PART I: THE STRUCTURE DETERMINATION OF MANGANESE TETRAPHENYLPORPHYRIN

PART II: THE REDETERMINATION OF THE STRUCTURE OF PORPHINE

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

BETTY MEI-HORNG LEE CHEN

1970

This is to certify that the

thesis entitled

Part I: The Structure Determination of Manganese Tetraphenylporphyrin.
Part II: The Redetermination of the Structure of Porphine.

presented by

Betty Mei-horng Lee Chen

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

A. Tulinsky
Major professor

Date April 9, 1971.

O-7639

C 121

220

ABSTRACT

PART I: THE STRUCTURE DETERMINATION OF MANGANESE TETRAPHENYLPORPHYRIN

PART II: THE REDETERMINATION OF THE STRUCTURE OF PORPHINE

By

Betty Mei-Horng Lee Chen

The structures of manganese tetraphenylporphyrin and porphine were determined by means of three dimensional X-ray crystallographic techniques. Both molecules crystallize in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The unit cell dimensions for manganese tetraphenylporphyrin are a = 14.56 Å, b = 21.77 Å, c = 17.02 Å, and $\beta = 135.6^0$, those for porphine are a = 10.27 Å, b = 12.09 Å, c = 12.36 Å, and $\beta = 102.2^0$.

Manganese tetraphenylporphyrin was shown to coordinate with an axial chlorine ion. The locations of the manganese and chlorine atoms were determined by the heavy atom method; the remaining atoms, including all the hydrogens, were located from difference syntheses. All atomic parameters were refined by the least squares method. The porphyrin molecules in the crystal were stacked approximately perpendicular to the $\vec{c}^*$ direction, with an acetone molecule from crystallization trapped between adjacent porphyrin molecules.

The Mn(III) ion in an approximately square-pyramidal geometry is displaced 0.27 Å from the mean plane of the four basal nitrogen atoms toward the axial chlorine ligand. The chlorine atom is slightly tilted ($\sim 5^0$) from the apical position to keep a reasonable contact distance (3.45 Å) to a carbon atom belonging to the phenyl group of an adjacent porphyrin molecule. The bond distances of Mn-Cl (2.36 Å) and Mn-N (2.01 Å), which are slightly shorter than expected, may be responsible for the high stability of this porphyrin. The porphyrin skeleton is ruffled since one pair of diagonal pyrrole groups is displaced below the NLS plane while the other pair is above it with apparent deviations of 0.3 - 0.5 Å for the peripheral carbon atoms. The porphyrin nucleus and phenyl groups were shown to be aromatic; the former was electronically separated from the latter by single bonds which join the phenyl rings to the porphyrin nucleus. The dihedral angles between individual phenyl groups and the NLS plane are 54.2^0, 123.5^0, 49.7^0 and 77.4^0 respectively.

The structure of porphine was determined previously by Webb and Fleischer, with an alleged copper impurity and a postulated "four half-hydrogen" structure for the central hydrogen atoms. Since the peak heights of the half-hydrogens were only slightly greater than background, and since the exact nature of these half-hydrogens with respect to van der Waals contacts was not reported, a redetermination

of the porphine structure was undertaken. In addition to collecting a complete set of all independent reflections, additional and more elaborate counting techniques were applied to those reflections which might contain a significant contribution to the hydrogen atom structure. The results indicated only two central hydrogen atoms bonded to one pair of diagonal nitrogen atoms. The central hydrogen atoms are coplanar to the porphine nucleus with N-H distances of 0.89 Å and 0.92 Å, respectively. The locations of H22 and H24 are inclined toward N21 and N23 at angles of 5.8^{0} and 4.5^{0} relative to the line joining the two opposite nitrogen atoms (N22-N24), respectively.

PART I: THE STRUCTURE DETERMINATION OF MANGANESE TETRAPHENYLPORPHYRIN

PART II: THE REDETERMINATION OF THE STRUCTURE OF PORPHINE

By

Betty Mei-Horng Lee Chen

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1970

ACKNOWLEDGMENT

The author wishes to express her appreciation to Professor Alexander Tulinsky for his guidance throughout the course of this study.

Appreciation is extended to Mr. Richard Vandlen and to Dr. N. V. Mani for their assistance.

Appreciation is also extended to Dr. Alan Adler for furnishing the samples of porphine and manganese tetraphenylporphyrin.

Appreciation is also extended to the Molecular Biology Section of the National Science Foundation for providing financial support.

Thanks are particularly due to her husband, Jing-shyong, for his constant encouragement and assistance.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

DEFINITIONS OF SYMBOLS USED

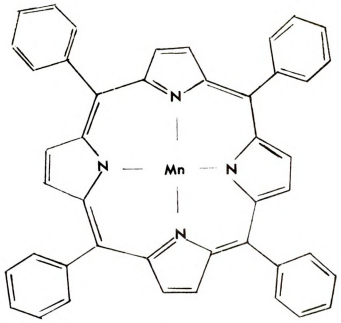
$\vec{a}, \vec{b}, \vec{c}$ or a, b, c	Primitive translations or unit cell axes of the crystal lattice, and their magnitudes.
β	Angle between $\vec{c}$ and $\vec{a}$.
$\vec{a}^*, \vec{b}^*, \vec{c}^*$	Primitive translations of the reciprocal lattice.
h, k, ℓ	Set of three integers with ranges from $-\infty$ to ∞.
$\bar{h}, \bar{k}, \bar{\ell}$	Negative of the above set
(h,k,ℓ)	Parallel lattice planes which intersect $\vec{a}$, $\vec{b}$, and $\vec{c}$ at intervals of a/h, b/k, and c/ℓ respectively.
f_j	Atom j's scattering factor or ability relative to a classical electron to scatter X-rays.
T_j	$= \exp - B_j(\sin\theta/\lambda)^2$ isotropic temperature factor of atom j $= \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)$ anisotropic temperature factor of atom j.
Z_i	Number of electrons belonging to atom i.
$\vec{r}_j$	$= x_j\vec{a} + y_j\vec{b} + z_j\vec{c}$. Position vector for atom j.
$F(hk\ell)$	$= \sum_{j=1}^{N} f_j\,(hk\ell) \exp 2\pi i(hx_j + ky_j + \ell z_j)$ structure factor for the reflection from (h,k,ℓ) planes. N atoms per unit cell.
$I(hk\ell)$	Intensity of the reflection from the (h,k,ℓ) planes.

$\|F_o(hk\ell)\|$	Observed structure amplitude, whose square is proportional to $I(hk\ell)$.
2θ	Scattering angle.
ϕ, χ, 2θ, ω	Angular settings for the diffractometer.
λ	Wavelength of X-ray radiation.
$\mathbf{A}(hk\ell)$	Absorption correction for the reflection from the (h,k,ℓ) planes.
μ	Linear absorption coefficient.
ρ_{oi}	Electron density calculated with structure factors whose phases, S_c, are those of i^{th} set of F_c $(hk\ell)$ and whose amplitudes are $\|F_o(hk\ell)\|$.
$\Delta\rho_i$	Difference synthesis calculated with coefficients $\|\|F_o\| - \|F_c\|\|$ and phases, S_c.
R	$= \dfrac{\Sigma\|\|F_o\| - \|F_c\|\|}{\Sigma\|F_o\|}$ Residual index.

GENERAL INTRODUCTION

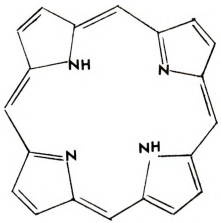
Porphyrins (Fig. 1a) are derivatives of porphine (Fig. 1b), a system in which four pyrrole rings are linked by four methine carbon atoms to give a sixteen-membered macrocyclic ring. The porphyrins are found to be essential for certain biological functions such as: (i) oxygen storage and transport, as in myoglobin and hemoglobin; (ii) cellular respiration involving electron transport, as in the cytochromes; and (iii) photosynthesis, as in the chlorophyll-containing chloroplasts. All these biologically active substances consist of three distinct parts: the porphyrin, a central metal atom, and a complicated molecular environment.

Recently, manganese porphyrins have been considered to be important in chloroplasts, since manganese is essential in the energy converting unit of the plant. There is evidence that the plant can restore its ability to reduce carbon dioxide and evolve oxygen by adding manganese ions back to the energy system. Although there is little evidence to indicate the function and environment of manganese, it has been suggested that manganese is complexed with ligands of biological interest such as porphyrins. Thus, the structural properties of manganese-containing porphyrins may be of importance and biological interest.



(a)

(a) Manganese tetraphenylporphyrin, $MnC_{44}H_{28}N_4$.



(b)

(b) Porphine, $C_{20}H_{14}N_4$

Figure 1.

Manganese tetraphenylporphyrin (Fig. 1a, hereafter referred to as MnTPP) is a synthetic porphyrin. Single crystals of MnTPP form in the monoclinic crystal system and contain four molecules in the unit cell. Since space group requirements dictate that each asymmetric unit contains one complete molecule, the molecular structure of MnTPP is not affected in any obvious way by crystal symmetry. For this reason and others already mentioned, an X-ray crystallographic study of the structure of MnTPP was undertaken in anticipation of perhaps providing information of biological interest and utility, as well as adding to the general understanding of metalloporphyrins.

In the other portion of this work, a redetermination of the structure of porphine was carried out. As the parent compound of the porphyrin series, the structure of porphine is particularly important because any understanding of the porphyrins must rest intimately upon the understanding of porphine.

The central hydrogen atoms of the free base of porphine and of porphyrins are known to influence the detailed structure of the porphyrin skeleton. Various techniques have been used to probe properties of these central hydrogen atoms. Low temperature visible spectroscopy suggested the existence of *cis* and *trans* isomers, *i.e.*, hydrogen atoms on adjacent and on opposite pyrrole nitrogen atoms, respectively. Attempts to detect hydrogen bonding between hydrogens and neighboring nitrogen atoms by infrared spectroscopy

were inconclusive. Nuclear magnetic resonance spectroscopy suggested the rapid exchange of the inner hydrogen atoms. On the other hand, the X-ray diffraction analysis of the triclinic form of tetraphenylporphyrin (tri-TPP) showed that the two inner hydrogen atoms were localized and located on opposite nitrogen atoms, whereas the results of a similar study of the tetragonal form of TPP indicated a disordered structure for the molecule (two equally probable positions in the plane of the molecule 90^0 apart). From the X-ray diffraction work of Webb and Fleischer, the porphine molecule was reported to be essentially planar with an average symmetry close to $D_{4h}(4/mmm)$ and to contain four inner half-hydrogen atoms. The latter were suggested to be due to a rapid interconversion of N-H tautomers. However, since the crystals were also reported to contain a 5-10% impurity of copper porphine and since the electron densities of the half-hydrogen atoms were only slightly above background, the situation of the central hydrogen atoms remained unceratin. For these reasons and others to be elaborated upon later, an X-ray crystallographic re-examination of the structure of porphine was undertaken.

PART I

THE STRUCTURE OF MANGANESE TETRAPHENYLPORPHYRIN

I. INTRODUCTION

1. Metalloporphyrins

The porphine skeleton with four pyrrole rings and four methine carbon atom bridges is shown in Figure 1b. There are fourteen replaceable hydrogen atoms, eight pyrrole hydrogens, four methine hydrogens, and two central hydrogen atoms bonded to nitrogen atoms. Derivatives which are produced by the replacement of inner hydrogen atoms by metals are the metalloporphines, while those whose outer hydrogens are replaced by other groups are called porphyrins. The four methine carbon atoms can also be replaced by aza-nitrogen atoms forming azaporphines which, in turn, are related to the phthalocyanines by fusion of a benzene ring to each pyrrole. The two inner hydrogens of phthalocyanine are also replaceable by a wide variety of metals.

