-6	10	2	48.37	49.50
-5	10	2	49.09	53.66
-4	10	2	21.16	24.56
-3	10	2	-13.52	12.17
-2	10	2	48.74	49.26
-1	10	2	45.52	46.83
0	10	2	44.76	41.91
1	10	2	21.52	21.76
2	10	2	60.83	61.56
3	10	2	31.88	27.86
4	10	2	-12.26	13.04
5	10	2	0.0	2.95
6	10	2	53.33	55.25
7	10	2	23.66	22.92
8	10	2	24.75	24.62
9	10	2	30.81	30.49
10	10	2	32.41	31.01
11	10	2	-12.30	13.25
-10	11	2	-7.42	1.03
-9	11	2	17.93	15.41
-8	11	2	25.55	27.39
-7	11	2	-12.95	11.48
-6	11	2	-8.51	3.91
-5	11	2	-9.15	8.41
-4	11	2	22.29	23.87
-3	11	2	-12.21	11.32
-2	11	2	19.17	16.51
-1	11	2	-10.47	13.63
0	11	2	27.27	26.35
1	11	2	16.29	15.15
2	11	2	23.25	23.16

h	k	l	F_o	F_c
3	11	2	-4.60	4.11
4	11	2	17.86	18.73
5	11	2	-11.51	9.34
6	11	2	-7.51	7.99
7	11	2	21.00	17.76
8	11	2	-9.39	3.76
9	11	2	-15.00	13.72
-8	12	2	-3.97	5.17
-6	12	2	0.0	4.10
-5	12	2	-6.09	0.67
-4	12	2	20.03	23.49
-3	12	2	16.02	15.81
-2	12	2	18.11	17.11
-1	12	2	-8.13	9.21
0	12	2	-5.69	1.11
1	12	2	0.0	1.48
2	12	2	16.74	20.42
3	12	2	19.73	22.60
4	12	2	-5.91	6.93
5	12	2	33.15	35.06
6	12	2	-15.14	16.43
7	12	2	-4.30	3.64
-4	13	2	-14.32	14.59
-3	13	2	-13.91	14.17
-2	13	2	31.10	31.23
-1	13	2	20.74	22.95
0	13	2	0.0	2.53
1	13	2	19.17	22.71
2	13	2	33.13	35.64
3	13	2	-8.32	7.83
4	13	2	-7.11	15.71
-17	1	3	0.0	2.25
-16	1	3	30.58	29.14
-15	1	3	18.75	17.86
-14	1	3	28.61	25.86
-13	1	3	0.0	6.50
-12	1	3	62.26	61.45
-11	1	3	17.44	15.26
-10	1	3	51.15	51.55
-9	1	3	49.11	50.68
-8	1	3	53.15	56.34
-7	1	3	-1.12	8.37
-6	1	3	21.34	26.50
-5	1	3	40.26	38.53
-4	1	3	31.99	34.31
-3	1	3	117.87	102.60
-2	1	3	25.06	31.22
-1	1	3	253.14	236.04
0	1	3	89.53	71.58
1	1	3	110.20	119.00
2	1	3	104.96	119.74
3	1	3	38.17	41.44
4	1	3	-11.21	13.79
5	1	3	39.54	41.57
6	1	3	55.66	61.18
7	1	3	55.63	62.24
8	1	3	39.30	40.79
9	1	3	15.83	15.25
10	1	3	33.17	34.83
11	1	3	43.72	43.80
12	1	3	27.63	26.67
13	1	3	19.39	22.42
14	1	3	42.34	39.94
15	1	3	-8.17	5.98
16	1	3	-14.43	13.13
-17	2	3	-9.63	2.59
-16	2	3	22.26	19.85
-15	2	3	15.60	19.62
-14	2	3	35.91	34.17
-13	2	3	-1.57	2.60
-12	2	3	74.92	73.54
-11	2	3	46.24	47.65
-10	2	3	14.90	13.08
-9	2	3	-9.60	6.73
-8	2	3	107.[illegible]	111.08
-7	2	3	134.25	137.10
-6	2	3	-7.47	9.49
-5	2	3	102.57	92.51
-4	2	3	41.44	33.19
-3	2	3	116.58	124.32
-2	2	3	52.07	51.35
-1	2	3	-10.41	3.82
0	2	3	145.83	142.28
1	2	3	0.0	1.16
2	2	3	-11.72	1.66
3	2	3	47.24	50.76
4	2	3	45.69	45.35
5	2	3	139.51	143.07
6	2	3	51.23	51.04
7	2	3	90.41	91.09
8	2	3	119.92	126.22
9	2	3	-7.57	11.50
10	2	3	23.17	15.67
11	2	3	62.54	61.86
12	2	3	56.79	64.18
13	2	3	35.02	30.21
14	2	3	29.11	31.02
15	2	3	16.78	17.69
16	2	3	55.20	52.50
-16	3	3	-7.55	9.12
-15	3	3	66.25	36.42
-14	3	3	-14.69	15.15
-13	3	3	-12.15	8.20
-12	3	3	-17.66	7.81
-11	3	3	29.10	29.56
-13	3	3	41.54	45.15
-9	3	3	35.54	35.20
-8	3	3	13.21	17.29
-7	3	3	50.63	51.76
-6	3	3	24.84	24.10
-5	3	3	12.39	11.56
-4	3	3	37.21	33.00
-3	3	3	57.65	53.44
-2	3	3	-2.78	2.03
-1	3	3	170.08	157.62
0	3	3	26.75	30.93
1	3	3	74.46	71.33
2	3	3	42.64	47.35
3	3	3	-10.43	4.06
4	3	3	62.33	61.78
5	3	3	22.83	17.34
6	3	3	55.65	59.17
7	3	3	34.48	32.55
8	3	3	32.43	33.01
9	3	3	26.07	24.98
10	3	3	21.79	19.15
11	3	3	-5.72	5.26
12	3	3	-6.84	7.24
13	3	3	-4.27	0.72
14	3	3	16.49	16.64
15	3	3	20.25	13.41
16	3	3	-13.27	1.24
-16	4	3	17.36	12.54
-15	4	3	24.51	23.71
-14	4	3	22.25	24.25
-13	4	3	-7.56	9.24
-12	4	3	19.63	14.37
-11	4	3	40.67	42.52
-10	4	3	-12.64	7.81
-9	4	3	-13.93	14.65
-8	4	3	94.05	89.55
-7	4	3	-8.67	14.14
-6	4	3	-7.69	4.19
-5	4	3	29.39	24.36
-4	4	3	103.37	92.44
-3	4	3	58.34	57.02
-2	4	3	17.51	16.46
-1	4	3	28.29	23.85
0	4	3	12.63	14.31
1	4	3	43.55	41.73
2	4	3	17.89	15.39

h	k	l	F_o	F_c
3	4	3	39.27	33.00
4	4	3	74.59	68.98
5	4	3	15.79	12.38
6	4	3	0.0	1.01
7	4	3	13.48	11.24
8	4	3	65.41	63.20
9	4	3	17.67	20.43
10	4	3	24.22	24.45
11	4	3	-2.71	3.13
12	4	3	35.10	34.08
13	4	3	0.0	1.33
14	4	3	-10.62	5.16
15	4	3	-8.13	6.47
-16	5	3	20.15	24.15
-15	5	3	24.44	26.28
-14	5	3	19.71	20.61
-13	5	3	-2.60	5.13
-12	5	3	29.84	30.04
-11	5	3	26.11	28.40
-10	5	3	62.22	65.66
-9	5	3	25.31	27.72
-8	5	3	27.30	28.90
-7	5	3	47.94	49.87
-6	5	3	43.65	43.06
-5	5	3	56.08	57.84
-4	5	3	42.94	40.75
-3	5	3	34.98	33.18
-2	5	3	61.72	57.35
-1	5	3	92.83	95.72
0	5	3	0.0	2.37
1	5	3	20.41	20.54
2	5	3	64.65	66.96
3	5	3	45.73	43.03
4	5	3	43.83	44.09
5	5	3	-8.63	5.84
6	5	3	17.56	19.96
7	5	3	93.47	88.20
8	5	3	-13.33	13.70
9	5	3	16.39	13.11
10	5	3	24.24	25.66
11	5	3	18.07	17.21
12	5	3	-11.12	5.86
13	5	3	-8.52	3.66
14	5	3	17.82	17.36
15	5	3	-10.94	7.77
-15	6	3	-11.52	14.24
-14	6	3	34.79	37.38
13	6	3	62.53	23.31
-12	6	3	24.15	27.21
-11	6	3	15.63	26.05
-10	6	3	30.69	32.55
-9	6	3	21.89	16.83
-8	6	3	72.81	69.79
-7	6	3	91.86	96.19
-6	6	3	34.95	34.25
-5	6	3	105.51	102.46
-4	6	3	35.17	33.10
-3	6	3	124.10	124.44
-2	6	3	54.19	64.21
-1	6	3	91.50	93.22
0	6	3	96.79	91.48
1	6	3	59.11	59.51
2	6	3	15.64	14.55
3	6	3	104.79	97.63
4	6	3	37.17	36.54
5	6	3	110.68	111.54
6	6	3	44.71	41.24
7	6	3	102.93	98.83
8	6	3	55.72	54.70
9	6	3	20.65	20.55
10	6	3	-3.38	2.48
11	6	3	68.65	65.21
12	6	3	23.55	27.40
13	6	3	27.07	29.34
14	6	3	33.47	27.36
-14	7	3	25.27	21.32
-13	7	3	0.0	3.15
-12	7	3	24.24	23.54
-11	7	3	14.95	12.14
-10	7	3	0.0	4.51
-9	7	3	17.55	9.62
-8	7	3	19.85	20.15
-7	7	3	51.34	44.92
-6	7	3	65.12	71.25
-5	7	3	47.72	44.05
-4	7	3	22.63	20.43
-3	7	3	45.50	40.05
-2	7	3	29.82	29.60
-1	7	3	-5.45	7.97
0	7	3	40.97	45.97
1	7	3	17.30	16.02
2	7	3	29.12	26.86
3	7	3	87.53	84.30
4	7	3	-4.63	3.74
5	7	3	18.46	13.38
6	7	3	52.69	51.57
7	7	3	63.45	59.71
8	7	3	-12.81	6.75
9	7	3	24.33	24.88
10	7	3	36.95	34.52
11	7	3	0.0	3.10
12	7	3	-13.44	12.74
13	7	3	-7.37	6.17
-13	8	3	-7.13	11.32
-12	8	3	-8.44	3.35
-11	8	3	39.09	34.45
-10	8	3	30.73	29.10
-9	8	3	27.90	31.16
-8	8	3	28.53	26.04
-7	8	3	39.90	43.41
-6	8	3	26.97	27.81
-5	8	3	27.44	26.62
-4	8	3	69.60	72.26
-3	8	3	83.28	83.63
-2	8	3	-5.15	9.47
-1	8	3	76.15	74.54
0	8	3	18.18	19.78
1	8	3	68.79	70.56
2	8	3	-12.26	13.83
3	8	3	59.98	61.46
4	8	3	47.99	43.62
5	8	3	33.22	35.82
6	8	3	-8.25	4.29
7	8	3	44.79	45.09
8	8	3	40.94	45.43
9	8	3	37.86	35.21
10	8	3	36.12	35.19
11	8	3	28.72	26.78
12	8	3	22.56	18.54
13	8	3	-12.17	12.22
-12	9	3	0.0	2.51
-11	9	3	42.18	44.64
-10	9	3	-13.91	10.92
-9	9	3	-2.66	9.20
-8	9	3	-9.93	13.90
-7	9	3	50.73	51.45
-6	9	3	-6.29	5.75
-5	9	3	19.49	18.36
-4	9	3	-4.81	4.75
-3	9	3	53.99	53.91
-2	9	3	-10.71	13.13
-1	9	3	-5.89	2.76
0	9	3	0.0	1.63
1	9	3	46.02	47.76
2	9	3	28.39	27.05
3	9	3	-7.26	7.09
4	9	3	-8.11	7.83
5	9	3	40.66	43.77
6	9	3	-6.87	8.41
7	9	3	15.48	14.65

h	k	l	F_o	F_c
8	9	3	16.70	16.46
9	9	3	23.62	19.33
10	9	3	-6.17	7.83
11	9	3	-12.03	12.43
12	9	3	-4.27	9.95
-11	10	3	-9.85	11.40
-10	10	3	-14.05	13.72
-9	10	3	0.0	8.86
-8	10	3	38.14	39.61
-7	10	3	-9.38	9.33
-6	10	3	-8.31	2.58
-5	10	3	29.87	29.20
-4	10	3	0.0	6.89
-3	10	3	21.72	24.98
-2	10	3	23.96	23.90
-1	10	3	22.84	26.11
0	10	3	30.85	33.01
1	10	3	25.01	28.93
2	10	3	18.84	16.59
3	10	3	45.70	51.69
4	10	3	23.62	23.63
5	10	3	29.38	29.79
6	10	3	15.88	20.12
7	10	3	28.96	31.79
8	10	3	-10.60	7.24
9	10	3	-9.12	1.96
10	10	3	0.0	5.60
-9	11	3	0.0	6.26
-8	11	3	-10.22	6.38
-7	11	3	0.0	1.14
-6	11	3	22.59	22.16
-5	11	3	-12.74	14.85
-4	11	3	-11.39	11.24
-3	11	3	-9.18	9.27
-2	11	3	-4.42	2.07
0	11	3	-12.54	13.83
1	11	3	15.87	17.87
2	11	3	-4.22	1.41
3	11	3	-9.38	15.72
4	11	3	29.44	20.47
5	11	3	20.47	27.37
6	11	3	0.0	3.25
7	11	3	-9.27	7.63
8	11	3	0.0	3.46
9	11	3	-5.11	4.93
-7	12	3	22.99	23.39
-6	12	3	18.07	15.66
-5	12	3	28.36	29.04
-4	12	3	15.55	13.71
-3	12	3	40.51	41.14
-2	12	3	15.23	12.04
-1	12	3	30.44	31.65
0	12	3	0.0	4.02
1	12	3	53.22	53.42
2	12	3	-12.53	3.06
3	12	3	46.82	49.98
4	12	3	22.06	20.95
5	12	3	19.17	21.20
6	12	3	0.0	2.92
-2	13	3	-6.02	4.45
-3	13	3	-14.29	15.27
-1	13	3	-10.57	7.71
0	13	3	-14.39	15.61
1	13	3	17.85	15.85
2	13	3	-9.32	17.04
-17	0	4	0.0	9.51
-16	0	4	-8.12	17.35
-15	0	4	-8.03	8.34
-14	0	4	26.24	26.27
-13	0	4	24.67	24.93
-12	0	4	51.36	53.77
-11	0	4	68.57	75.52
-10	0	4	99.97	110.34
-9	0	4	56.13	55.79
-8	0	4	77.86	95.57
-7	0	4	79.61	97.47
-6	0	4	136.08	149.77
-5	0	4	57.35	61.5[illegible]
-4	0	4	85.95	85.97
-3	0	4	38.34	50.35
-2	0	4	33.32	1.77
-1	0	4	-2.94	7.44
0	0	4	210.79	223.93
1	0	4	222.77	250.11
2	0	4	-7.73	9.26
3	0	4	40.13	39.28
4	0	4	18.73	21.39
5	0	4	169.72	175.75
6	0	4	97.44	105.49
7	0	4	34.14	32.12
8	0	4	0.0	4.21
9	0	4	156.87	169.63
10	0	4	18.81	19.83
11	0	4	-10.26	12.74
12	0	4	0.0	1.45
13	0	4	62.52	61.72
14	0	4	18.43	15.95
15	0	4	-10.51	17.76
-17	1	4	-14.75	12.09
-16	1	4	-12.66	14.26
-15	1	4	-8.11	4.27
-14	1	4	45.10	45.09
-13	1	4	-13.19	15.12
-12	1	4	25.23	25.09
-11	1	4	55.79	59.82
-10	1	4	20.24	19.08
-9	1	4	41.85	47.37
-8	1	4	19.39	22.39
-7	1	4	36.94	40.16
-6	1	4	52.03	50.31
-5	1	4	34.92	33.02
-4	1	4	11.35	14.39
-3	1	4	59.79	51.59
-2	1	4	34.63	36.63
-1	1	4	23.12	13.17
0	1	4	120.23	124.21
1	1	4	25.97	29.19
2	1	4	36.24	32.93
3	1	4	-11.79	8.79
4	1	4	34.77	45.66
5	1	4	74.64	70.10
6	1	4	-1.51	0.61
7	1	4	0.0	1.72
8	1	4	0.0	5.27
9	1	4	17.19	19.56
10	1	4	-4.16	7.94
11	1	4	-13.01	12.49
12	1	4	-9.72	5.07
13	1	4	-8.46	12.41
14	1	4	16.85	15.63
15	1	4	-9.18	7.49
-16	2	4	18.56	13.02
-15	2	4	-4.11	1.25
-14	2	4	24.75	23.06
-13	2	4	16.05	21.43
-12	2	4	28.77	30.01
-11	2	4	-12.43	11.73
-10	2	4	51.37	54.26
-9	2	4	-6.73	10.85
-8	2	4	20.34	23.03
-5	2	4	25.97	33.83
-4	2	4	113.07	121.45
-3	2	4	56.93	51.82
-2	2	4	46.73	37.16
-1	2	4	23.46	28.85
0	2	4	97.20	84.19
1	2	4	68.35	66.74
2	2	4	20.53	15.70
3	2	4	31.19	34.26
4	2	4	34.29	33.99

h	k	l	F_o	F_c
5	2	4	97.15	94.40
6	2	4	15.00	15.22
7	2	4	31.94	29.07
8	2	4	18.79	21.94
9	2	4	43.46	45.82
10	2	4	14.62	5.37
11	2	4	16.62	14.07
12	2	4	16.03	20.73
13	2	4	29.82	28.73
14	2	4	-6.77	4.45
15	2	4	-5.98	1.22
-16	3	4	22.72	22.12
-15	3	4	21.15	22.66
-14	3	4	35.67	39.95
-13	3	4	-11.39	11.37
-11	3	4	69.42	71.93
-10	3	4	15.69	17.72
-9	3	4	14.23	17.34
-8	3	4	41.71	39.87
-7	3	4	74.82	73.76
-6	3	4	48.17	45.71
-5	3	4	28.61	24.64
-4	3	4	62.90	54.35
-3	3	4	108.23	105.40
-2	3	4	36.56	24.50
-1	3	4	39.28	23.69
0	3	4	-9.47	14.87
1	3	4	71.17	71.61
2	3	4	32.37	32.62
3	3	4	36.22	32.34
4	3	4	65.16	62.55
5	3	4	95.60	102.98
6	3	4	24.81	24.25
7	3	4	26.39	25.72
8	3	4	-12.89	13.22
9	3	4	30.74	35.37
10	3	4	30.04	31.43
11	3	4	22.59	24.59
12	3	4	-8.23	10.75
13	3	4	24.04	22.27
15	3	4	-10.12	9.42
-16	4	4	-11.94	15.66
-15	4	4	-7.30	11.99
-14	4	4	-3.74	5.42
-13	4	4	33.29	35.47
-12	4	4	-7.79	7.70
-10	4	4	43.58	44.71
-9	4	4	-9.91	12.41
-8	4	4	15.45	22.44
-7	4	4	80.58	74.77
-6	4	4	123.96	117.94
-5	4	4	59.32	54.47
-3	4	4	100.27	93.34
-1	4	4	29.30	24.51
0	4	4	0.0	7.62
1	4	4	183.06	165.59
2	4	4	46.70	43.71
3	4	4	-5.77	3.94
4	4	4	64.27	62.13
5	4	4	109.91	176.89
6	4	4	126.07	123.94
7	4	4	-9.02	11.37
8	4	4	65.65	61.91
9	4	4	121.12	133.96
10	4	4	-13.81	10.55
11	4	4	15.33	14.09
12	4	4	38.94	33.32
13	4	4	38.90	34.56
14	4	4	27.31	26.42
15	4	4	-14.01	9.49
-15	5	4	20.02	20.61
-14	5	4	35.39	37.31
-13	5	4	-3.75	4.01
-12	5	4	27.66	24.35
-11	5	4	-7.51	7.09
-10	5	4	19.38	13.34
-9	5	4	37.56	41.29
-8	5	4	31.47	35.59
-7	5	4	18.45	14.10
-6	5	4	110.31	102.53
-5	5	4	31.14	24.92
-4	5	4	42.59	42.45
-3	5	4	44.26	41.66
-2	5	4	60.11	42.54
-1	5	4	21.23	24.07
0	5	4	102.42	100.97
1	5	4	82.49	83.14
2	5	4	63.26	64.36
3	5	4	41.93	38.93
4	5	4	23.73	16.35
5	5	4	55.39	57.20
6	5	4	19.24	21.21
7	5	4	49.37	47.07
9	5	4	46.41	43.01
10	5	4	29.45	30.12
11	5	4	22.10	24.85
12	5	4	0.0	2.43
13	5	4	-11.83	12.13
14	5	4	15.68	14.11
-15	6	4	-13.44	15.26
-14	6	4	31.35	30.19
-13	6	4	21.69	22.21
-12	6	4	26.42	27.47
-11	6	4	-9.33	6.41
-10	6	4	44.11	44.51
-9	6	4	16.48	13.68
-9	6	4	35.59	33.36
-7	6	4	87.77	85.90
-6	6	4	38.57	39.41
-5	6	4	-10.01	8.49
-4	6	4	90.29	97.37
-3	6	4	126.83	124.79
-2	6	4	83.05	77.37
-1	6	4	33.01	32.13
0	6	4	28.62	29.94
1	6	4	92.29	99.73
2	6	4	36.03	35.26
3	6	4	-8.53	5.12
4	6	4	61.47	55.44
5	6	4	131.10	131.91
6	6	4	26.94	24.52
7	6	4	-12.80	10.37
8	6	4	17.23	15.41
9	6	4	83.57	83.03
10	6	4	17.15	16.27
11	6	4	16.03	14.50
12	6	4	-6.79	9.68
13	6	4	45.51	47.35
14	6	4	-5.81	2.76
-14	7	4	41.55	42.47
-13	7	4	26.34	27.11
-11	7	4	-4.93	5.85
-10	7	4	43.59	44.39
-9	7	4	22.67	23.32
-8	7	4	-7.11	4.23
-7	7	4	-9.71	9.79
-6	7	4	88.66	86.41
-5	7	4	-5.26	2.41
-4	7	4	19.77	22.51
-3	7	4	40.54	39.02
-2	7	4	74.67	70.49
-1	7	4	15.32	23.09
0	7	4	-12.23	16.04
1	7	4	25.37	28.11
2	7	4	59.99	56.37
3	7	4	0.0	1.73
4	7	4	-8.69	11.27
5	7	4	28.96	29.33
6	7	4	49.98	50.56
7	7	4	0.0	2.45