Porphine is a planar molecule, made up of eleven conjugate double bonds, with considerable flexibility to fold as demanded by environmental stresses and strains. Some forces which can affect the conformation of the porphyrin moiety are: (1) a central metal atom, (2) side-chain substitutions on the porphyrin ring, and (3) intermolecular forces from the environment of the molecule. Of greatest

concern in this work is the coordination of the central metal atom and its effect on the porphyrin system.

2. Review of Porphyrins and Metalloporphyrins

Extensive reviews of structural studies of porphyrins and metalloporphyrins have been written by Hoard[1] and Fleischer.[2] The following on the geometry of metals in metalloporphyrins is intended as a brief summary of these reviews (see Fig. 2).

Since porphyrins consist of large conjugated systems which can serve as tetradentate ligands, metallic cations are able to be accommodated at the center of the system with the four nitrogen atoms serving as ligands. The metals of metalloporphyrins have been found in a variety of coordinations. Four coordinate compounds formed by central metal atoms bonded with the four pyrrole nitrogen atoms have approximate square planar geometry. Although the porphine skeleton of these porphyrins is a conjugated system and is usually assumed to be planar, some of the metalloporphyrins, such as CuTPP[3] and nickel etio-I porphyrin[4] have been found to possess nonplanar porphyrin rings. Furthermore, there are small variations of metal-nitrogen (M-N) distances from one porphyrin to another. The reasons for the nonplanarity and the variation in M-N bond distances are as yet not well understood.

Five coordinate metalloporphyrins are found to have square pyramidal geometry. In general, the metal is

Figure 2. Geometry of metals in metalloporphyrins.

(1) four-coordinate with a square planar geometry.

(2) tetragonal pyramid coordination of five-coordinate metalloporphyrins.

(3) six-coordinate metalloporphyrins.

(4) possible seven-coordinate metalloporphyrins.

(5) square antiprism of the eight-coordinate tin phthalocyanine complex.

(6) manganese(III) phthalocyanine dimer.

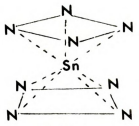
(7) μ-oxo-bis(porphyriniron(III) dimer.

(1)

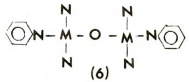
(2)

(3)

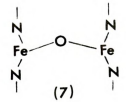
(4)



(5)



(6)



(7)

Figure 2.

displaced from the mean plane of the pyrrole nitrogen atoms toward the apical ligand. For example, iron in high spin ClFeTPP[5] shows an out-of-plane displacement of about 0.4 Å, and vanadium in vanadyl-substituted etioporphyrin[6] is 0.48 Å out of the plane. In some of these porphyrins, there is a significant shortening of the axial bond between the apical ligand and the metal. For example, the axial length of Fe-Cl in ClFeTPP is 2.19 Å, while the corresponding value listed in International Tables for X-Ray Crystallography is 2.38 Å. Similar shortening effects are also observed in the O-Mg (2.07 A) bond of $(H_2O)MgTPP$[7].

Six coordinate compounds display distorted octahedral geometry; eight coordination is found as a square-antiprism sandwich in the tin phthalocyanine complex,[8] and higher coordinate metalloporphyrins do not seem to form. On the other hand, dimeric metalloporphyrins such as μ-oxo-bis(porphyriniron(III))[9] are known. Here, the iron atom has five coordination and is about 0.5 Å out of the nitrogen plane in the direction toward the oxygen bridge, with the Fe-O-Fe angle being about 170^0.

In general, the bond distances of the porphine core as determined from X-ray studies do not correspond to an average of single and double bond distances nor a single-bond-double-bond array of a conjugated double bond system. The average carbon-nitrogen distance[10] of most metalloporphyrins is about 1.37 Å, which is shorter than the 1.42 Å distance expected for a trigonally hybridized C-N σ-bond,

but longer than the 1.27 Å distance observed for the C=N double bond. In the pyrrole ring, the average C_a-C_b bond length (where C_a is the carbon atom adjacent to the pyrrole nitrogen while C_b is the carbon adjacent to C_a) is about 1.45 Å, a definitely shorter value than the bond length of 1.49 Å expected between trigonally hybridized carbon atoms, while the average C_b-C_b bond length of 1.35 Å indicates a lengthening of the double bond value of 1.33 Å.

The center-nitrogen distance (Ct-N), which indicates the radius of the central hole of the porphyrin core, has been observed in most cases to be smaller in metalloporphyrins than that of the corresponding free base porphyrins. The bond distances of the metal-nitrogen (M-N) of metalloporphyrins have been observed to vary from 2.05 Å in ferric porphyrin to 1.95 Å in nickel etio-I porphyrin. There seems to be no direct relationship between the M-N bond length and the size of metal atom. Furthermore, the metal atom can be in or out of the mean plane of the four nitrogen atoms. This effect has been carefully examined in iron porphyrins by Hoard,[10] who predicted that a low-spin iron porphyrin would have iron in the nitrogen plane while the metal in high-spin iron porphyrin would be 0.5 Å out of the mean plane. Indeed, this prediction has been verified by the structure analysis of bisimidazoleiron(III) tetraphenylporphyrin.[11]

3. Manganese Porphyrins

Porphyrin complexes of Mg, Co, and Fe are known to occupy central roles in chlorophyll, vitamin B_{12}, and hemeproteins. Recently, manganese porphyrins have received a great deal of attention because of their possible link to chloroplasts. Two reasons for this interest are: (1) the relationship of manganese porphyrins in photosynthesis, and (2) the coordination chemistry of this transition metal in a porphyrin environment.

The chloroplast, which is the most essential component in photosynthesis, contains protein, lipid, chlorophyll, inorganic ions and carotenoids. Among these components, chlorophylls and inorganic ions, such as manganese ions, have been considered to be most important in the energy transfer process.[12,13] Chloroplasts can be broken down into subunits, with the smallest subunit, a quantasome, being about 200 Å in diameter. For each quantasome, there are precisely two manganese atoms per 300 chlorophyll molecules. In addition, there is evidence that manganese is an essential element for the oxygen evolving step of photosynthesis. When manganese ions are re-added to the plant's environment, its ability to evolve oxygen is restored, and the plant can perform its normal function of reducing CO_2 and evolving oxygen. All the evidence indicates that the presence of manganese is a functional requirement of the chloroplasts. However, the manganese is difficult to remove from chloroplasts, and its physical properties as such are not easily observed.

Calvin[14] has suggested that the manganese atoms in the chloroplast are bound to porphyrin type ligands. He has demonstrated that manganese porphyrin can undergo reversible oxidation-reduction changes between Mn(II)-Mn(III) and Mn(III)-Mn(IV), with the Mn(III) species being unusually stable. This initial work supported the relevance of manganese porphyrin as a possible photosynthetic model compound.

The physical and chemical properties of manganese porphyrins have been studied by Boucher.[15,16] Magnetic susceptibility measurements in the solid and in solution, at a number of different temperatures, yield an effective magnetic moment in the range of 4.5 to 5.0 B.M. The expected value for a spin-free d^4 manganese(III) complex is 4.9 B.M. These measurements suggest that there is no spin pairing. The far infrared spectra show metal-anion stretching absorptions in the region of 160 to 500 cm^{-1}, consistent with the strong binding of an additional ligand in the axial coordinate position of the metal. In solution, electronic spectra showed that six-coordinated manganese porphyrins were present with various ligands. From these spectra it was concluded that manganese porphyrins have significant metal-porphyrin π-bonding; however, the porphyrin-metal d-orbital π interaction is difficult to describe quantitatively. Two possible geometries of the molecule have been predicted. One possibility is that of tetragonal geometry with the metal ion in the plane of four pyrrole

nitrogen atoms, with an axial anion and a solvent molecule at somewhat larger distances from the metal. The other possibility is that the metal atom is out of the plane of the porphyrin (about 0.5 Å), coming closer to the axial anion. The latter geometry can be rationalized by saying that because of the large size of the metal ion, it cannot fit into the nitrogen cavity. In any case, the exact molecular structure of manganese porphyrins was still in question. For such reasons, it seemed particularly appropriate to carry out a detailed structural determination of a manganese porphyrin.

II. EXPERIMENTAL

1. Photographic Studies

Photographic methods provide a quick and easy way to obtain a general view of the geometry of a diffraction pattern, the symmetry of the reciprocal lattice, and the relative intensity distribution of a large number of reflections. Methods available to obtain such information are oscillation and moving film photography (Weissenberg and precession methods).

In the oscillation method, the crystal is mounted in a manner such that some principle axis coincides with the oscillation axis and the crystal is oscillated through a small angle, i.e., $5\text{-}10^{0}$, around this axis by means of some threaded gear or other mechanism. The photographic film is placed in a cylindrical camera around the oscillation axis. A small number of planes will come into a reflecting position with this oscillating motion and will produce spots on a film in the form of a series of separated layer lines. The diffraction pattern recorded in this way can provide useful information regarding the symmetry of the crystal lattice and the spacing of the lattice along the oscillation axis.

Single crystals of MnTPP were grown by slow evaporation of an acetone solution. The dark purple crystals exhibited polyhedral morphology with many well-defined faces. A crystal of suitable size (approximately 0.4 x 0.2 x 0.3 mm) and with good morphological quality was chosen for photographic examination. A 10^0 oscillation photograph of a crystal mounted with its largest dimension perpendicular to the spindle oscillation axis showed that the intensity distribution of the upper and lower halves of the photograph were symmetrical with respect to the zero layer line. This distribution indicated the presence of a mirror plane of symmetry in the direct lattice perpendicular to the oscillation axis and either a monoclinic lattice or one with higher crystal symmetry (i.e., orthorhombic or higher).

In the Weissenberg film method, a single layer line normal to the oscillation axis is selected for observation by means of a slotted screen which allows only the reflections in that layer to be recorded on the photographic film. As the crystal rotates, the film moves past the screen slot in a synchronous way and reflections which occur at different times are recorded at different translational positions on the film. The moving film photograph displays the reciprocal lattice plane which is perpendicular to the oscillation axis and can be used to determine the symmetry of these planes and to index reflections. Photographs of several successive layers of the MnTPP crystal were taken. The lack of any further symmetry elements showed that MnTPP crystallized in a monoclinic lattice. The unique b axis of the

monoclinic crystal system coincided with the oscillation axis and the a* and c* reciprocal axes were selected so that the zero layer photograph showed the reflections (h0ℓ) absent when the ℓ index was odd. This characteristic extinction is due to a c-axis glide plane, and corresponds to a reflection across a plane accompanied by a translation of c/2 parallel to the plane along the c axis.

In the precession method, the crystal oscillates about an axis with the latter also undergoing an oscillation. The net motion closely resembles a precession motion. During these motions, the film always remains parallel to the reciprocal lattice plane which is perpendicular to the X-ray beam in the absence of a precession angle, and thus records the true, undistorted, geometry of the reciprocal lattice plane. Precession photographs of MnTPP taken of the reciprocal planes parallel to the b-axis (hk0 and 0kℓ) showed that 0k0 reflections were absent whenever k was odd. This absence indicates the presence of a 2-fold screw axis along the b axis of the crystal (i.e., 2-fold rotation plus b/2 translation along the rotational axis).

Thus, the preliminary studies of the crystal MnTPP showed that the crystal belongs to a monoclinic system with a space group possessing the following conditions for systematically absent reflections:

0k0 reflections, $k = (2n + 1) = \text{odd}$

h0ℓ reflections, $\ell = (2n + 1) = \text{odd}$.

From these conditions, the space group was uniquely

determined as $P2_1/c$, space group No. 14, subgroup number 2, as tabulated by the International Tables for X-ray Crystallography.