Table 15

continued :-

h	k	l	F_o	F_c
8	7	4	-24.48	22.55
9	7	4	-4.54	10.32
10	7	4	22.02	21.05
11	7	4	-7.84	3.90
12	7	4	18.54	19.86
13	7	4	-6.80	3.21
-13	8	4	49.22	47.80
-12	8	4	-10.34	7.05
-11	8	4	28.73	29.62
-10	8	4	-10.57	11.10
-9	8	4	47.71	52.14
-8	8	4	37.90	30.35
-7	8	4	26.65	27.50
-6	8	4	24.84	27.44
-5	8	4	67.33	71.39
-4	8	4	82.06	81.56
-3	8	4	0.0	1.52
-2	8	4	27.44	24.72
-1	8	4	68.28	67.45
0	8	4	55.21	55.16
1	8	4	29.69	26.75
2	8	4	80.28	81.95
3	8	4	46.43	44.15
4	8	4	54.62	54.41
5	8	4	0.0	1.34
6	8	4	53.17	52.11
7	8	4	21.15	20.42
8	8	4	54.54	54.96
9	8	4	-4.99	3.34
10	8	4	-8.43	2.53
11	8	4	16.15	17.49
12	8	4	40.22	35.73
-12	9	4	-8.31	6.32
-11	9	4	-11.67	12.06
-10	9	4	14.48	17.35
-9	9	4	-7.74	1.04
-8	9	4	-6.17	5.53
-7	9	4	-11.63	13.19
-6	9	4	29.34	27.75
-5	9	4	28.14	27.59
-4	9	4	-3.43	4.27
-3	9	4	25.07	24.30
-2	9	4	-12.27	4.76
-1	9	4	22.34	26.53
0	9	4	36.74	34.19
1	9	4	23.14	23.25
2	9	4	0.0	1.46
3	9	4	-6.07	1.52
4	9	4	-12.52	17.34
5	9	4	17.57	19.52
6	9	4	16.45	19.29
7	9	4	-3.62	4.22
8	9	4	25.28	25.61
9	9	4	-10.91	5.31
11	9	4	-14.43	7.01
-11	10	4	-13.47	13.66
-10	10	4	22.41	25.60
-9	10	4	48.76	49.94
-8	10	4	20.01	23.31
-7	10	4	44.53	40.73
-6	10	4	0.0	1.15
-5	10	4	28.45	33.22
-4	10	4	-2.43	3.67
-3	10	4	42.27	43.79
-2	10	4	24.79	22.44
-1	10	4	23.17	23.95
0	10	4	40.84	39.85
1	10	4	26.94	27.64
2	10	4	15.14	21.26
3	10	4	28.97	29.49
4	10	4	30.52	32.42
5	10	4	51.75	51.53
6	10	4	0.0	6.28
7	10	4	-14.44	13.66
8	10	4	30.34	24.24
9	10	4	23.24	24.66
-9	11	4	-9.04	9.82
-8	11	4	-13.55	14.12
-7	11	4	15.43	17.90
-6	11	4	44.47	47.59
-5	11	4	-4.43	9.32
-4	11	4	21.92	22.18
-3	11	4	-13.44	7.58
-2	11	4	50.41	52.74
-1	11	4	0.0	2.36
0	11	4	-8.71	10.54
1	11	4	-10.47	14.27
2	11	4	40.53	44.37
3	11	4	-13.69	13.75
4	11	4	0.0	7.33
5	11	4	-11.33	14.09
6	11	4	44.43	43.82
7	11	4	0.0	1.38
8	11	4	-11.93	10.85
-6	12	4	21.99	24.65
-5	12	4	-12.11	15.45
-4	12	4	16.42	16.40
-3	12	4	0.0	1.65
-2	12	4	23.82	27.55
-1	12	4	0.0	3.56
0	12	4	16.14	14.59
1	12	4	-4.99	1.60
2	12	4	29.40	34.66
3	12	4	-3.42	2.53
4	12	4	34.66	35.23
5	12	4	-8.95	2.16
-16	1	5	-4.16	2.18
-15	1	5	37.03	37.79
-14	1	5	0.0	2.30
-13	1	5	40.66	40.76
-12	1	5	0.0	3.49
-11	1	5	61.86	56.80
-10	1	5	77.91	73.69
-9	1	5	33.19	33.16
-8	1	5	12.72	11.13
-7	1	5	74.09	74.09
-6	1	5	46.03	44.49
-5	1	5	78.69	79.10
-4	1	5	25.61	24.93
-3	1	5	53.54	52.30
-2	1	5	144.57	136.54
-1	1	5	19.95	18.33
0	1	5	36.02	26.63
1	1	5	56.64	56.15
2	1	5	110.54	104.79
3	1	5	40.42	34.45
4	1	5	35.54	37.65
5	1	5	76.21	82.85
6	1	5	94.62	95.53
7	1	5	-8.11	14.46
8	1	5	35.36	35.77
9	1	5	27.25	27.25
10	1	5	58.11	63.66
11	1	5	-13.46	13.76
12	1	5	-4.30	2.37
13	1	5	25.09	24.23
14	1	5	42.22	41.89
15	1	5	19.95	19.15
-16	2	5	26.95	27.25
-15	2	5	29.57	29.74
-14	2	5	29.94	27.08
-13	2	5	37.07	39.80
-12	2	5	26.85	29.26
-11	2	5	16.72	16.86
-10	2	5	-5.13	1.17
-9	2	5	125.21	134.48
-8	2	5	-5.02	9.90
-7	2	5	34.54	33.02
-6	2	5	41.33	32.42
-5	2	5	140.82	141.96
-4	2	5	40.36	32.63
-3	2	5	45.67	45.46
-2	2	5	14.12	11.76
-1	2	5	179.96	167.97
0	2	5	21.25	26.57
1	2	5	-5.42	13.07
2	2	5	23.33	14.78
3	2	5	227.17	222.66
4	2	5	-6.66	2.17
5	2	5	73.84	73.19
6	2	5	32.27	33.63
7	2	5	178.21	172.94
8	2	5	24.34	25.45
9	2	5	20.15	13.11
10	2	5	49.77	49.28
11	2	5	44.06	44.24
12	2	5	17.27	17.43
13	2	5	19.33	20.19
14	2	5	0.0	4.75
-16	3	5	35.49	35.95
-15	3	5	0.0	1.12
-14	3	5	0.0	5.50
-13	3	5	18.76	10.15
-12	3	5	35.72	35.74
-11	3	5	-5.27	5.17
-10	3	5	44.33	45.23
-9	3	5	-6.33	1.47
-8	3	5	59.29	61.36
-7	3	5	-11.47	15.17
-6	3	5	37.25	37.93
-5	3	5	64.11	66.12
-4	3	5	28.31	25.26
-3	3	5	35.76	44.73
-2	3	5	19.71	17.97
-1	3	5	14.49	11.92
0	3	5	21.44	25.13
1	3	5	30.97	33.42
2	3	5	-9.65	5.72
3	3	5	37.52	32.23
4	3	5	16.67	17.99
5	3	5	-10.14	10.71
6	3	5	-6.37	3.43
7	3	5	-3.47	9.74
8	3	5	23.63	22.72
9	3	5	42.01	44.12
10	3	5	0.0	3.95
11	3	5	-6.90	6.64
12	3	5	0.0	5.37
13	3	5	0.0	4.65
14	3	5	0.0	1.59
-15	4	5	-7.23	1.92
-14	4	5	32.53	31.33
-13	4	5	27.75	37.32
-12	4	5	14.72	12.27
-11	4	5	21.33	15.60
-10	4	5	48.47	52.06
-9	4	5	91.11	94.92
-8	4	5	16.23	15.06
-7	4	5	47.72	33.85
-6	4	5	51.32	51.67
-5	4	5	125.71	117.67
-4	4	5	34.29	31.43
-3	4	5	0.0	.24
-2	4	5	55.35	57.45
-1	4	5	165.24	135.62
0	4	5	46.75	44.84
1	4	5	-2.13	5.26
2	4	5	67.21	61.49
3	4	5	149.92	146.32
4	4	5	29.73	31.59
5	4	5	24.97	31.64
6	4	5	0.0	1.53
7	4	5	115.49	111.44
8	4	5	43.33	44.59
9	4	5	0.0	1.73
10	4	5	-5.75	4.92
11	4	5	65.69	65.16
12	4	5	27.84	27.95
13	4	5	-17.34	16.51
14	4	5	-14.46	17.30
-15	5	5	26.19	27.45
-14	5	5	16.13	16.70
-13	5	5	41.16	44.60
-12	5	5	15.17	13.14
-11	5	5	33.96	34.38
-10	5	5	54.60	56.72
-9	5	5	25.04	30.15
-8	5	5	-10.34	16.75
-7	5	5	51.34	51.19
-6	5	5	69.55	66.21
-5	5	5	84.13	83.54
-4	5	5	39.67	35.77
-3	5	5	63.13	54.44
-2	5	5	95.27	94.55
-1	5	5	25.74	19.64
0	5	5	65.43	66.86
1	5	5	44.43	42.31
2	5	5	61.75	64.27
3	5	5	20.31	31.89
4	5	5	23.92	25.29
5	5	5	32.36	33.71
6	5	5	62.71	62.12
7	5	5	-7.74	1.13
8	5	5	-13.24	12.12
9	5	5	-8.91	13.37
10	5	5	16.63	17.56
11	5	5	-13.51	12.99
12	5	5	-5.72	3.54
13	5	5	20.93	21.71
-14	6	5	27.11	31.05
-13	6	5	-11.23	7.32
-12	6	5	26.41	22.52
-11	6	5	37.42	37.11
-10	6	5	52.72	54.59
-9	6	5	17.40	19.76
-8	6	5	51.73	53.25
-7	6	5	-14.89	19.35
-6	6	5	57.07	54.96
-5	6	5	20.24	16.41
-4	6	5	101.75	102.19
-3	6	5	13.23	13.60
-2	6	5	110.05	104.47
-1	6	5	15.15	15.57
0	6	5	56.92	55.21
1	6	5	28.23	25.65
2	6	5	101.23	93.65
3	6	5	47.52	48.51
4	6	5	75.51	78.36
5	6	5	75.43	74.03
6	6	5	55.75	50.69
7	6	5	42.56	43.47
8	6	5	46.42	45.07
9	6	5	33.72	37.96
10	6	5	37.55	37.30
11	6	5	-5.43	6.39
12	6	5	22.14	21.71
13	6	5	35.37	30.37
-13	7	5	-11.34	11.24
-12	7	5	23.21	22.19
-11	7	5	28.26	22.60
-10	7	5	-5.71	6.88
-9	7	5	-13.42	14.60
-8	7	5	37.60	39.60
-7	7	5	51.38	51.50
-6	7	5	36.47	39.06
-5	7	5	44.47	41.75
-4	7	5	19.95	21.41
-3	7	5	68.52	66.80
-2	7	5	27.74	33.54
-1	7	5	0.0	2.24
0	7	5	49.91	45.32
1	7	5	71.93	72.43
2	7	5	52.02	55.75
3	7	5	43.14	41.47
4	7	5	-13.47	15.35
5	7	5	30.63	23.25
6	7	5	51.71	54.24
7	7	5	28.40	29.24
8	7	5	24.54	25.07
9	7	5	53.52	52.27
10	7	5	15.41	13.86
11	7	5	21.83	22.33
12	7	5	-12.52	5.06
-12	8	5	-13.95	15.80
-11	8	5	-10.09	5.52
-10	8	5	0.0	5.65
-9	8	5	30.15	32.52
-8	8	5	37.42	36.86
-7	8	5	-12.55	3.08
-5	8	5	44.79	46.55
-4	8	5	30.16	31.61
-3	8	5	0.0	1.17
-2	8	5	19.46	15.17
-1	8	5	73.83	71.74
0	8	5	28.55	26.12
1	8	5	45.95	47.12
2	8	5	-13.69	11.15
3	8	5	55.53	57.23
4	8	5	27.96	29.70
5	8	5	-5.17	11.56
6	8	5	26.04	21.11
7	8	5	47.34	51.34
9	8	5	35.04	34.51
10	8	5	0.0	1.13
11	8	5	36.29	37.72
-11	9	5	-7.76	4.47
-10	9	5	-2.54	6.95
-9	9	5	-5.63	4.52
-8	9	5	42.71	44.02
-7	9	5	18.57	18.19
-6	9	5	-6.77	6.62
-5	9	5	20.45	22.65
-4	9	5	55.17	54.58
-3	9	5	21.16	13.33
-2	9	5	-6.38	6.66
-1	9	5	26.37	29.69
0	9	5	55.71	57.06
1	9	5	44.17	43.43
2	9	5	-3.42	7.30
3	9	5	24.59	30.17
4	9	5	36.09	33.67
5	9	5	24.56	26.11
6	9	5	-11.15	[illegible]
7	9	5	32.76	30.70
8	9	5	25.15	25.44
9	9	5	-15.53	17.70
10	9	5	-14.82	14.92
-10	10	5	36.56	31.69
-9	10	5	-9.36	4.67
-8	10	5	31.27	25.82
-7	10	5	0.0	4.23
-6	10	5	14.52	17.06
-5	10	5	27.14	26.72
-4	10	5	33.95	37.24
-3	10	5	-6.74	3.91
-2	10	5	47.23	42.55
-1	10	5	32.93	31.77
0	10	5	25.40	22.42
1	10	5	17.02	17.40
2	10	5	30.41	47.57
3	10	5	0.0	1.71
4	10	5	43.51	47.71
5	10	5	21.57	22.72
6	10	5	29.04	25.46