2. Diffractometer Intensity Data Collection

A second crystal, which was slightly smaller than the one used for photographic studies, with dimensions of about 0.25 x 0.15 x 0.15 mm (see Fig. 6) was used for intensity measurements. The crystal was mounted on a goniometer head whose axis was coincident with the Φ circle of a quarter circle crystal orienter (see Fig. 31 given in Appendix 1). The orientation of the crystal with respect to the diffractometer axis was such that the unique b axis of the crystal was also coincident to the Φ axis of the diffractometer. The a* c* plane was thus located in the equatorial plane ($\chi = 0^{\circ}$). The unit cell dimensions of the crystal were determined by measuring the angular orientation which centered the intensity of 12 moderately intense reflections well-distributed in reciprocal space and with large 2θ angles. The angular coordinates were used with the method of least squares to obtain the best unit cell parameters and least squares orientation of the crystal. The results are listed in Table 1.

The density of a single crystal of MnTPP was measured by flotation in an aqueous silver nitrate solution and indicated that there were four molecules in the unit cell.

The observed density of the crystal was 1.30 g/cm^3; however, the calculated density based on four MnTPP molecules in the unit cell was only 1.17 g/cm^3. The high observed molecular weight (738 instead of 667) suggested the presence of additional material in the unit cell. This material could have been introduced at the time of preparation(ions) or crystallization(solvent). The discrepancy was resolved later during the structure determination.

Table 1. Crystallographic Data for MnTPP

Space Group	Monoclinic $P2_1/c$	$Z^* = 4$
a	14.588 ± 0.005 Å	Empirical formula $MnC_{44}H_{28}N_4$
b	21.765 ± 0.006	M.W. = 667
c	17.023 ± 0.006	D_{obs} = 1.30 ± 0.01 g cm^{-3}
β	135.62 ± 0.04 degree	D_{cal} = 1.17 g cm^{-3}

Volume 3773.8 ± 3.4 Å^3

*Number of molecules in the unit cell.

The quality of the crystal chosen and the best quadrant for data collection can be ascertained by measurement of the mosaic spreads of the crystal, essentially a measurement of the degree of misalignment of the mosaic blocks (minute perfect crystal blocks) which make up the real crystal. For MnTPP, the reflections (080), (300), ($\bar{3}$00), (006) and (00$\bar{6}$) were chosen to measure the mosaic spreads. The mosaic spreads of ($\bar{3}$00), (300), (006), and (00$\bar{6}$)

reflections (at $\chi = 0^0$) were measured by: (1) presetting 2θ at the center of the reflection as determined by use of a left/right device which allows either the left half or the right half of the diffracted beam to be selectively examined, (2) off-setting the Φ angular setting to the background level of the peak, and recording the intensity, I, of the diffracted beam as a function of the angle Φ in increments of 0.05^0 from background to background. The mosaic spreads of the (080) reflection (at $\chi = 90^0$) were measured by: (1) presetting $2\theta_{max}$, (2) presetting Φ at the value of the a*, c*, -a*, and -c* axes, (3) offsetting the ω angle to the background level and recording the intensity, I, as a function of the ω angle in increments of 0.05^0 from background to background. The mosaic spread of $(00\bar{6})$ was found to have the maximum basal peak width which was 0.45^0. All the remaining mosaic spreads were about 0.3^0 in width and symmetrical in shape. The data collection was thus restricted to the quadrant defined by the -a* axis ($\Phi = 298.5^0$), and a* axis ($\Phi = 118.5^0$) and including the c* axis at $\Phi = 38.9^0$.

A set of intensity data was collected with a Picker 4-Circle Automatic Diffractometer using the moving crystal-moving counter technique (2θ scan). In this technique, the reflection was scanned and counted with the radiation filtered through a nickel filter (β filter) in order to remove Cu Kβ radiation. A second scan was then made with a balanced cobalt filter (α filter), i.e., one whose

absorption edge is at a wavelength just longer than the $K\alpha$ radiation being used. A flow chart of the data collection procedure is shown in Figure 3. Within a 2θ limit of 100^0, the total number of reflections measured was 3978. In order to ascertain which reflections should be considered as unobserved, the lower limit of intensity corresponding to the average background intensity fluctuation was determined as follows. Any measured intensity of reflections which are systematically absent, i.e., $(h0\ell)$ and $(0k0)$ reflections k or ℓ odd, should be mainly due to the effects of background radiation. Using this assumption, an average intensity of 7 counts/10 sec was obtained by measuring 93 systematically absent reflections. Thus the minimum observable intensity for reflection was set to be slightly larger than this average background value. Eliminating the unobserved reflections, systematically absent reflections, and all redundant reflection ($\pm$ hk0 reflections), a total of 2977 unique and observable reflections remained for the structure determination of MnTPP.

If during the course of data collection procedure the intensity of any of the monitor reflections (004), $(\bar{7}00)$ and (080) was outside the expected counting statistic error, approximately the square-root of the original intensity ($\sqrt{I}$), the crystal was realigned and data collection was resumed. Throughout the data collection the intensity of the monitors did not fluctuate by more than 10% of their original value. Since there was no systematic

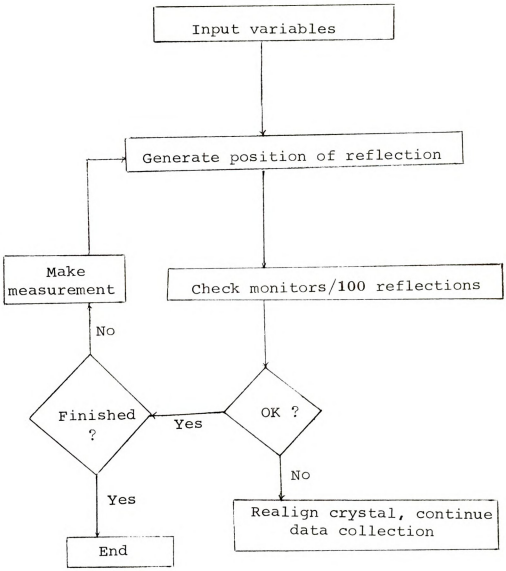


Figure 3. Flow chart for data collection procedure.

intensity decrease a decay correction was not considered necessary.

The absorption of X-rays by the crystal (see Appendix 1) showed a functional dependence on both 2θ and Φ. Although initially only an approximate absorption correction was applied to the data in terms of both these angles, a more accurate correction was applied later.

The intensities of all the independent reflections were subsequently corrected for Lorentz and polarization effects, and converted to a set of relative structure amplitudes ($|F|$).

III. STRUCTURE DETERMINATION

1. Introduction

It is well known that an X-ray wave scattered by the atoms of a crystal can be characterized by a quantity $F(hk\ell)$ called the structure factor. This quantity is a complex number whose magnitude is the amplitude of the scattered wave and whose orientation in the complex plane is determined by the phase of the scattered wave. The structure factors depend on the arrangement of atoms in the crystal. If the magnitudes and phases of the structure factors are known, the electron density distribution in the unit cell can be calculated; conversely if the electron density is known, structure factors can be obtained. The fundamental difficulty encountered in crystallography is that the magnitudes of the structure factors are obtainable from measured intensities, but the phases cannot be measured directly. Determination of the phases of the structure factors is known as the phase problem.

There is no general solution for the phase problem. However, it has been found that structures in which one or a few atoms are markedly heavier than the remainder are usually more easily solved than those in which all the atoms

are alike. The reasons for this are: (1) it is possible to locate the heavy atoms in the crystal by methods which do not require knowledge of the phases, and (2) once the heavy atoms have been found they can serve as a trial phase model from which the remaining atoms can be found.

2. Location of the Manganese Atom

The Patterson function is a Fourier series whose coefficients are the squares of the structure amplitudes, $|F(hk\ell)|^2$. The structure amplitudes are directly derivable from X-ray intensities. The Patterson function is related to the electron density function, both of which can be expressed mathematically as the following Fourier series

electron density:

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

Patterson function:

$$P(uvw) = \frac{1}{V^2} \sum_{hk\ell} \sum \sum |F(hk\ell)|^2 \cos 2\pi(hu + kv + \ell w) \quad (2)$$

Then, (1) has a peak at each atom location, while (2) has peaks corresponding to the end of the vectors between atom locations. The coordinates of the r^{th} peak in (2) are related to those of i^{th} and j^{th} peaks in (1) by

$u_r = x_j - x_i$, $v_r = y_j - y_i$, and $w_r = z_j - z_i$.

Thus for every pair of peaks in (1), there is a specific peak in (2).

Harker (1936)[17] pointed out that in some cases much useful information is concentrated in certain planes of the three-dimensional Patterson function. For space group $P2_1/c$, there are four equivalent positions:

(a) x_i , y_i , z_i

(b) $\bar{x}_i$, $\bar{y}_i$, $\bar{z}_i$

(c) $\bar{x}_i$, $1/2 + y_i$, $1/2 - z_i$

(d) x_i , $1/2 - y_i$, $1/2 + z_i$.

For atoms which are related by equivalent positions (a) and (c), there is a corresponding peak in the section $v = 1/2$, ($u = 2\bar{x}_i$, $w = 1/2 - 2z_i$). This section ($v = 1/2$) is called a Harker section. The same reasoning applies to atoms related by (b) and (c), with the corresponding vector occuring on the Harker line with coordinates, ($u = 0$, $v = 1/2 + 2y$, $w = 1/2$).

If the crystal contains only a few heavy atoms in the unit cell, the locations of these atoms can be solved by the use of the Patterson function. The Patterson peaks are approximately proportional to the product of atomic number of the atoms giving rise to them ($Z_i Z_j$); thus the peaks due to the heavy atoms stand out against the background of other smaller peaks. The overlapping of peaks which is caused by finite widths can be reduced by a process known as sharpening. Thus, the Patterson coefficients can be modified to make the heavy-atom vectors appear approximately as vectors between point atoms. Normally the scattering

power of an atom decreases as a function of $(\sin \theta/\lambda)$, but sharpening can remove this fall-off characteristic by making the scattering power equal to atomic number Z for all $(\sin \theta/\lambda)$. A common expression used for sharpening[18] is

$$|F_{point}| = |F_0|/\bar{f} \text{ , where } \bar{f} = \sum_{i=1} (f_m)_i / \sum_{i=1} (Z_m)_i$$

Z_m is the number of electrons in an atom of m type.

f_m is atomic scattering factor of atom m.

Once the $|F_{point}|$'s are obtained from the observable $|F_0|$'s, they can be squared and used as the coefficients for a sharpened Patterson function. The effect of sharpening enhances the heavy-atom vectors and makes peaks more resolved.

MnTPP contains four Mn atoms in the unit cell and their positions were found by the use of Patterson function. The Patterson coefficients were sharpened with the Mn atomic scattering factor

$$|F_{point}| = (Z_{Mn}/f_{Mn}) \ |F_0|,$$

where Z_{Mn} is the number of electrons of the Mn atom (25), and the denominator is the atomic scattering factor of Mn atom, as obtained from the f-curve tabulated in International Tables for X-ray Crystallography.[54] The vector peak due to Mn-Mn interactions showed clearly in the Harker section of the Patterson map (shown in Fig. 4). The coordinates of Mn atoms from the Harker section and Harker line (Fig. 5) are

Figure 4. Harker section of ClMnTPP. Peak 1 is Mn-Mn vector, peak 2 is Cl-Cl vector.

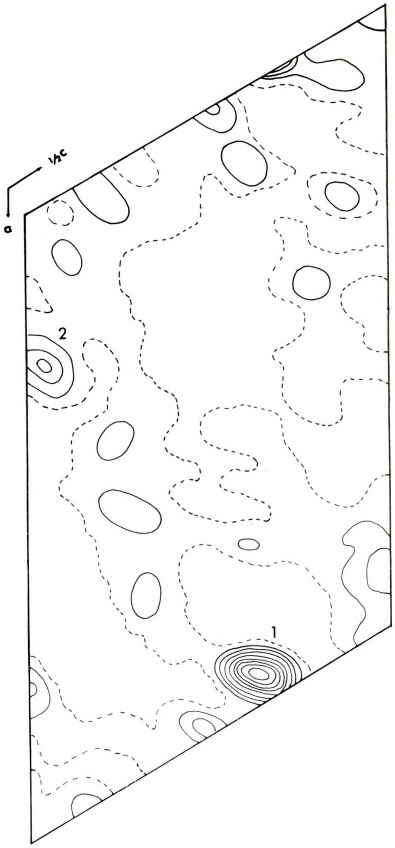


Figure 4.

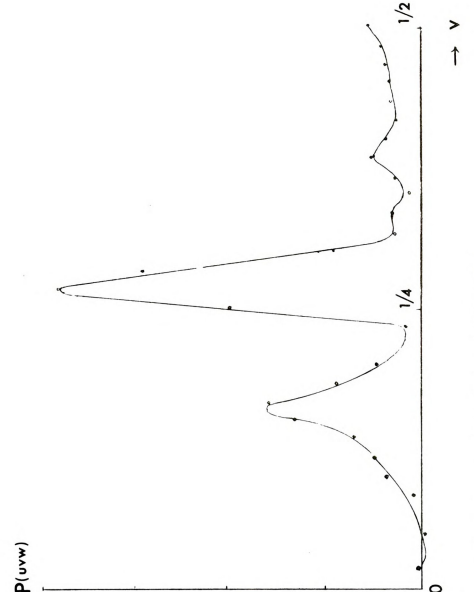


Figure 5. Harker line of ClMnTPP.

(in fractions of a unit cell):

$x = -0.4766$

$y = 0.1142$

$z = 0.0875.$

The remaining atoms in the unit cell were found by using electron density methods.

3. Electron Density

The structure factor with one heavy atom in the unit cell can be written as

$$F(hk\ell) = f_H \exp 2\pi i(hx_H + ky_H + \ell z_H) + \sum_n f_n \exp 2\pi i(hx_n + ky_n + \ell z_n) \quad (3)$$

where f_H is the scattering factor of the heavy atom, whose positional parameters are x_H, y_H, z_H. If f_H is much greater than f_n, then the first term will tend to dominate the scattering factor expression. To a first approximation, the structure factor can then be represented as

$$F_c \cong f_H \exp 2\pi i(hx_H + ky_H + \ell z_H)$$

or in centrosymmetrical case

$$F_c \cong |F(hk\ell)| \cdot S_c(hk\ell) \quad (3a)$$

where S_c is the sign of the calculated structure factor, F_c, and $|F(hk\ell)|$ is the observed structure amplitude. By use of equation (3a), an electron density can be computed from the calculated heavy atom phases and the magnitudes

of the $|F_o|$'s'

$$\rho(xyz) = \frac{1}{V} \sum\sum\sum_{hk\ell} |F_o(hk\ell)| \, S_c(hk\ell) \cos 2\pi (hx + ky + \ell z) \quad (4)$$

where $|F_o|$ is observed structure amplitude. Light atoms found in this approximate electron density can then be used to generate a new set of better phases. By continuing this "bootstrapping" procedure, all atoms except the very light ones can usually be found.

In the present work, an electron density was calculated on the basis of the manganese atomic position derived from the Patterson function. In this calculation some small and phase undetermined reflections ($|F_o| < 10$) were excluded. Many peaks which were ascribed as light atoms appeared in an approximate plane in the unit cell. However, at this stage it was impossible to discern the expected molecular geometry, probably because the phases based on just the Mn atom contained considerable errors and introduced many spurious peaks in the density along with the correct ones. However, one strong peak was found approximately 2.5 Å away from the manganese atom and approximately perpendicular to mean plane of peaks. The Harker section was re-examined, and indeed, there was a vector due to an atom with approximately fourteen electrons. Anions that could possibly be coordinated with manganese, introduced either during preparation or crystallization, were considered.

Manganese porphyrin can be synthesized[15] from a mixture of divalent manganese acetate and free base porphyrin in a

reaction medium such as glacial acetic acid or N,N¹-dimethylformamide.[19] Dilute sodium halide solution is used to extract and to purify the product. In the presence of air, Mn(II) porphyrin is rapidly oxidized to the very stable Mn(III) porphyrin, for which a halide complex has been reported under these prepartory conditions.

Among possible anions, it was decided from the above that chloride was the most likely anion bound to the manganese atom; moreover, it also corresponded to about the correct number of electrons. Thus, the peak from Harker section and Harker line with coordinates,

$$x = 0.6350$$
$$y = 0.1667$$
$$z = 0.2467$$

was assigned as chlorine. This increased the expected molecular weight to 702 a.m.u. and the calculated crystal density based on four ClMnTPP molecules was 1.23 g/cm^3 (D_{obs} = 1.30 g/cm^3).

Another electron density phased with the Mn and Cl contributions was calculated. This new map showed little improvement of the light atom structure over the original one except for the appearance of the chlorine atom.

4. Difference Synthesis

The difference synthesis is a Fourier series whose coefficients are the quantities $F_o - F_c$, ΔF,

$$\Delta\rho = \frac{1}{V} \sum_{hk\ell} \sum \sum (|F_o| - |F_c|) \cdot S_c \cos 2\pi(hx + ky + \ell z) \quad (5)$$

where S_c is the sign of the calculated structure amplitudes $|F_c|$. In the early stages of a structure determination, when the exact phases of $|F_o|$ are not known well, a trial structure can sometimes be arrived at by calculating a difference synthesis where dominating heavy atom contributions are removed. Three criteria should be considered in selecting the coefficients. In the first case, when $|F_o|$ is approximately equal to $|F_c|$ ($|F_o| \approx |F_c|$), the calculated phase is probably close to the true phase. The second case is then $|F_o|$ is much larger than $|F_c|$ ($|F_o| >> |F_c|$). Here, because F_c is small, the calculated phase is fairly uncertain due to the fact that small changes could cause fairly large changes in F_c. Thus, use of the calculated phase for $|F_o|$ becomes very unreliable and can introduce large errors. In the third case, where $|F_c|$ is much larger than $|F_o|$ ($|F_c| >> |F_o|$), even though the discrepancy is large the sign of the difference is correct. Therefore, the reflections used in a difference synthesis should be mostly those satisfying the first and third cases.

Because an unambiguous location of the light atoms could not be obtained from the $|F_o|$ synthesis due to the many spurious peaks, a difference synthesis was computed. Since the difference synthesis is very sensitive to the scale constant between $|F_o|$ and $|F_c|$, an accurate scale constant must be applied to either the F_c or $|F_o|$ (if $|F_o|$

is not on the absolute scale). The scale constant k can be obtained from a Wilson plot of the data. A Wilson plot is based on the equation[20,21]

$$\ln(\langle |F_o|^2 \rangle / \sum_{i=1}^{N} f_{oi}^2) = \ln k - 2B(\sin\theta/\lambda)^2 \qquad (6)$$

where $\langle |F_o|^2 \rangle$ is related to the average intensity, f_{oi} is the scattering factor of i^{th} atom, N is the total number of atoms in the unit cell and B is an average thermal parameter. By plotting the quantity $\ln(\langle |F_o|^2 \rangle / \sum_{i=1}^{N} f_{oi}^2)$ vs $(\sin\theta/\lambda)^2$, a straight line can be obtained from which the intercept is ln k and the slope is 2B. In applying the Wilson plot to the intensity data of MnTPP, the reflections were separated into 12 ranges of 2θ, where each range contained about the same number of reflections (approximately 250). Values for $\langle |F_o|^2 \rangle$ and $(\sin\theta/\lambda)$ were calculated for each range. The quantity f_{oi} was taken from f-curves at the average $(\sin\theta/\lambda)$ for each range. The result of this plot gave for B the value of approximately 4.0 Å^2. The value of the isotropic thermal parameter obtained was about that expected for organic compounds (between 3 to 5 Å^2).[22] The summation of observed and calculated structure factors suggested for the scale constant a value of approximately 0.82. Since the value of k obtained from the Wilson plot seemed unreasonable this latter value was used in the structure factor calculations.

Initially, isotropic temperature factors of 3.5 Å^2 and 4.5 Å^2 were assigned to Mn and Cl atoms, respectively. The

R-factor of the calculation, where R is defined as $\Sigma \; ||F_o| - |F_c||/\Sigma \; |F_o|$, based on the Mn atom alone was 0.69, while the R-factor including both Mn and Cl atoms was 0.52. The observed and difference syntheses calculated were based on the latter structure.

The structure determination can be divided into three stages. In the first stage, a difference, $\Delta\rho_1$, and observed electron density, ρ_{o1}, were computed using 1266 reflections whose calculated structure factors were greater than 14 electrons (on an absolute scale). By considering only those peaks which occurred in both densities as possible atoms, four nitrogen atoms and thirteen carbon atoms were located with reasonable bond distances in the approximately expected geometry. The structure factor calculation with these seventeen atoms had an R-factor of 0.458. The same structure factor calculation excluding the chlorine atom from the calculation increased the R-factor to 0.507. Thus, at this stage, it was decided that Cl atom was truly in the crystal.

In the second stage, new observed and difference syntheses, ρ_{o2}, and $\Delta\rho_2$ were calculated with 2037 terms whose magnitudes were greater than 8 electrons (based on the structure factor calculation with R = 0.458). Twelve additional carbon atoms were located. The observed electron and difference densities were plotted in the vicinity of each atom to obtain better coordinates and to approximate individual temperature factors. The heights of two peaks from ρ_{o1}

decreased in ρ_{02}, with two new peaks forming near the original peaks. Furthermore, the distances between the new peaks and their adjacent peaks were closer to acceptable bond lengths. Thus, the coordinates assigned to the old peaks were replaced by those of the two new peaks for the next calculation. A structure factor calculation using a new scale constant of 0.75, including the Mn atom, the Cl atom, four nitrogen atoms, and 23 carbon atoms had an R-factor of 0.385.

In the third stage of the structure determination, new difference and observed electron density maps, $\Delta\rho_3$ and ρ_{03}, including 2725 terms, were calculated from which the remaining 21 carbon atoms were found. Individual isotropic temperature factors were then assigned to each atom by comparing the peak heights and shapes in the observed and calculated density maps. A structure factor calculation including the complete molecule, except hydrogen atoms, had an R-factor of 0.235.

5. Refinement by the Method of Least Squares

Once a model of a trial structure has been proposed, it is usual to improve the preliminary coordinates of the atoms. This process is known as refinement. Of the several methods of refinement which can be used in crystal structure analysis, that of least squares was used for ClMnTPP.

The principle of least squares, applied to a structure refinement, is that the best values for a set of parameters are those which minimize the sum of the squares of the properly weighted differences between the observed and calculated structure amplitudes for all independent reflections. The quantity to be minimized can be written

$$R = \sum_{i=1}^{N} w_i \left(|F_o| - |F_c| \right)^2 ,$$

where N is the total number of the independent reflections, and w_i is the individual weight of the observed structure factor. The weight of the reflection is defined to be the inverse of the square of the standard deviation of the corresponding observation

$$w_i = \frac{1}{\sigma_i^2} .$$

Usually, only relative weights can be estimated easily.