7	10	5	-12.96	12.50
8	10	5	25.38	26.19
-8	11	5	-14.74	12.62
-7	11	5	15.97	11.56
-6	11	5	-12.22	13.75
-5	11	5	22.81	23.45
-4	11	5	77.53	20.61
-3	11	5	-7.24	2.58
-2	11	5	-6.01	11.03
-1	11	5	-15.46	13.14
0	11	5	-10.42	5.50
1	11	5	-4.33	2.55
2	11	5	-11.74	7.46
3	11	5	-5.56	1.72
4	11	5	20.32	27.45
5	11	5	-16.17	12.11
6	11	5	-12.74	9.33
-4	12	5	25.43	21.40
-3	12	5	0.0	4.71
-1	12	5	-9.54	5.60
0	12	5	45.19	45.77
1	12	5	22.30	21.64
2	12	5	32.94	30.26
3	12	5	-7.61	2.59
-16	0	6	-9.24	3.49
-15	0	6	42.13	42.64
-14	0	6	16.92	15.45
-13	0	6	24.95	19.74
-12	0	6	23.23	27.12
-11	0	6	48.31	53.23
-10	0	6	-6.24	1.56
-9	0	6	25.69	33.51
-8	0	6	59.60	70.16
-7	0	6	95.06	106.85
-6	0	6	69.53	67.72
-5	0	6	-5.49	6.59
-4	0	6	44.75	46.82
-3	0	6	93.67	135.05
-2	0	6	15.29	26.40
-1	0	6	20.31	16.15
0	0	6	161.16	175.51
1	0	6	49.34	65.58
2	0	6	-6.93	1.95
3	0	6	31.67	17.54
4	0	6	158.09	171.54
5	0	6	57.85	71.16
6	0	6	60.93	64.24
7	0	6	25.83	24.79
8	0	6	105.44	109.57
9	0	6	-9.13	6.73
10	0	6	15.96	16.14
11	0	6	17.93	15.23
12	0	6	50.42	53.80
13	0	6	0.0	2.19
14	0	6	23.72	22.39
-15	1	6	29.97	31.19
-14	1	6	-4.69	4.17
-13	1	6	-14.23	12.21
-12	1	6	29.23	29.92
-11	1	6	-11.92	13.13
-10	1	6	35.33	32.57
-9	1	6	-6.91	4.03
-8	1	6	65.53	55.65
-7	1	6	10.29	11.72
-6	1	6	20.26	20.25
-5	1	6	84.93	91.33
-4	1	6	96.47	103.01
-3	1	6	13.45	13.99
-2	1	6	57.12	59.35
-1	1	6	57.52	55.17
0	1	6	39.73	43.45
1	1	6	12.47	12.40
2	1	6	35.03	36.04
3	1	6	-3.72	4.76
4	1	6	117.34	121.90
5	1	6	19.43	22.52
6	1	6	13.42	4.41
7	1	6	-12.57	17.56
8	1	6	26.57	32.53
9	1	6	21.47	25.32
10	1	6	-6.86	5.64
11	1	6	-11.25	15.21
12	1	6	17.49	11.91
13	1	6	15.74	16.37
14	1	6	-11.43	11.06
-15	2	6	-13.72	14.53
-14	2	6	-13.27	13.74
-13	2	6	23.50	21.43
-12	2	6	-12.11	14.60
-11	2	6	38.27	37.78
-10	2	6	23.96	26.66
-9	2	6	25.81	22.41
-8	2	6	-13.42	18.60
-7	2	6	20.26	21.07
-6	2	6	55.17	57.10
-5	2	6	35.50	37.48
-4	2	6	0.0	11.25
-3	2	6	14.85	14.59
-2	2	6	64.21	62.35
-1	2	6	65.71	62.55
0	2	6	42.54	32.06
1	2	6	34.85	36.29
2	2	6	44.67	44.76
3	2	6	40.07	34.27
4	2	6	67.57	75.52
5	2	6	15.12	15.86
6	2	6	31.73	31.36
7	2	6	-11.47	17.44
8	2	6	47.21	44.12
9	2	6	-10.54	14.15
10	2	6	25.59	31.57
11	2	6	-10.47	11.14
12	2	6	37.53	35.21
13	2	6	-10.74	5.44
14	2	6	0.0	2.03
-15	3	6	22.44	21.12
-14	3	6	-8.25	11.32
-13	3	6	26.93	25.35
-12	3	6	67.57	73.06
-11	3	6	-7.14	1.21
-10	3	6	10.11	11.59
-9	3	6	-7.41	3.73
-8	3	6	195.13	170.45
-7	3	6	-11.12	11.26
-6	3	6	41.26	40.73
-5	3	6	58.19	57.16
-4	3	6	192.42	177.92
-3	3	6	27.12	23.21
-2	3	6	81.16	66.88
-1	3	6	-8.44	6.41
0	3	6	137.57	131.22
1	3	6	20.65	13.75
2	3	6	44.01	42.43
3	3	6	23.45	23.91
4	3	6	133.44	134.81
5	3	6	49.53	47.79
6	3	6	36.57	33.05
7	3	6	-4.01	5.91
8	3	6	47.63	51.47
9	3	6	-12.94	11.05
10	3	6	22.44	21.73
11	3	6	-13.57	16.74
12	3	6	32.15	35.43
13	3	6	25.25	25.69
-15	4	6	29.72	23.47
-14	4	6	-1.94	5.71
-13	4	6	0.0	7.93
-12	4	6	36.14	47.91
-11	4	6	17.77	13.25
-10	4	6	33.71	31.95
-9	4	6	-1.73	3.31
-8	4	6	53.37	59.93
-7	4	6	63.79	63.77
-6	4	6	-10.25	3.90
-5	4	6	30.29	29.43
-4	4	6	76.56	75.56
-3	4	6	32.37	33.37
-2	4	6	49.16	46.68
-1	4	6	100.37	95.65
0	4	6	123.56	127.58
1	4	6	-5.59	7.39
2	4	6	24.51	25.09
3	4	6	55.79	53.13
4	4	6	23.75	24.20
5	4	6	51.73	51.97
6	4	6	0.0	2.79
7	4	6	55.34	61.05
8	4	6	64.34	63.24
9	4	6	-12.71	17.69
10	4	6	-12.57	1.26
11	4	6	38.43	32.49
12	4	6	23.47	25.70
13	4	6	-10.54	9.92
-14	5	6	0.0	1.24
-13	5	6	27.01	31.56
-12	5	6	35.42	32.74
-11	5	6	25.53	24.43
-10	5	6	26.91	25.27
-9	5	6	62.77	62.97
-8	5	6	27.52	21.40
-7	5	6	57.36	56.23
-5	5	6	-1.59	4.98
-4	5	6	28.27	23.96
-3	5	6	20.59	24.75
-2	5	6	20.94	17.47
-1	5	6	96.23	94.68
0	5	6	81.95	79.87
1	5	6	79.34	67.24
2	5	6	27.17	21.10
3	5	6	17.09	17.83
4	5	6	-6.03	4.91
5	5	6	39.33	38.56
6	5	6	43.86	44.53
7	5	6	-11.74	5.61
8	5	6	41.12	43.76
9	5	6	63.22	65.51
10	5	6	51.02	51.77
11	5	6	-8.94	4.16
12	5	6	21.60	22.19
-13	6	6	-14.21	14.26
-12	6	6	0.0	3.56
-11	6	6	46.53	45.28
-10	6	6	23.47	23.45
-9	6	6	-13.15	13.55
-8	6	6	30.72	37.06
-7	6	6	31.17	29.73
-6	6	6	-12.21	16.57
-5	6	6	40.54	34.01
-4	6	6	54.07	55.72
-3	6	6	45.35	46.66
-2	6	6	36.90	36.27
-1	6	6	22.22	22.69
0	6	6	72.76	70.61
1	6	6	46.79	47.98
2	6	6	25.48	26.98
3	6	6	24.25	22.17
4	6	6	64.85	62.59
5	6	6	26.45	24.88
6	6	6	-4.23	7.54
7	6	6	0.0	7.38
8	6	6	51.26	50.57
9	6	6	0.0	0.95
10	6	6	21.12	18.89
11	6	6	-8.92	5.58
12	6	6	32.63	30.55
-13	7	6	-5.89	6.30
-12	7	6	28.41	25.71
-11	7	6	30.53	31.52
-10	7	6	16.37	19.15
-9	7	6	21.22	23.97
-8	7	6	19.07	21.12
-7	7	6	48.05	52.47
-6	7	6	19.95	23.03
-5	7	6	25.32	27.64
-4	7	6	50.65	50.27
-3	7	6	54.67	57.26
-2	7	6	-8.43	3.44
-1	7	6	16.21	14.67
0	7	6	33.34	32.51
1	7	6	50.27	49.55
2	7	6	13.42	12.77
3	7	6	-4.51	4.55
4	7	6	33.10	31.82
5	7	6	31.14	31.62
6	7	6	-7.19	5.70
7	7	6	-4.37	3.02
8	7	6	-12.46	4.46
9	7	6	16.87	13.44
10	7	6	0.0	5.63
11	7	6	-13.59	10.86
-12	8	6	-7.29	4.07
-11	8	6	18.66	21.15
-10	8	6	48.51	49.52
-9	8	6	21.37	17.62
-8	8	6	23.15	25.56
-7	8	6	0.0	1.40
-6	9	6	41.55	44.93
-5	8	6	48.94	44.84
-4	8	6	-7.56	1.93
-3	8	6	18.52	11.35
-2	8	6	62.11	52.54
-1	8	6	75.64	74.92
0	8	6	-11.95	11.02
1	8	6	21.57	17.22
2	8	6	52.65	54.99
3	8	6	59.61	69.37
4	8	6	-12.97	10.51
5	8	6	17.27	14.76
6	8	6	26.85	29.16
7	8	6	52.61	55.96
8	8	6	-8.34	1.21
9	8	6	-5.28	1.55
10	8	6	25.04	27.08
-10	9	6	18.91	13.72
-9	9	6	27.16	29.95
-8	9	6	24.65	25.61
-7	9	6	-8.43	14.22
-6	9	6	-8.53	5.42
-5	9	6	0.0	6.28
-4	9	6	30.43	32.54
-3	9	6	22.55	21.71
-2	9	6	-5.49	1.67
-1	9	6	45.81	46.28
0	9	6	49.68	51.43
1	9	6	27.63	26.57
2	9	6	-14.17	11.73
3	9	6	16.13	13.44
4	9	6	-11.57	13.64
5	9	6	-14.13	13.14
6	9	6	-4.35	4.72
7	9	6	-7.66	5.17
8	9	6	21.59	22.84
-8	10	6	23.93	25.43
-7	10	6	-11.95	10.12
-6	10	6	34.69	36.21
-5	10	6	22.77	24.25
-4	10	6	25.79	20.76
-3	10	6	-10.74	1.43
-2	10	6	21.39	20.14
-1	10	6	30.20	31.02
0	10	6	19.24	19.76
1	10	6	14.69	17.09
2	10	6	30.02	29.96
3	10	6	45.67	49.75
4	10	6	19.70	21.14
5	10	6	-12.75	12.19
6	10	6	33.45	30.11
7	10	6	41.10	42.69
-6	11	6	-10.31	15.43
-5	11	6	29.35	31.92
-4	11	6	-5.35	5.70
-3	11	6	44.51	49.84
-2	11	6	-4.57	2.45
-1	11	6	24.03	24.37
0	11	6	-9.71	4.64
1	11	6	42.92	47.59
2	11	6	25.77	26.44
3	11	6	19.24	17.31
4	11	6	21.97	20.43
-15	1	7	-3.67	3.06
-14	1	7	49.71	52.33
-13	1	7	-4.72	1.39
-12	1	7	14.04	15.40
-11	1	7	34.13	35.66
-10	1	7	37.65	35.75
-9	1	7	15.99	23.93
-8	1	7	27.07	24.53
-7	1	7	59.64	64.82
-6	1	7	94.24	94.22
-5	1	7	37.13	21.55
-4	1	7	66.10	66.55
-2	1	7	107.78	97.61
-1	1	7	48.71	43.10
0	1	7	24.20	22.13
1	1	7	87.15	78.30
2	1	7	42.73	44.02
3	1	7	14.94	11.18
4	1	7	28.77	31.47
5	1	7	77.91	84.62
6	1	7	0.0	4.76
7	1	7	0.0	0.60
8	1	7	-7.53	0.66
9	1	7	24.92	23.70
10	1	7	27.91	25.72
11	1	7	-8.24	2.43
12	1	7	0.0	4.12
13	1	7	36.43	36.34
-14	2	7	30.44	32.15
-13	2	7	30.22	29.15
-12	2	7	-10.44	1.93
-11	2	7	-6.85	16.34
-10	2	7	49.93	51.54
-9	2	7	-10.82	13.15
-8	2	7	14.59	19.57
-7	2	7	28.01	27.92
-6	2	7	138.76	141.61
-5	2	7	-11.63	3.43
-4	2	7	101.40	95.17
-3	2	7	26.85	19.72
-2	2	7	160.22	141.42
-1	2	7	51.67	47.87
0	2	7	90.60	75.06
1	2	7	26.39	25.66
2	2	7	128.44	125.40
3	2	7	-3.40	9.72
4	2	7	26.34	23.96
5	2	7	-13.57	12.39
6	2	7	104.42	110.54
7	2	7	34.61	34.92
8	2	7	27.72	27.47
9	2	7	27.34	35.98
10	2	7	64.07	47.41
11	2	7	26.67	26.26
-14	3	7	27.34	31.60