(1) Weighting Scheme

In order for the method of least squares to work best, it is necessary to have a reasonable weighting scheme applied to the observed structure factors. The weighting scheme, similar to that described by Hughes,[47] which was chosen for the refinement of ClMnTPP structure was

when $|F_o| \leq 15.0$, $\sigma = 2.0$

and when $|F_o| > 15.0$, $\sigma = 0.1 \times |F_o|$.

Thus, when $|F_o|$ was greater than 15.0, the standard deviation

of the reflection was assumed to be directly related to the magnitude of the observed structure amplitude; when less than 15.0, the error was assumed constant.

(2) The Method of Least Squares

In the least squares refinement, the parameters which are varied are the three coordinates of each atom, the overall scale constant, and the individual temperature factors. For the latter, each atom can be assumed to have an isotropic temperature correction of the form of $\exp(-B \sin^2 \theta/\lambda^2)$, or an anisotropic temperature correction in terms of six parameters which describe a thermal ellipsoid as:

$$T(hk\ell) = \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell) \ .$$

Individual isotropic temperature factors can be converted to the anisotropic form by the relationships

$$\beta_{11} = Ba^{*2}/4 \quad , \quad \beta_{12} = B\vec{a}^* \cdot \vec{b}^*/4 \quad , \quad \text{etc}$$

where a^* , b^* , etc are reciprocal cell constants.

The isotropic thermal parameters of the last structure factor calculation, which had an R-factor of 0.235, were converted into anisotropic parameters, and the weighting scheme described above was applied before a least squares calculation was performed using the program ORFLS.[23] After completion of one complete cycle of refinement in which

atomic coordinates and anisotropic temperature factors were varied, (atomic parameters of the 24 inner atoms were allowed to vary first followed by the atomic parameters of the outer atoms) the residual index, R, decreased to 0.173. By readjusting the scale constant from 0.75 to 0.72, the R-factor decreased further to 0.157. After another cycle of refinement in which the anisotropic temperature factors of only the Mn and Cl atoms were varied, the R-factor was 0.149. One further cycle of refinement on all parameters brought the R-factor to 0.125. At this time the bond distances and angles of the model were calculated, and were found to deviate in a significant way from those expected on the basis of other porphyrin structures.

Because of the manner in which the crystal was mounted (long direction perpendicular to the ϕ-axis), the data were affected by serious absorption problem. Since this effect was only corrected in an approximate way, it was decided to apply a more nearly accurate absorption correction at this time based on a method proposed by Phillips.[24]

(3) Phillips' Absorption Correction

Generally, as a crystal rotates about the goniometer axis at the angular setting $\chi = 90^0$, the intensities of an axial reflection vary as a function of the azimuthal angular setting, ϕ, for the corresponding reciprocal lattice level. By measuring the intensities of an axial reflection as a function of ϕ, a relative transmission T

(or absorption, A) curve can be obtained. The transmission and absorption coefficients of the axial reflections have the relationship:

$$A = 1/T = I_{max}(\phi_0)/I(\phi)$$

where ϕ_0 is the particular angular setting which gives the maximum intensity.

In the Phillips' absorption correction, the transmission coefficients for any general reflection $(hk\ell)$ are given approximately by the expression

$$T(hk\ell) = [T(\phi_{inc}) + T(\phi_{ref})]/2$$

where ϕ_{inc} and ϕ_{ref} are the azimuthal angles of the incident and reflected beams. Both ϕ_{inc} and ϕ_{ref} can be expressed in terms of $\phi_{hk\ell}$, the crystal setting at which the reflection plane $(hk\ell)$ is parallel to the incident X-ray beam, more explicitly

$$\phi_{inc} = (\phi_{hk\ell} - \epsilon_{hk\ell}) \text{ , and } \phi_{ref} = (\phi_{hk\ell} + \delta_{hk\ell})$$

where $\epsilon_{hk\ell}$ and $\delta_{hk\ell}$ are the angular differences between $\phi_{hk\ell}$ and the angles of the incident and diffracted beams projected on the equatorial plane. For a four-circle diffractometer, $\epsilon_{hk\ell}$ and $\delta_{hk\ell}$ are given as

$$\epsilon_{hk\ell} = \delta_{hk\ell} = \sin^{-1}(\sin\theta \cos\chi)$$

It should be pointed out that this semi-empirical method can give only the relative values for each absorption correction; the additional scale constants corresponding to

the reciprocal lattice levels must be obtained from other sources.

The absorption factor A can be obtained either by experimental observation or by calculation by evaluating the integral

$$A = \int_V \frac{1}{V} \exp\left[-\mu(\gamma_\alpha + \gamma_\beta)\right] d\bar{V}$$

where V is the volume of the crystal, μ is its linear absorption coefficient, γ_α the path length along the primary beam direction, and γ_β that along the diffracted beam direction. This integral can be solved by numerical methods (computer program, ORABS)[25]. Input to ORABS consists of the unit cell dimensions, the linear absorption coefficient, and the distances from the surface boundary planes to an internal reference point. The absorption curve can then be computed as a function of azimuthal angles Φ and reciprocal lattice levels. The relative scale constants between the corresponding reciprocal lattice levels can be evaluated by considering the direction of least absorption from each absorption curve.

The dimensions of an idealized ClMnTPP crystal and the orientation of the three axes of the unit cell within the crystal are shown in Figure 6. The linear absorption coefficient of ClMnTPP is 41.0 cm^{-1}, and the six boundary planes and their distances from the center of the crystal are listed in Table 2. The calculated absorption curves were in good agreement with the observed ones in both shape

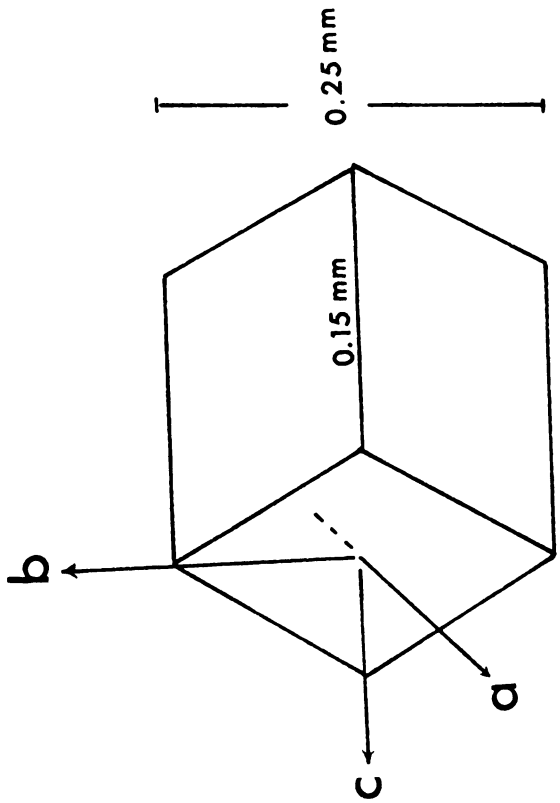


Figure 6. Approximate crystal geometry for computing absorption factors.

and magnitude, in Table 3 are listed the maximum absorption factors obtained from these observed and calculated absorption curves. The scale constants obtained on the basis of the least absorption in each absorption curve are also presented in Table 4.

Table 2. Boundary Planes and Their Distances from the Center of the Crystal.

Planes	Distances (cm)
100	0.0100
$\bar{1}00$	0.0100
$11\bar{1}$	0.0075
$\bar{1}11$	0.0078
$1\bar{1}\bar{1}$	0.0076
$\bar{1}\bar{1}1$	0.0075

A new data reduction was computed using this new absorption correction, but no significant improvement resulted in the R-factor of the last cycle of refinement. At this stage it became increasingly more evident that the discrepancy between the observed and calculated crystal densities was probably an important factor affecting the residual index. After substracting the contribution to the crystal density due to ClMnTPP, there still remained approximately 40 a.m.u. of additional mass.

Table 3. Maximum Calculated and Observed Absorption Factors.

Absorption Curves in the Reciprocal Level of	$(A_{max})_{ob}$	$(A_{max})_{cal}$
020	1.70	1.70
040	1.73	1.69
060	1.68	1.65
080	1.60	1.57
0,10,0	1.54	1.55
0,12,0	1.47	1.52
0,14,0	1.43	1.43
0,16,0	1.33	1.36
0,18,0	1.26	1.29
0,20,0	1.17	1.22

Table 4. Scale Constants for each Reciprocal Level

Reciprocal Levels	Scale Constant
020	1.00
040	1.00
060	1.01
080	1.01
0,10,0	1.02
0,12,0	1.03
0,14,0	1.04
0,16,0	1.06
0,18,0	1.08
0,20,0	1.11

(4) Finding the Acetone Molecule

A difference electron density (at R = 0.125) was computed and four relatively large peaks (~ 3 electron/$\mathring{A}^3$) were found in the vicinity of the Cl atom and the porphyrin molecule. From an examination of the distances between peaks, the corresponding angles, and the peak electron densities, they were found to display the geometry expected of an acetone molecule. By including Mn, Cl, the TPP molecule, and an acetone molecule into the next structure factor calculation, the R-factor was 0.129. After one cycle of refinement on coordinates and anisotropic temperature factors of all the atoms, the R-factor decreased to 0.085. After one more cycle on the coordinates and the anisotropic temperature factors of Mn, Cl, and the acetone molecule, the R-factor decreased to 0.078. Since the R-factor had improved significantly, the convergence of the least squares calculation was assumed. An attempt was now made to locate the hydrogen atoms.

(5) Finding the Hydrogen Atoms

The nomenclature of the atoms in the porphyrin molecule is shown in Figure 7. Hydrogen atoms are named corresponding to the carbon atoms to which they are bonded. A difference electron density based on the structure at an R-factor of 0.078 was calculated to see if hydrogen atoms would be observable. All hydrogen atoms were found at

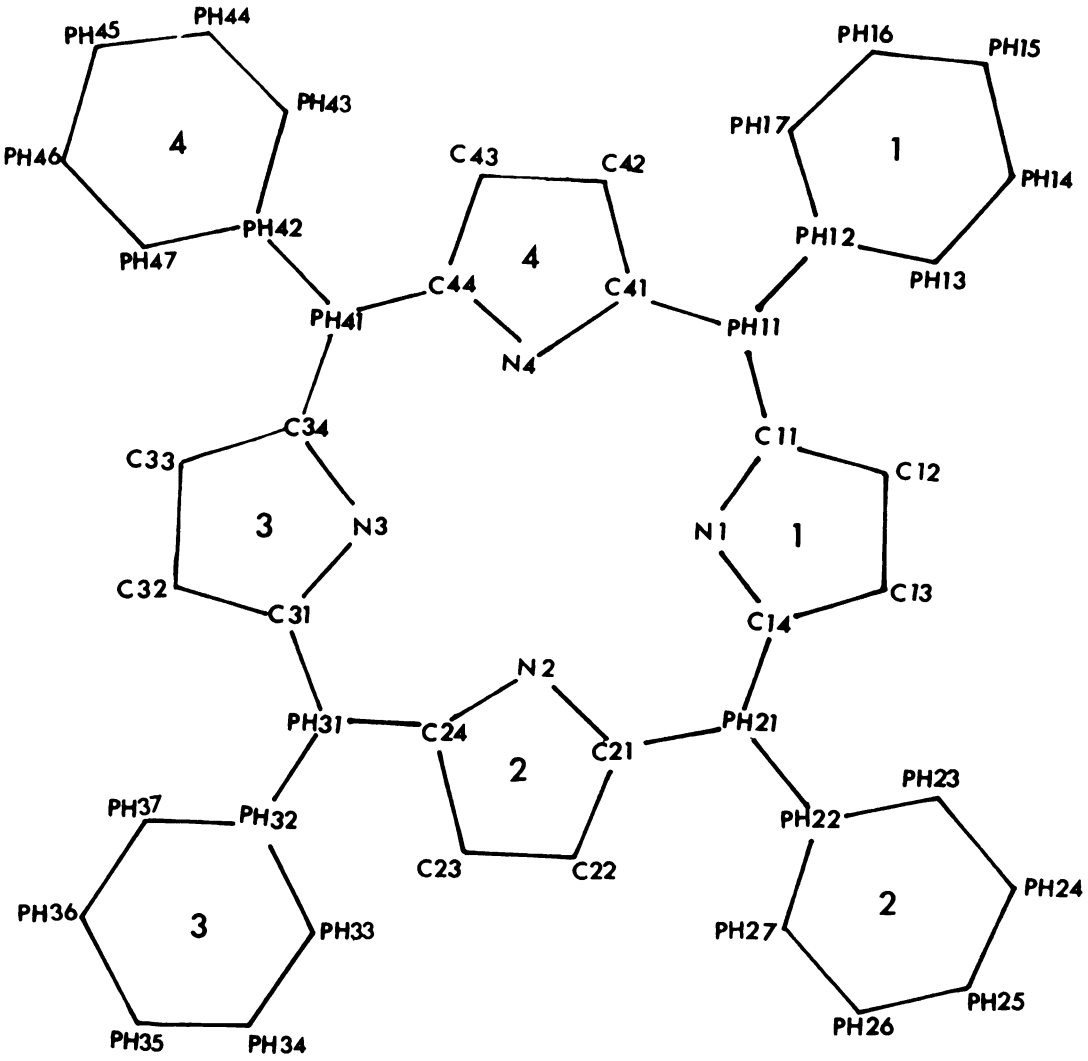


Figure 7. Porphyrin skeleton nomenclature. Numbering of phenyl and pyrrole groups is also indicated.

approximately the correct locations, but only 13 hydrogen atoms which had the better peak heights and shapes were selected to be included in the next structure factor calculation. The isotropic temperature factors of the hydrogen atoms were assumed to be approximately 20% greater than those of their adjacent carbon atoms before the former had been converted to anisotropic values. One cycle of least squares refinement in which the coordinates of all the atoms (including H) and the anisotropic temperature factors of all the atoms except the 13 hydrogen atoms were varied, decreased the R-factor to 0.072. Another difference map was calculated and it showed the remaining hydrogens much improved in peak heights and positions. These were included in calculations and the R—factor became 0.067 after one more cycle of refinement on all the coordinates and anisotropic temperature factors. Since the acetone molecule seemed to occupy the crystal lattice incompletely, a weight of 75% was applied to all of its atoms. The final structure factor calculation gave R = 0.069 and the least squares refinement was terminated at this point.

The calculated crystal density based on ClMnTPP and including a 0.75 occupancy of acetone is 1.31 g/cm^3, while the observed density is 1.30 g/cm^3.

IV. STRUCTURAL RESULTS

The final coordinates, anisotropic temperature factors, the mean square atomic displacement ($\bar{u}^2$) in the direction of each principal axis, and peak heights of all the atoms in ClMnTPP are listed in Table 5. The labeling of the atoms has already been shown in Figure 7. The coordinates, the peak heights, and the isotropic temperature factors of the hydrogen atoms are shown in Table 6. The atomic parameters of the acetone molecule are listed in Table 7.

The procedure for fitting a set of points to a plane or a line by a least squares method was described by Schomaker[51] The equation of a plane can be denoted as $m_1x + m_2y + m_3z = d$, where d is the distance from an origin to the fitting plane. The parameters m_1, m_2, m_3, and d for the equations which best describe the individual pyrrole rings, the phenyl groups, the four inner nitrogen atoms, the sixteen-inner atoms of the porphyrin and the nuclear least squares plane (NLS) which encompasses the four pyrrole rings and four bridge carbon atoms are listed in Table 8. The dihedral angles (in degrees) between the NLS plane and those of each individual phenyl ring and the angle between the NLS plane and the line between the Mn and Cl atom are given in Table 9.

Table 5. The Final Atomic Coordinates, Thermal Parameters,

	Coordinates in Fractions			Anisotropic Temperature		
Atom	x	y	z	β_{11}	β_{22}	β_{33}
Mn	-0.4773	0.1150	0.0900	0.0067	0.0011	0.0056
Cl	0.6276	0.1673	0.2585	0.0010	0.0019	0.0061
N1	0.4000	0.0619	0.0756	0.0052	0.0013	0.0054
C11	0.2801	0.0789	0.0336	0.0093	0.0015	0.0074
C12	0.2413	0.0356	0.0695	0.0103	0.0016	0.0077
C13	0.6626	0.4926	0.3672	0.0078	0.0016	0.0081
C14	0.4342	0.0077	0.1351	0.0068	0.0015	0.0054
N2	0.6437	0.0427	0.1493	0.0067	0.0011	0.0064
C21	0.3663	0.4865	0.3183	0.0074	0.0013	0.0056
C22	0.2666	0.4461	0.2867	0.0079	0.0014	0.0065
C23	0.1951	0.4777	0.2963	0.0095	0.0013	0.0066
C24	0.7512	0.0381	0.1666	0.0063	0.0012	0.0058
N3	0.6266	0.1595	0.0721	0.0067	0.0012	0.0053
C31	0.7493	0.1448	0.1195	0.0063	0.0016	0.0057
C32	0.7238	0.2445	0.0747	0.0089	0.0021	0.0092
C33	0.8108	0.1974	0.1222	0.0111	0.0014	0.0092
C34	0.6085	0.2211	0.0415	0.0092	0.0016	0.0066
N4	0.3738	0.3243	0.4839	0.0063	0.0013	0.0063
C41	0.2497	0.3269	0.4387	0.0069	0.0013	0.0063
C42	0.1744	0.2749	0.3665	0.0073	0.0019	0.0072
C43	0.2549	0.2397	0.3722	0.0088	0.0018	0.0060
C44	0.3810	0.2695	0.4464	0.0081	0.0014	0.0065
PH11	0.2046	0.3704	0.4644	0.0078	0.0014	0.0065
PH12	0.0727	0.3606	0.4201	0.0057	0.0017	0.0074
PH13	0.9734	0.4045	0.3491	0.0087	0.0034	0.0105
PH14	0.8479	0.3964	0.3065	0.0090	0.0052	0.0127
PH15	0.8246	0.3440	0.3352	0.0117	0.0040	0.0160
PH16	0.9247	0.3004	0.4079	0.0157	0.0037	0.0190
PH17	0.0475	0.3099	0.4512	0.0123	0.0023	0.0125
PH21	0.4586	0.4712	0.3179	0.0083	0.0009	0.0057
PH22	0.4388	0.4128	0.2605	0.0073	0.0015	0.0047
PH23	0.5304	0.3659	0.3225	0.0117	0.0012	0.0085
PH24	0.5125	0.3112	0.2694	0.0131	0.0016	0.0111
PH25	0.4037	0.3038	0.1563	0.0127	0.0019	0.0091
PH26	0.3123	0.3498	0.0952	0.0126	0.0023	0.0095
PH27	0.3307	0.4052	0.1470	0.0119	0.0022	0.0065
PH31	0.8071	0.0864	0.1575	0.0061	0.0015	0.0053
PH32	0.9326	0.0772	0.1929	0.0074	0.0013	0.0072
PH33	0.0460	0.0598	0.3016	0.0064	0.0023	0.0076
PH34	0.1642	0.0541	0.3320	0.0070	0.0028	0.0122
PH35	0.1730	0.0664	0.2579	0.0114	0.0024	0.0140
PH36	0.0611	0.0846	0.1509	0.0117	0.0021	0.0145
PH37	0.9406	0.0895	0.1173	0.0114	0.0021	0.0093

and Peak Heights of MnClTPP.

Parameters			Mean Square Atomic Displacements* ($\AA^2$)			Peak Height ($e/\AA^3$)
β_{12}	β_{13}	β_{23}	$8\pi^2\bar{u}_1^2$	$8\pi^2\bar{u}_2^2$	$8\pi^2\bar{u}_3^2$	ρ_0
0.0002	0.0047	0.0002	2.01	2.36	3.22	34.9
0.0003	0.0057	-0.0004	2.59	3.89	4.59	19.9
0.0006	0.0039	0.0003	1.57	2.82	3.25	7.1
0.0000	0.0070	0.0001	2.25	2.85	4.36	6.1
0.0002	0.0071	0.0002	2.91	3.03	4.54	5.5
-0.0000	0.0062	-0.0000	2.53	3.13	4.54	5.3
-0.0003	0.0049	-0.0001	1.97	2.73	3.22	5.5
-0.0000	0.0051	-0.0001	1.85	2.12	3.68	7.0
-0.0004	0.0051	-0.0007	1.87	2.56	3.62	5.9
-0.0007	0.0059	-0.0002	1.72	3.03	3.89	5.4
-0.0004	0.0061	-0.0003	2.39	3.09	4.07	5.3
0.0002	0.0044	-0.0002	2.05	2.67	3.45	6.2
0.0003	0.0046	0.0004	1.97	2.26	3.25	7.6
0.0000	0.0048	-0.0000	1.92	2.94	3.25	6.0
0.0004	0.0071	0.0008	2.70	3.65	5.76	5.3
-0.0003	0.0081	0.0004	2.10	3.82	5.30	5.5
0.0005	0.0062	0.0005	2.59	2.85	4.18	5.8
-0.0004	0.0049	-0.0002	1.87	2.70	3.68	6.6
-0.0004	0.0050	0.0001	1.78	3.10	3.65	5.7
-0.0009	0.0049	-0.0009	2.39	3.75	5.01	5.2
-0.0007	0.0055	-0.0006	2.82	3.00	4.18	5.5
-0.0009	0.0059	-0.0006	1.94	2.56	4.10	5.8
0.0001	0.0055	0.0003	2.31	2.97	4.25	6.6
-0.0008	0.0046	-0.0011	1.92	2.79	5.34	5.7
0.0002	0.0072	0.0000	3.00	6.37	6.59	4.7
-0.0003	0.0077	-0.0001	3.16	8.19	9.78	4.1
-0.0022	0.0111	-0.0005	2.33	8.55	9.73	4.1
-0.0017	0.0154	-0.0006	2.23	7.44	10.87	4.1
-0.0007	0.0100	-0.0000	2.97	5.01	7.11	4.8
-0.0002	0.0054	-0.0001	1.75	2.53	3.51	6.3
-0.0004	0.0045	-0.0002	2.23	2.61	3.35	6.3
-0.0002	0.0082	-0.0003	2.20	3.00	5.17	6.5
-0.0000	0.0100	-0.0002	2.94	3.42	6.41	5.3
-0.0005	0.0082	-0.0008	3.13	4.55	5.63	5.2
-0.0006	0.0075	-0.0013	3.45	5.38	6.64	4.7
-0.0003	0.0070	-0.0006	2.53	4.44	5.01	5.2
0.0002	0.0044	0.0002	2.10	2.76	3.19	6.2
0.0001	0.0059	-0.0000	2.10	2.56	5.18	5.8
0.0007	0.0042	0.0004	2.42	4.55	5.76	5.1
0.0007	0.0058	0.0001	2.56	5.34	9.13	4.7
-0.0000	0.0101	-0.0001	3.38	4.55	8.24	4.7
-0.0001	0.0110	-0.0004	2.76	4.03	8.39	4.9
-0.0003	0.0084	-0.0006	2.88	3.96	5.59	4.7

Table 5. Continued.