Table 15

continued:-

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-10	3	7	-11.55	2.37
-9	3	7	45.90	47.39
-8	3	7	-7.73	7.63
-7	3	7	-9.03	7.94
-6	3	7	23.87	23.15
-5	3	7	17.29	16.91
-4	3	7	29.72	26.60
-3	3	7	14.47	8.03
-2	3	7	22.17	22.60
-1	3	7	57.59	54.41
0	3	7	65.17	67.89
1	3	7	25.80	25.53
2	3	7	34.46	33.27
3	3	7	18.84	14.62
4	3	7	-10.39	8.50
5	3	7	45.93	42.57
6	3	7	22.23	21.37
7	3	7	0.0	6.32
8	3	7	17.16	16.45
10	3	7	30.43	30.88
11	3	7	-12.31	12.89
12	3	7	0.0	1.89
-14	4	7	23.91	22.77
-13	4	7	-6.86	5.53
-12	4	7	-14.55	17.56
-11	4	7	36.27	36.52
-10	4	7	44.97	46.24
-9	4	7	-8.76	7.26
-8	4	7	40.04	41.84
-7	4	7	30.93	35.92
-6	4	7	29.39	32.41
-5	4	7	27.91	27.77
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2	4	7	86.33	87.14
3	4	7	30.03	29.35
4	4	7	-1.44	3.33
5	4	7	-9.55	8.32
6	4	7	64.34	63.21
7	4	7	26.04	29.28
8	4	7	-1.09	2.68
9	4	7	-5.42	3.62
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11	4	7	24.85	27.90
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6	5	7	18.57	23.94
7	5	7	-3.66	3.77
8	5	7	-14.11	15.67
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6	6	7	23.23	21.58
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-3	0	10	-5.52	11.42
-2	0	10	61.31	66.98
-1	0	10	0.0	7.14
0	0	10	27.04	17.91
1	0	10	-7.75	4.10
2	0	10	51.43	55.52
3	0	10	25.34	34.97
4	0	10	-14.96	15.95
5	0	10	28.27	29.66
7	0	10	17.67	14.28
8	0	10	-12.26	10.58
-10	1	10	24.79	26.39
-9	1	10	21.35	22.15
-8	1	10	27.07	28.67
-7	1	10	45.29	49.40
-6	1	10	14.74	17.65
-5	1	10	24.14	23.12
-4	1	10	30.15	33.61
-3	1	10	53.49	48.53
-2	1	10	39.35	35.70
-1	1	10	0.0	4.06
0	1	10	-4.76	3.73
1	1	10	35.25	28.67
2	1	10	21.44	17.89
3	1	10	-11.52	10.07
4	1	10	18.50	19.24
5	1	10	47.02	53.64
6	1	10	-7.25	7.26
7	1	10	0.0	1.23
8	1	10	-8.75	5.11
-10	2	10	28.92	27.73
-9	2	10	-6.54	5.49
-8	2	10	-9.64	1.25
-7	2	10	15.35	14.57
-6	2	10	49.06	45.99
-5	2	10	-12.65	7.46
-4	2	10	-11.32	2.34
-3	2	10	-11.69	9.20
-2	2	10	45.52	42.97
-1	2	10	26.21	23.14
0	2	10	-9.23	6.53
1	2	10	-8.67	8.75
2	2	10	29.44	30.14
3	2	10	21.06	20.28
4	2	10	-6.51	6.82
5	2	10	0.0	0.41
6	2	10	22.39	23.28
7	2	10	-14.08	11.37
-10	3	10	34.59	36.90
-9	3	10	-8.72	10.99
-8	3	10	54.59	50.89
-7	3	10	53.37	53.87
-6	3	10	32.73	34.49
-5	3	10	21.05	16.90
-4	3	10	55.26	53.04
-3	3	10	72.94	69.76
-2	3	10	31.42	33.83
-1	3	10	-11.59	5.02
0	3	10	41.08	39.69
1	3	10	68.56	69.06
2	3	10	24.99	23.45
3	3	10	0.0	4.95
4	3	10	35.69	33.26
5	3	10	76.24	77.65
6	3	10	-1.56	1.33
7	3	10	-5.33	1.83
-9	4	10	-7.56	1.48
-8	4	10	-9.94	1.79
-7	4	10	0.0	0.37
-6	4	10	15.03	17.14
-5	4	10	-12.40	10.27
-4	4	10	22.89	18.94
-3	4	10	15.99	15.44
-2	4	10	-9.07	14.08
-1	4	10	22.14	23.35
0	4	10	-14.33	9.72
1	4	10	-15.21	16.49
2	4	10	-10.33	11.19
3	4	10	-14.12	11.59
4	4	10	-7.19	3.62
5	4	10	29.54	25.36
6	4	10	20.96	19.32
-8	5	10	24.91	23.93
-7	5	10	-12.97	12.71
-6	5	10	-2.29	2.95
-5	5	10	-10.77	6.46
-4	5	10	19.74	11.64
-3	5	10	-13.42	11.37
-2	5	10	33.09	33.59
-1	5	10	28.74	27.89
0	5	10	50.72	50.81
1	5	10	36.35	36.54
2	5	10	16.45	15.49
3	5	10	17.07	16.67
4	5	10	22.31	24.85
5	5	10	-11.92	3.19
-7	6	10	-12.75	13.79
-6	6	10	27.85	23.45
-5	6	10	-6.57	2.67
-4	6	10	-6.67	3.48
-3	6	10	-4.57	5.35
-2	6	10	39.94	37.17
-1	6	10	25.50	24.58
0	6	10	0.0	1.80
1	6	10	-10.39	1.22
2	6	10	30.98	27.24
3	6	10	21.24	17.91
4	6	10	0.0	1.72
-4	7	10	0.0	4.56
-3	7	10	35.97	33.89
-2	7	10	30.29	31.51
-1	7	10	22.47	23.13
0	7	10	0.0	3.55
1	7	10	38.79	35.51
-8	1	11	-14.90	14.26
-7	1	11	16.73	17.30
-6	1	11	-9.71	2.75
-5	1	11	53.89	56.21
-4	1	11	19.64	16.08
-3	1	11	-7.37	3.71
-2	1	11	-12.42	4.51
-1	1	11	63.56	61.25
0	1	11	-9.50	3.15
1	1	11	-10.91	12.85
2	1	11	-7.47	5.52
3	1	11	54.60	49.06
4	1	11	0.0	7.75
5	1	11	-5.94	7.11
-7	2	11	23.42	24.37
-6	2	11	32.56	31.30
-5	2	11	28.03	27.77
-4	2	11	24.65	23.07
-3	2	11	24.79	22.94
-2	2	11	-5.33	6.71
-1	2	11	18.66	17.58
0	2	11	14.19	17.44
1	2	11	48.04	41.62
2	2	11	20.12	19.96
3	2	11	47.20	53.47
4	2	11	-3.55	2.36
-7	3	11	0.0	4.14
-6	3	11	35.71	34.18
-5	3	11	-8.58	9.26
-4	3	11	-11.15	3.35
-3	3	11	-9.44	8.00
-2	3	11	20.23	19.40
-1	3	11	23.48	18.42
0	3	11	35.75	34.72
1	3	11	-12.59	14.74
2	3	11	-7.13	7.55
3	3	11	0.0	6.75
4	3	11	19.42	13.05
-6	4	11	24.61	26.96
-5	4	11	32.06	25.76
-4	4	11	37.35	33.50
-3	4	11	34.25	33.27
-2	4	11	31.83	30.74
-1	4	11	31.26	29.99
0	4	11	-6.72	4.45
1	4	11	32.47	30.55
2	4	11	32.17	30.15
-3	5	11	-5.17	2.90
-2	5	11	-10.25	5.07
-1	5	11	47.26	47.49
0	5	11	31.63	30.11