Atom	Coordinates in Fractions			Anisotropic Temperature		
	x	y	z	β_{11}	β_{22}	β_{33}
PH41	0.4927	0.2457	0.4808	0.0095	0.0015	0.0080
PH42	0.4930	0.1810	0.4509	0.0091	0.0017	0.0090
PH43	0.4717	0.1680	0.3612	0.0250	0.0021	0.0158
PH44	0.4901	0.1085	0.3432	0.0232	0.0034	0.0161
PH45	0.5244	0.0636	0.4146	0.0089	0.0046	0.0152
PH46	0.5412	0.4254	0.0041	0.0198	0.0025	0.0128
PH47	0.5238	0.3650	0.0233	0.0184	0.0011	0.0089
$\sigma x10^4$	0.9-10	0.3-5	0.8-9	0.3-64	1 - 9	1 - 45

*In the direction of each principal axis.

Parameters			Mean Square Atomic Displacements* ($\AA^2$)			Peak Height ($e/\AA^3$)
β_{12}	β_{13}	β_{23}	$8\pi^2\bar{u}_1^2$	$8\pi^2\bar{u}_2^2$	$8\pi^2\bar{u}_3^2$	ρ_0
-0.0007	0.0075	-0.0006	2.02	2.70	4.90	5.9
-0.0015	0.0073	-0.0019	1.92	2.67	6.37	5.5
-0.0036	0.0175	-0.0040	1.38	4.97	12.50	4.6
-0.0044	0.0168	-0.0032	3.72	4.62	12.70	4.4
-0.0002	0.0083	-0.0037	2.45	4.86	14.80	4.5
-0.0013	0.0068	0.0003	4.36	6.41	15.99	3.7
-0.0013	0.0070	-0.0002	1.82	5.05	11.28	4.9
1 - 11	1 - 45	1 - 19				

Table 6. Coordinates, Isotropic Temperature Factors, and Peak Heights of the Hydrogen Atoms.

Atom	x	y	z	B	Peak Heights e/A^3
HC12	0.1460	0.0419	0.0461	5.0	0.4
HC13	0.6644	0.4472	0.3372	4.6	0.4
HC22	0.2521	0.4055	0.2724	4.1	0.5
HC23	0.1339	0.4528	0.2940	4.3	0.4
HC32	0.8952	0.1971	0.1435	5.4	0.5
HC33	0.7306	0.2926	0.0662	5.4	0.4
HC42	0.0663	0.2663	0.3201	4.2	0.5
HC43	0.2319	0.1957	0.3274	4.3	0.5
HPH13	0.9900	0.4520	0.3388	6.3	0.4
HPH14	0.7801	0.4309	0.2810	7.7	0.3
HPH15	0.7495	0.3310	0.3030	7.3	0.3
HPH16	0.9145	0.2574	0.4471	10.4	0.5
HPH17	0.1045	0.2772	0.4941	6.8	0.5
HPH23	0.6089	0.3745	0.3935	5.2	0.4
HPH24	0.5867	0.2796	0.3119	6.4	0.4
HPH25	0.4036	0.2602	0.1263	8.3	0.5
HPH26	0.2275	0.3440	0.0002	6.0	0.4
HPH27	0.2656	0.4466	0.0937	5.3	0.5
HPH33	0.0347	0.0476	0.3632	4.2	0.6
HPH34	0.2588	0.0500	0.4203	5.7	0.5
HPH35	0.2658	0.0548	0.2839	7.2	0.3
HPH36	0.0577	0.1032	0.0888	7.4	0.5
HPH37	0.8660	0.0994	0.0365	5.9	0.5
HPH43	0.4000	0.2000	0.2830	10.6	0.3
HPH44	0.4332	0.1167	0.2667	10.9	0.3
HPH45	0.5373	0.0242	0.3870	8.0	0.3
HPH46	0.5297	0.3564	0.0944	8.4	0.4
HPH47	0.5827	0.4534	0.0673	5.8	0.3

Table 7. Atomic Parameters of the Acetone Molecule.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}
O1	0.8601	0.0380	0.5021	0.0285	0.0050	0.0212	0.0015
C2	0.9001	0.0860	0.5075	0.0152	0.0020	0.0105	0.0025
C3	0.9576	0.1030	0.4626	0.0192	0.0092	0.0113	0.0054
C4	0.9120	0.3621	0.0686	0.0320	0.0067	0.0110	-0.0096
$\sigma x10^4$	18-54	8 - 30	3 - 30	8 - 14	1 - 27	11-16	1 - 16

Atom	β_{13}	β_{23}	$8\pi^2\bar{u}_1^2$	$8\pi^2\bar{u}_2^2$	$8\pi^2\bar{u}_3^2$	Peak Height $e/Å^3$
O1	0.0139	0.0016	8.44	11.95	18.27	3.0
C2	-0.0013	0.0027	0.81	6.28	23.89	3.3
C3	0.0133	0.0028	2.02	6.41	19.43	2.8
C4	0.0121	-0.0013	3.65	5.97	25.83	2.6
$\sigma x10^4$	3 - 40	4 - 16				

Table 8. Parameters for the Equation, $m_1x + m_2y + m_3z = d$ Selected to Fit Planes.

Planes	m_1	m_2	m_3	d
1st Pyrrole	2.321	11.87	11.76	0.682
2nd Pyrrole	-1.338	6.826	12.39	1.298
3rd Pyrrole	-5.342	5.542	15.14	-1.385
4th Pyrrole	-5.590	10.781	13.97	-0.404
1st Phenyl	-5.536	-10.58	14.01	-2.980
2nd Phenyl	1.319	- 8.341	-13.22	4.960
3rd Phenyl	-0.008	20.86	3.433	2.280
4th Phenyl	11.60	- 4.116	- 2.852	4.521
NLS	-3.757	8.992	1.356	0.021
Inner 16 Atoms	-3.727	9.049	13.53	0.047
Inner 4 Nitrogen	-3.753	9.190	13.50	0.041

Table 9. Dihedral Angles between the NLS Plane and the Individual Phenyl Planes and the Angle between NLS Plane and Mn-Cl Line.

Plane	Dihedral Angle (degrees)
1st Phenyl	54.2
2nd Phenyl	123.5
3rd Phenyl	49.7
4th Phenyl	77.4

Angle between NLS plane and Mn-Cl line* -- 85.3^0

*The equations for the line between Mn and Cl atoms are: $x = 0.575 + 0.004\ t$, $y = 0.141 + 0.022\ t$, and $z = 0.174 + 0.071\ t$, where t is a parameter with real values.

The atomic deviations from the calculated least squares planes on the basis of different groups of atoms are listed in Tables 10 and 11. The atomic deviation for each atom in the porphyrin skeleton from the NLS plane is shown in Figure 8, and the atomic deviation for each atom from the least squares plane of the inner sixteen atoms is shown in Figure 9. The various bond distances of the porhyrin skeleton are presented in Figure 10a, and Figure 10b, with the corresponding bond angles in Figure 10c. The MnTPP molecule drawn in perspective in terms of its vibration ellipsoids is shown in Figure 11 (ORTEP).[26]

The structure of ClMnTPP crystal viewed on the bc plane is shown in Figure 12. There are four molecules packed in each unit cell, with the molecules stacking nearly perpendicular to the $\vec{c}^*$ direction. The molecules in the unit cell are related by the following symmetry operations: molecule II can be generated by rotating molecule I about a 2-fold axis at $z = 1/4$ and $x = 1/2$, followed by a translation of 1/2 along the b axis; the same rotation and translation generate molecule IV from molecule III; the pair of molecules I and IV and the pair II and III are related by a center of symmetry.

Table 10. The Atomic Deviations from the Least-Squares Planes of the Individual Pyrrole and Phenyl Rings.

Atom	d,(Å)	Atom	d,(Å)
First Pyrrole		Second Pyrrole	
N-1	0.011	N-2	-0.018
C-11	-0.005	C-21	0.012
C-12	-0.003	C-22	-0.002
C-13	0.010	C-23	-0.009
C-14	-0.013	C-24	0.016
s.d*	0.011	s.d	0.014
Third Pyrrole		Fourth Pyrrole	
N-3	0.012	N-4	-0.017
C-31	-0.008	C-41	0.017
C-32	0.006	C-42	-0.010
C-33	0.001	C-43	0.000
C-34	-0.011	C-44	0.010
s.d	0.010	s.d	0.014
First Phenyl		Second Phenyl	
PH12	-0.017	PH22	0.002
PH13	0.001	PH23	0.005
PH14	0.013	PH24	-0.005
PH15	-0.011	PH25	-0.004
PH16	-0.006	PH26	0.011
PH17	0.020	PH27	-0.010
s.d	0.014	s.d	0.008
Third Phenyl		Fourth Phenyl	
PH32	-0.002	PH42	0.026
PH33	0.008	PH43	-0.019
PH34	-0.005	PH44	0.001
PH35	-0.003	PH45	0.011
PH36	0.009	PH46	-0.013
PH37	-0.006	PH47	-0.005
s.d	0.007	s.d	0.016

* Standard deviation.

Table 11. Atomic Deviations from the Least Squares Plane of Four Nitrogen Atoms.

Atoms	d(Å)
N1	0.047
N2	-0.047
N3	0.047
N4	-0.047
s.d	0.054

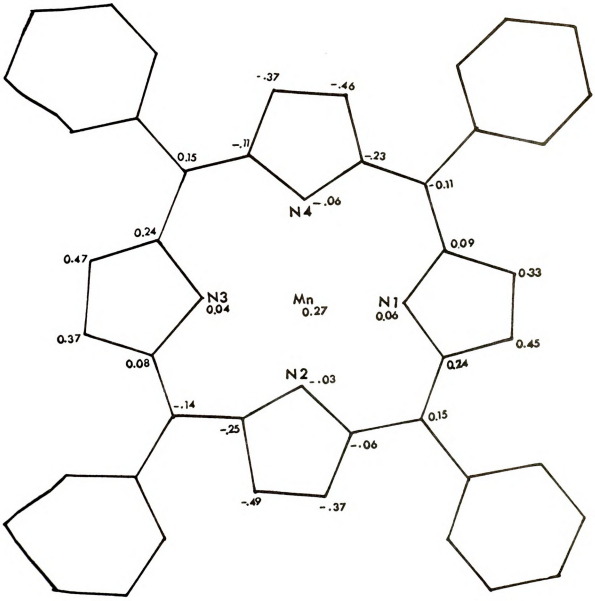


Figure 8. Atomic deviations in (Å) from the nuclear least squares plane (NLS).

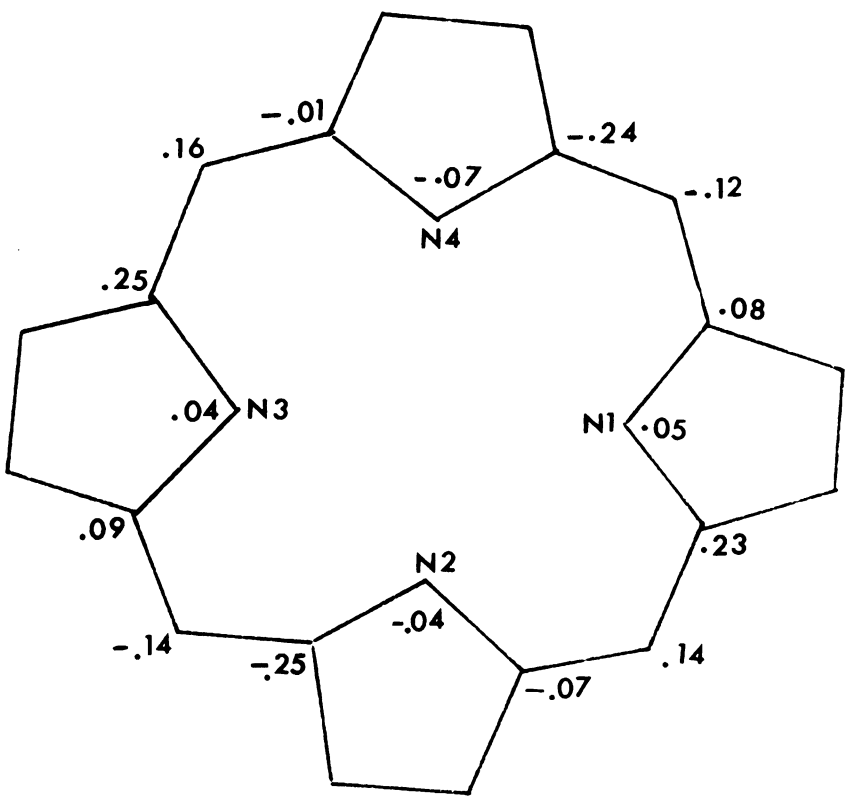


Figure 9. Atomic deviations in (Å) from the least squares plane based on the inner sixteen atoms of ClMnTPP.