h	k	l	F_o	F_c
1	1	1	102.43	104.31
-6	12	1	-13.59	4.16
8	0	2	82.37	92.44
-10	4	2	-5.49	4.49
8	4	2	18.42	13.08
-3	5	2	48.65	46.85
7	9	2	0.0	5.08
8	9	2	-12.43	17.23
-7	12	2	17.14	17.72
-1	11	3	-13.21	11.59
-12	3	4	35.23	39.22
-7	2	4	72.73	73.42
-6	2	4	28.47	29.90
14	3	4	29.25	26.57
-11	4	4	59.78	70.39
-4	4	4	51.15	52.32
-2	4	4	56.52	51.14
8	5	4	16.95	20.05
-12	7	4	-1.17	5.42
10	9	4	25.39	27.58
-2	12	5	25.93	24.59
-6	8	5	-3.78	14.29
8	8	5	-9.64	7.24
-6	5	6	21.83	24.30
-3	1	7	104.69	102.15
12	2	7	-13.37	10.65
9	3	7	-14.10	14.85
-8	0	8	0.0	1.09
1	8	8	-13.79	8.06
5	2	9	28.34	33.12
-3	4	9	24.89	23.37
-1	6	9	45.34	45.56
6	0	10	56.11	60.59
1	2	1	418.95	418.25
4	0	0	379.47	425.59

COORDINATES AND MOLECULAR DIMENSIONS

The numbering system used is shown in the diagram of the structure in Figure 9, and the final positional and thermal parameters are listed in Table 16. Bond lengths and valency angles are given in Table 17, and Table 18 gives the equations of the mean planes through the cyclopentadienyl rings with the angles between the normals of these planes. Figure 10 shows a view of the ferrocenyl groups along the normals of these planes, and Figure 11 is a packing diagram viewed along the c crystallographic axis.

Figure 9

A diagram of the structure, which shows the numbering system used.

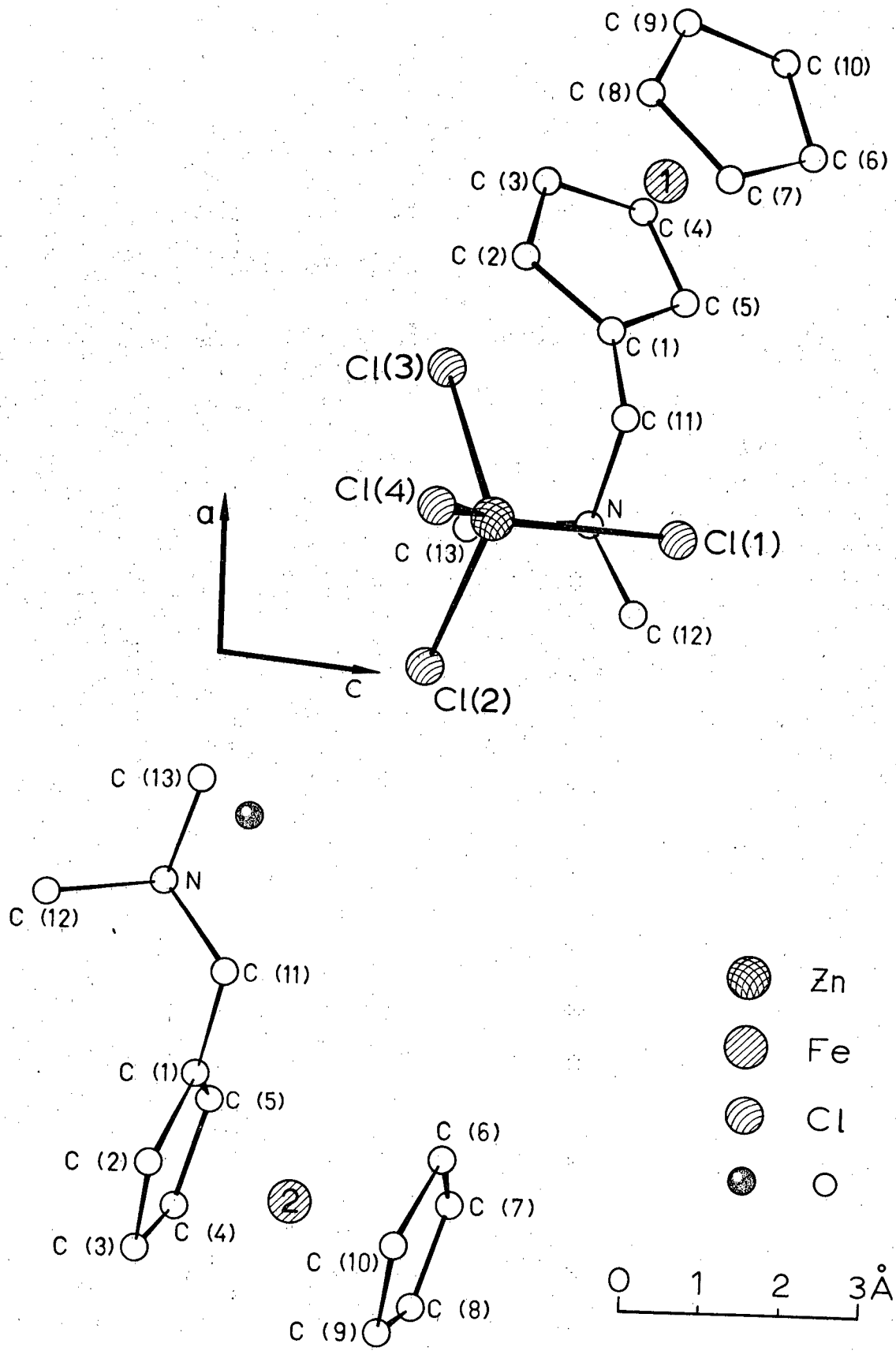

C (9)
C (10)
C (8)
C (6)
C (7)
C (3)
C (4)
C (2)
C (5)
C (1)
Cl(3)
C (11)
Cl(4)
N
Cl(1)
C (13)
C (12)
a
c
Cl(2)
C (13)
N
C (12)
C (11)
C (1)
C (5)
C (2)
C (4)
C (3)
C (6)
C (7)
C (10)
C (8)
C (9)
Zn
Fe
Cl
O
0 1 2 3Å

Table 16

Final positional (fractional × 10^4) and thermal parameters ($Å^2 \times 10^2$ for anisotropic; $Å^2$ for isotropic), with standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	3640(2)	1096(2)	4383(3)	5.41(18)	5.69(19)	5.19(18)	-1.15(33)	1.78(31)	-1.56(32)
Fe(2)	-3735(2)	1086(2)	0954(2)	5.41(18)	4.69(17)	3.61(15)	0.77(31)	2.22(28)	0.35(29)
Zn	1170(2)	4360(2)	2753(2)	6.39(16)	5.49(15)	5.34(14)	-0.51(27)	1.00(26)	0.26(26)
Cl(1)	1190(4)	4281(5)	4631(5)	10.98(48)	6.59(36)	5.04(32)	-6.01(72)	3.00(67)	-1.56(61)
Cl(2)	0090(4)	3641(6)	2099(6)	7.21(39)	10.98(54)	7.60(41)	-3.58(78)	-0.44(70)	-0.95(81)
Cl(3)	2148(4)	3599(5)	2198(5)	7.87(38)	7.19(40)	7.82(39)	1.79(68)	5.88(63)	1.91(68)
Cl(4)	1188(5)	5901(5)	2185(6)	11.64(54)	5.69(37)	7.97(42)	0.77(77)	-3.33(82)	2.95(69)

	Cation 1				Cation 2			
Atom	x	y	z	B	x	y	z	B
C(1)	2547(11)	0890(15)	3870(16)	3.8(4)	-2928(12)	1194(16)	-0077(16)	4.6(4)
C(2)	2980(14)	0865(19)	2965(19)	5.5(5)	-3588(12)	1682(16)	-0528(16)	4.4(4)
C(3)	3525(14)	0097(20)	3177(21)	5.6(5)	-4184(14)	0982(18)	-0652(18)	5.9(5)
C(4)	3407(15)	-0322(16)	4167(22)	7.4(7)	-3870(13)	0086(18)	-0258(19)	4.7(5)
C(5)	2813(12)	0165(16)	4627(19)	4.6(5)	-3099(12)	0218(15)	0082(17)	3.9(4)
C(6)	3926(15)	1735(20)	5866(22)	6.3(6)	-3316(14)	1545(21)	2458(18)	6.4(6)
C(7)	3702(16)	2427(18)	5035(24)	7.3(7)	-3601(16)	0627(22)	2551(20)	6.7(6)
C(8)	4218(15)	2311(19)	4184(25)	7.4(7)	-4350(14)	0642(21)	2182(18)	6.9(6)
C(9)	4732(16)	1568(21)	4535(23)	6.3(6)	-4562(14)	1514(22)	1842(18)	7.2(6)
C(10)	4543(15)	1220(20)	5550(22)	5.8(5)	-3943(17)	2139(18)	1999(18)	7.0(6)
C(11)	1972(12)	1593(16)	4080(18)	4.2(4)	-2204(12)	1684(18)	0224(19)	4.8(4)
C(12)	0630(15)	1756(23)	4214(24)	7.5(7)	-1811(14)	1415(19)	-1676(20)	5.8(5)
C(13)	1063(14)	1134(19)	2472(20)	5.7(5)	-0864(15)	1801(21)	-0131(23)	6.4(6)
N	1214(10)	1184(14)	3723(15)	4.7(4)	-1613(10)	1314(13)	-0480(16)	4.5(3)
O	-1110(13)	4391(17)	0389(20)	10.2(6)				

Table 17

Bond lengths (Å) and valency angles (degrees) with standard deviations in parentheses.

Cyclopentadienyl Rings:

	Cation 1	Cation 2
Fe-C(1)	2.03(2)	2.03(2)
Fe-C(2)	2.03(2)	2.04(2)
Fe-C(3)	2.03(3)	2.06(2)
Fe-C(4)	2.05(2)	2.04(2)
Fe-C(5)	2.03(2)	2.05(2)
Fe-C(6)	2.05(3)	2.03(2)
Fe-C(7)	2.03(3)	2.05(2)
Fe-C(8)	2.03(3)	2.05(3)
Fe-C(9)	2.07(3)	2.03(3)
Fe-C(10)	2.07(3)	2.02(2)
		Mean = 2.04
C(1)-C(2)	1.42(3)	1.44(3)
C(2)-C(3)	1.46(4)	1.46(3)
C(3)-C(4)	1.38(4)	1.44(3)
C(4)-C(5)	1.44(4)	1.43(3)
C(5)-C(1)	1.43(3)	1.42(3)
C(6)-C(7)	1.44(4)	1.40(4)
C(7)-C(8)	1.48(4)	1.38(4)
C(8)-C(9)	1.43(4)	1.34(4)
C(9)-C(10)	1.41(4)	1.42(4)
C(10)-C(6)	1.41(4)	1.47(4)
		Mean = 1.43
C(5)-C(1)-C(2)	108(2)	109(2)
C(1)-C(2)-C(3)	107(2)	107(2)
C(2)-C(3)-C(4)	108(2)	107(2)
C(3)-C(4)-C(5)	109(2)	109(2)
C(4)-C(5)-C(1)	108(2)	108(2)

..../continued

Table 17, continued

C(10)-C(6)-C(7)	109(2)	106(2)
C(6)-C(7)-C(8)	106(2)	108(3)
C(7)-C(8)-C(9)	108(2)	111(3)
C(8)-C(9)-C(10)	108(3)	109(2)
C(9)-C(10)-C(6)	109(2)	106(2)
		Mean = 108

Side Chains:

C(1)-C(11)	1.47(3)	1.49(3)
N-C(11)	1.51(3)	1.53(3)
N-C(12)	1.50(4)	1.48(3)
N-C(13)	1.53(3)	1.54(3)
C(2)-C(1)-C(11)	127(2)	123(2)
C(5)-C(1)-C(11)	124(2)	127(2)
C(1)-C(11)-N	109(2)	110(2)
C(11)-N-C(12)	110(2)	114(2)
C(11)-N-C(13)	112(2)	110(2)
C(12)-N-C(13)	111(2)	111(2)

Tetrachlorozincate group:

Zn-Cl(1) = 2.299(7)	Cl(1)-Zn-Cl(2) = 105.2(3)
Zn-Cl(2) = 2.270(8)	Cl(1)-Zn-Cl(3) = 110.2(3)
Zn-Cl(3) = 2.229(7)	Cl(1)-Zn-Cl(4) = 110.6(3)
Zn-Cl(4) = 2.274(7)	Cl(2)-Zn-Cl(3) = 111.1(3)
	Cl(2)-Zn-Cl(4) = 110.7(3)
	Cl(3)-Zn-Cl(4) = 109.0(3)

Table 18

Equations of mean planes, in the form $\ell X' + mY' + nZ' = p$ where X', Y' and Z' are coordinates in Å referred to orthogonal axes a, b and c*.

	Atoms in plane	ℓ	m	n	p	max. displ. (Å).
Cation 1:						
1	C(1)-C(5)	0.6056	0.6440	0.4673	5.5153	0.010
2	C(6)-C(10)	0.5725	0.6704	0.4720	8.6592	0.005
Cation 2:						
3	C(1)-C(5)	-0.3197	0.2112	0.9237	1.9555	0.006
4	C(6)-C(10)	-0.3202	0.2127	0.9232	5.2432	0.006

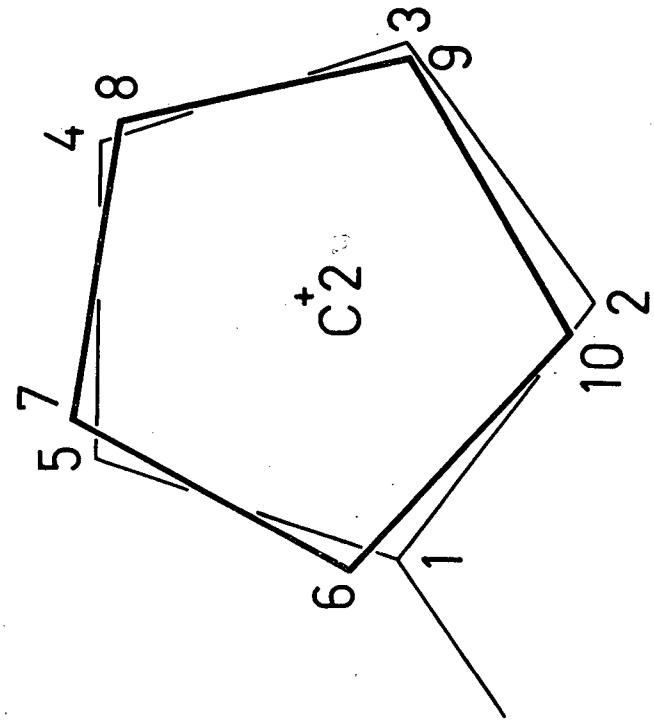
Angles between plane normals;

1 - 2 2.4°

3 - 4 0.1°

Figure 10

Views of the cyclopentadienyl rings normal to their planes. Heavier lines are nearer the viewer.


C2
+
1
2
3
4
5
6
7
8
9
10

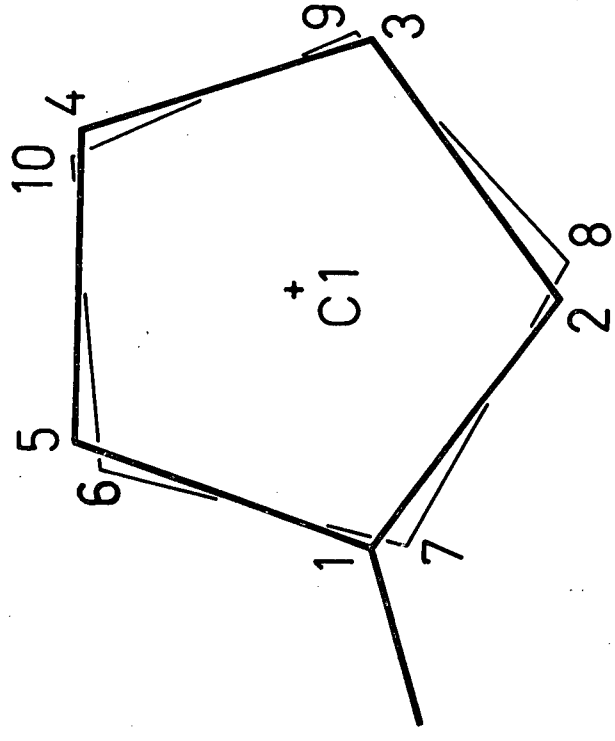
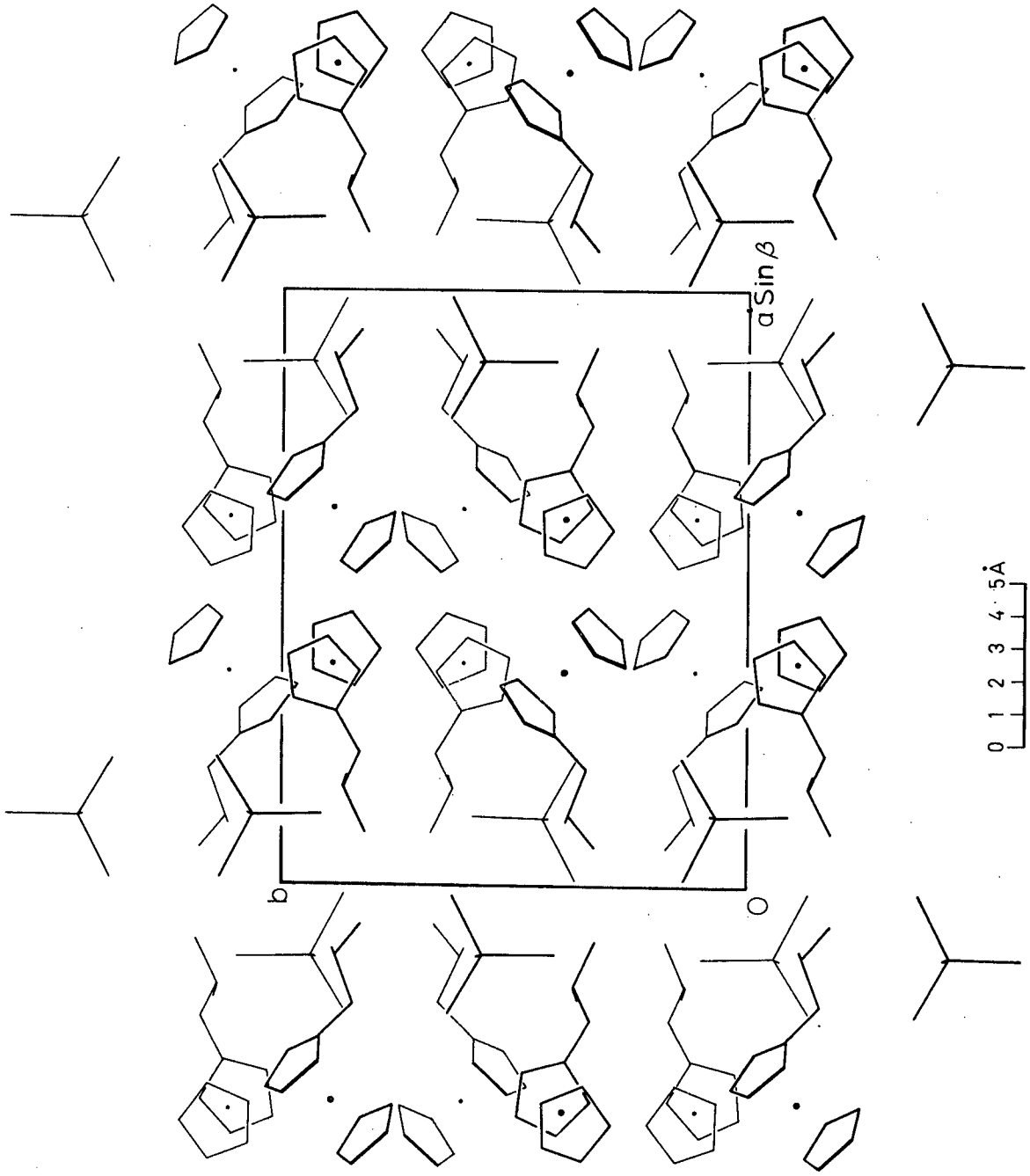

C1
+
1
2
3
4
5
6
7
8
9
10

Figure 11

Packing diagram viewed along the c crystallographic axis.


a Sin β
b
O
0 1 2 3 4 5Å

RESULTS AND DISCUSSION

The crystal analysis has confirmed the formulation of the compound as the tetrachlorozincate, and precludes any possibility of N→Zn coordination. The lack of absorption in the NH^+ stretching region (3.8-4.2μ) for the crystalline compound[28] is probably related to the strong hydrogen bonding from N-H to O and Cl (discussed below).

As shown in the packing diagram (Figure 11), the structure is composed of 'ionic layers' parallel to (100) which contain the $ZnCl_4^{-2}$ groups; the nitrogen-containing side chains are directed into the layers, with the Fe-hydrocarbon portions between layers. Within the ionic layers groups of four cations, two anions and two water molecules (two formula units) are linked around centres of symmetry by N-H...Cl (3.11 Å), N-H...O (2.76 Å), and O-H... Cl (3.05, 3.17 Å) hydrogen bonds as illustrated in Figure 12. The layer is extended in the (100) plane by weaker C...Cl interactions ranging upwards in length from 3.56 Å (Table 19). These involve primarily the N-methyl carbon atoms of adjacent side chains. The shortest contact between layers is C...C = 3.65 Å.

The two chlorine atoms which are hydrogen bonded to the water molecule subtend an angle of 127° at the oxygen atom so that the hydrogen atoms of the water molecule are most probably directed not far from the O...Cl vectors.

Figure 12

The environment of a $ZnCl_4^{-2}$ group, which shows the hydrogen bonding around a centre of symmetry.

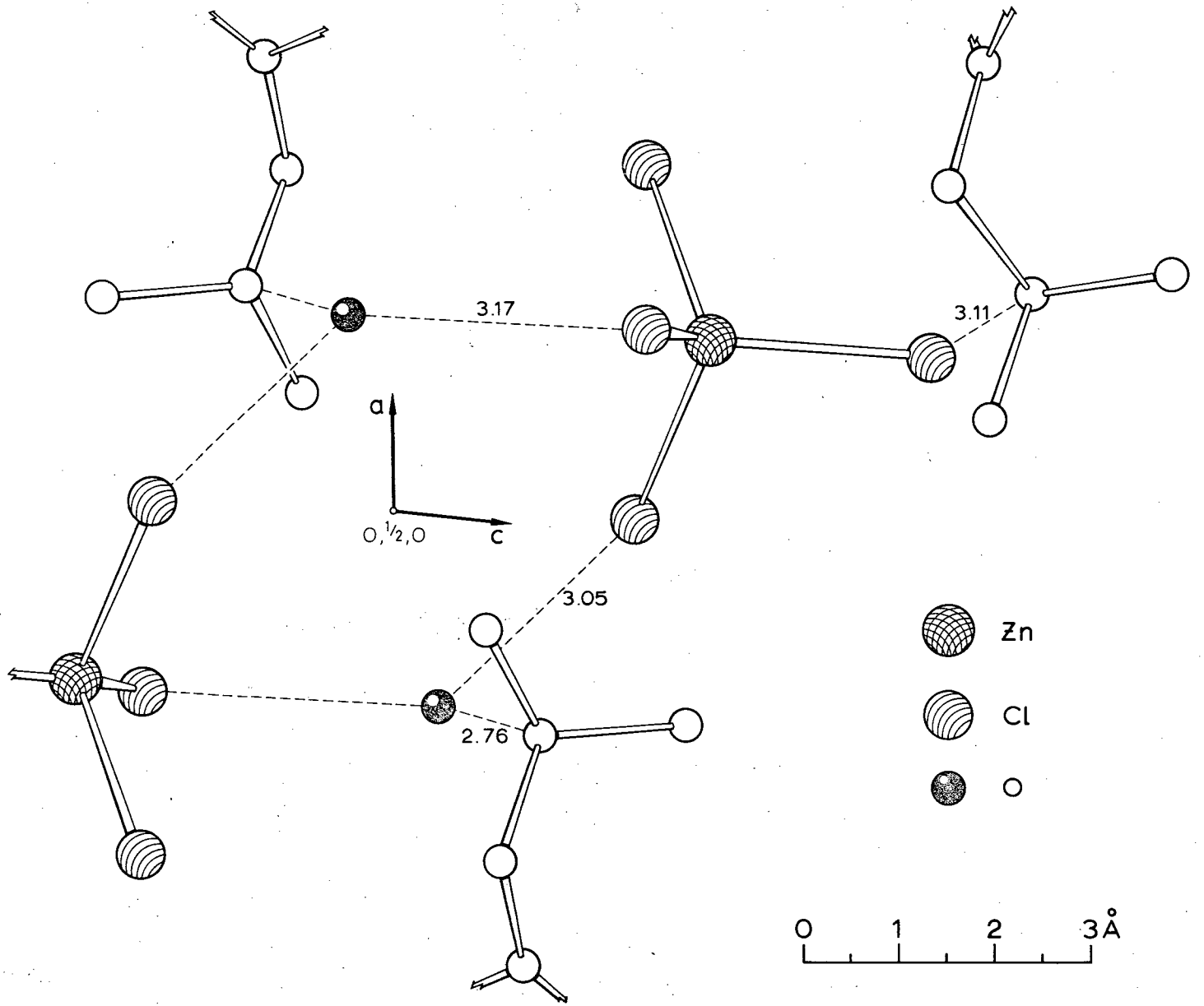

3.17
3.11
3.05
2.76
a
c
0,½,0
Zn
Cl
O
0 1 2 3Å

Table 19

All crystallographically independent distances < 3.7 Å between atoms in different asymmetric units.

Atom[I] to Atom	distance (Å)
O . . . .H - N(1)[III]	2.76
O - H . . . Cl(2)[I]	3.05
O - H . . . Cl(4)[II]	3.17
Cl(1). . H - N(2)[III]	3.11
Cl(1). . . .C^1(13)[IV]	3.56
Cl(1). . . .C^2(13)[III]	3.65
Cl(3). . . .C^1(11)[I]	3.67
Cl(4). . . .C^2(11)[III]	3.67
C^1(9). . . .C^2(9)[V]	3.65
C^1(12). . . C^2(13)[IV]	3.53
C^2(12). . . C^2(10)[VI]	3.46
C^2(2) . . . C^2(6)[VI]	3.57

[1] Cation 1 [2] Cation 2

I	x	y	z
II	- x	1 - y	- z
III	- x	½ + y	½ - z
IV	x	½ - y	½ + z
V	1 + x	y	z
VI	x	½ - y	-½ + z

The N...O...Cl angles are 97° and 121°, and the C-N...O and C-N...Cl angles are very close to the tetrahedral value at 109°, 105° and 110°, and 107°, 117° and 98° respectively.

The extent to which the chlorine atoms take part in hydrogen bonding is reflected in the Zn-Cl bond lengths (Table 17). Cl(2) and Cl(4) each interact with an oxygen atom at distances of 3.05 and 3.17 Å respectively, and have similar Zn-Cl lengths (2.270 and 2.274 Å respectively). Cl(1) is hydrogen bonded to a nitrogen atom at 3.11 Å, and the corresponding Zn-Cl distance is somewhat longer (2.299 Å), while Cl(3) has no contacts less than 3.6 Å, and is involved in the shortest Zn-Cl distance (2.229 Å). A similar situation has been reported for the $ZnCl_4^{-2}$ groups in the $Li_2ZnCl_4 \cdot 2H_2O$ structure[34]. Two hydrogen bonds to one chlorine atom lengthen the Zn-Cl distance to 2.30 Å, and a single interaction for two other chlorine atoms result in lengths of 2.28 Å, while the chlorine atom which is not involved in hydrogen bonding has the shortest Zn-Cl distance of 2.25 Å. These values may be compared with the normal distance for covalent tetrahedral zinc-chlorine bonds[35] of 2.30 Å. Comparable Zn-Cl distances have been reported for the three modifications of $ZnCl_2$[36], and for several related compounds[37-39].

The iron atoms are sandwiched between two cyclopentadienyl rings which are planar within experimental error (Table 18), approximately parallel, and separated by

3.28 Å (cf. ref. 40). The rings are nearly eclipsed as shown in Figure 10, and can be described in terms of the rotation of one of the rings from the eclipsed position as determined by the vectors from each carbon atom to the Fe atoms in the projection shown. The angles listed in Table 20 show that both ferrocene groups differ by only approximately 7° from the fully eclipsed position (0°) compared with the fully staggered position (36°), and are best described as approximately eclipsed. Similar small rotations from the eclipsed position have been reported for other ferrocene derivatives, for example, 5° in diferrocenyl ketone[40], 12° in α-keto-1,1'-trimethyleneferrocene[41] and 9° in 1,1'-tetramethylethyleneferrocene[42].

The bond lengths and angles in the cyclopentadienyl rings and the side chains do not differ from expected values[17] (Table 17), and the iron atoms appear to be bound equally to all the carbon atoms of the rings, the mean values being Fe-C = 2.04 and C-C (rings) = 1.43 Å.

Table 20

Angles from the eclipsed position for the cyclopentadienyl rings of the cations.

Cation 1		Cation 2	
C(1)-Fe-C(7)	6.6	C(1)-Fe-C(6)	11.2
C(2)-Fe-C(8)	7.5	C(2)-Fe-C(10)	5.5
C(3)-Fe-C(9)	4.4	C(3)-Fe-C(9)	2.1
C(4)-Fe-C(10)	7.3	C(4)-Fe-C(8)	6.4
C(5)-Fe-C(6)	8.0	C(5)-Fe-C(7)	9.7
Mean	6.8	Mean	7.0

SUMMARY

One of the objects of this work has been to show how the various methods of X-ray diffraction can be used to overcome the phase problem and deduce crystal and molecular structure. Although it is extremely useful and interesting to examine a series of related compounds and to correlate the results in terms of bonding, intermolecular interactions, etc., it is also of value to gain familiarity with the methods of X-ray crystallography by applying them to as diversified a set of problems as possible.

Examples have been chosen from organic (natural products), inorganic and organometallic compounds, and, while all contained heavy atoms, structure elucidation was not always straightforward because of problems peculiar to each compound. These differences are also reflected in the final results; one involved hydrogen bonding interactions between molecules; others ionic coordination to build up the crystal network (Ag...O and Ag...C).

Since in this case there can be no continuing of a series, and since the analyses have provided answers to the immediate problems proposed, an appropriate project to follow might be the investigation of compounds of higher symmetry, as all those studied were either monoclinic or orthorhombic. This would logically involve mineral or metallic crystals, and is not inconsistent with the author's interests.

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