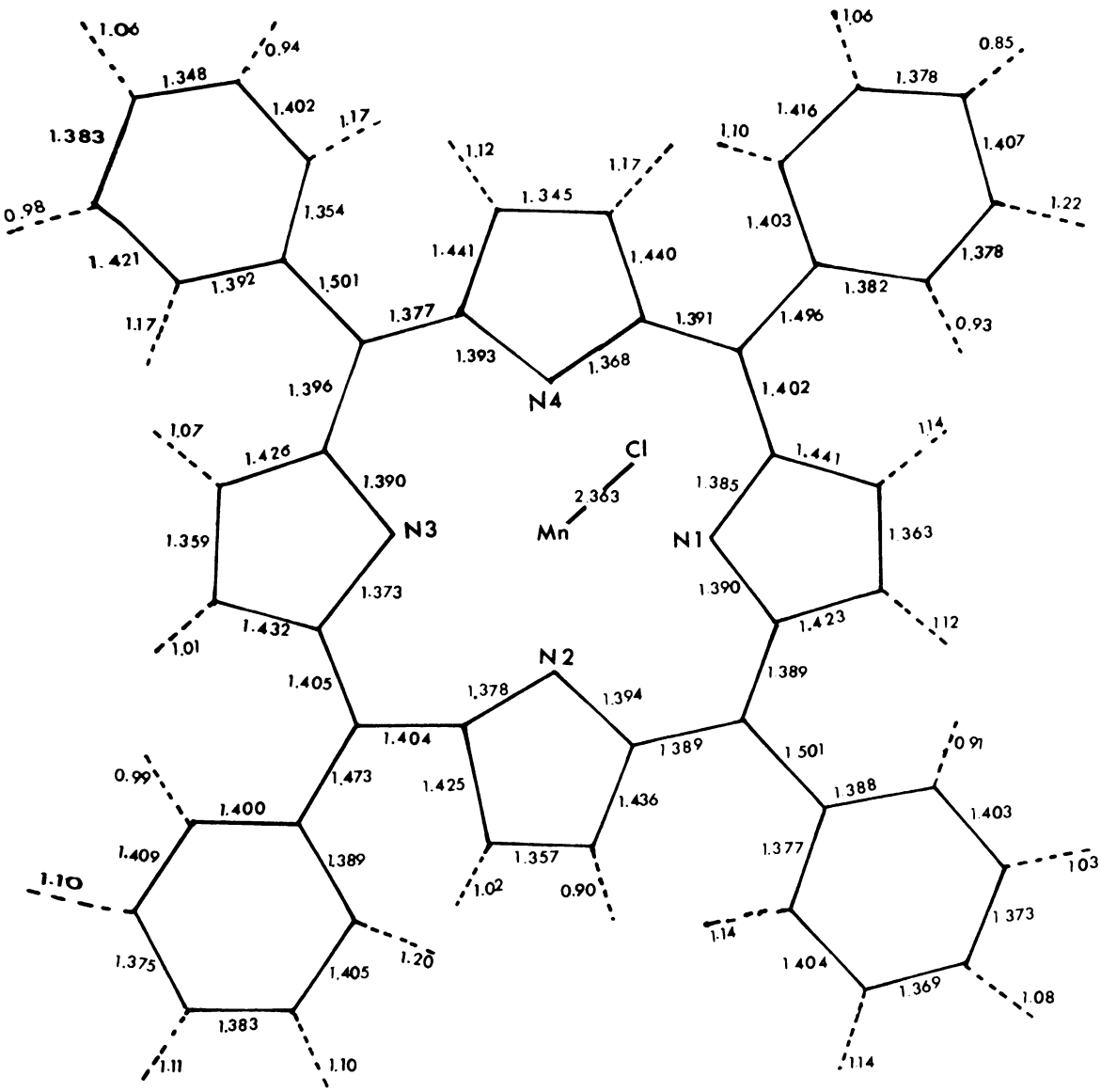


Figure 10a. Bond distances (in Å). Broken lines indicate C-H bond distances.

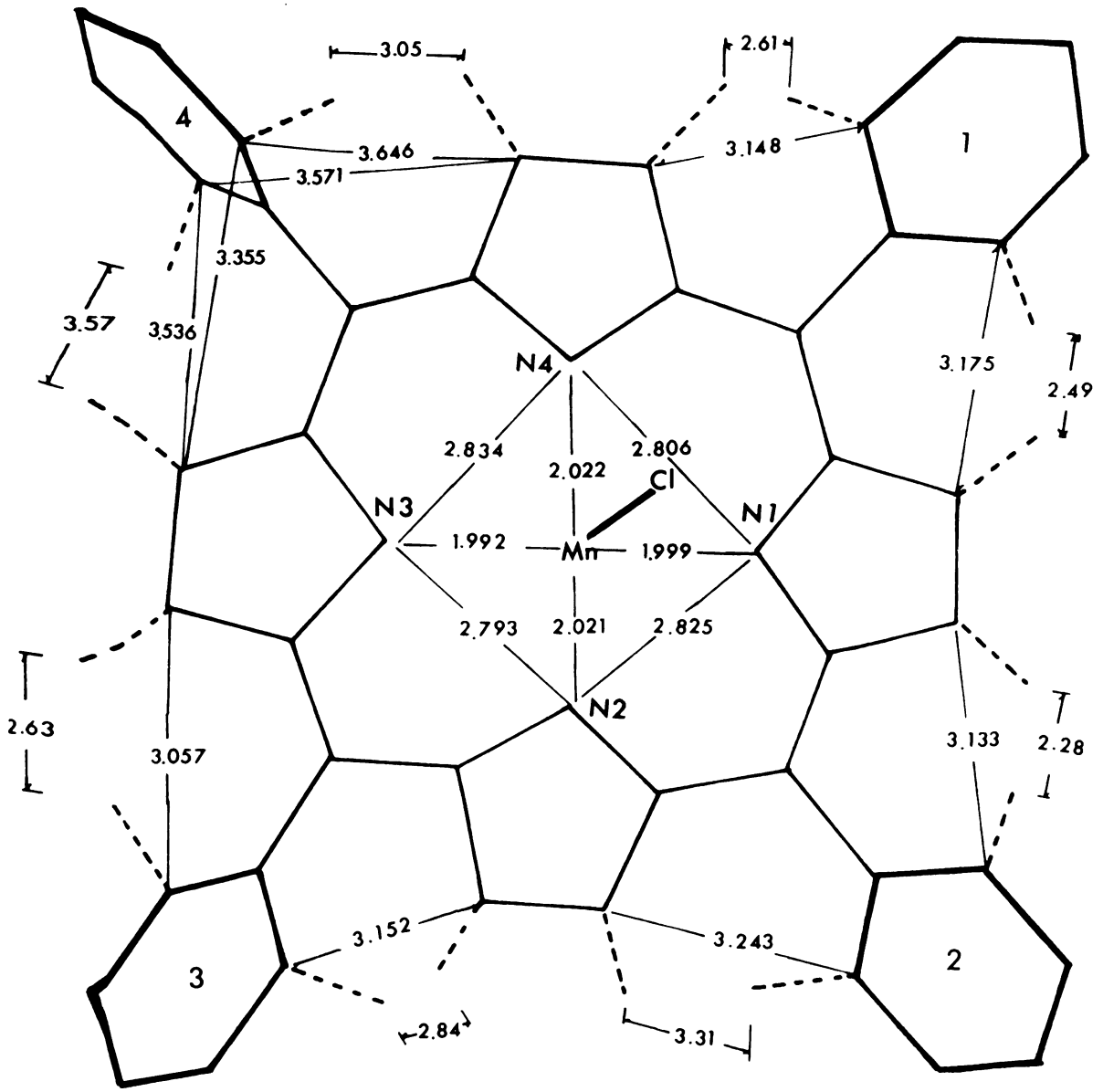


Figure 10b. Intramolecular distances. The numbering of the phenyl groups is indicated in the figure. The dihedral angles from phenyl groups 1,2,3, and 4 to the NLS plane are 54.2^0, 123.5^0, 49.7^0, and 77.4^0, respectively.

Figure 10c. ClMnTPP bond angles (degrees). Angle between line Mn-Cl and NLS plane is 85.5^0.

$\angle$ N1,Mn,N3 = 166.9^0

$\angle$ N2,Mn,N4 = 161.7^0

$\angle$ N1,Mn,Cl = 100.0^0

$\angle$ N2,Mn,Cl = 101.0^0

$\angle$ N3,Mn,Cl = 93.1^0

$\angle$ N4,Mn,Cl = 97.2^0

the standard deviation of the angles of the carbon-carbon and carbon-nitrogen bonds is approximately 0.6 $\sim$ 1.0 degree.

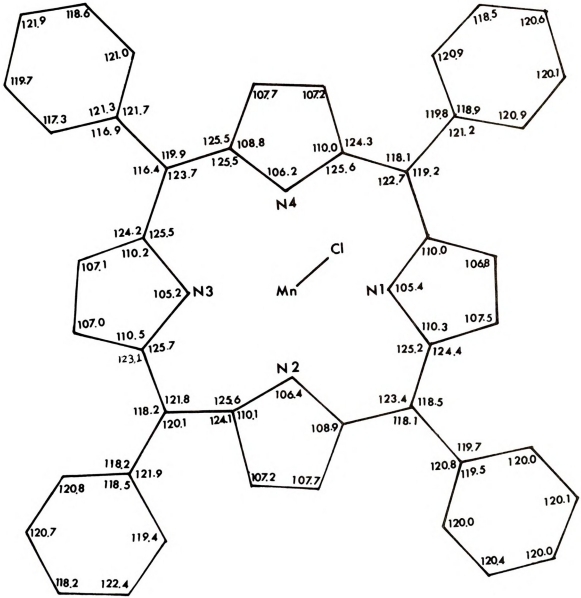

121.9
118.6
121.0
119.7
117.3
121.3
121.7
116.9
119.9
116.4
123.7
125.5
107.7
107.2
108.8
125.5
106.2
110.0
124.3
125.6
N4
118.1
122.7
119.2
118.5
120.6
120.9
120.1
119.8
118.9
120.9
121.2
124.2
125.5
110.2
107.1
105.2
N3
Cl
Mn
N1
110.0
106.8
105.4
107.5
110.3
107.0
110.5
125.7
123.1
125.2
124.4
N2
121.8
125.6
106.4
123.4
118.5
118.2
120.1
124.1
110.1
108.9
118.1
119.7
120.8
119.5
120.0
118.2
121.9
120.8
118.5
107.2
107.7
120.1
120.0
120.7
119.4
120.4
120.0
118.2
122.4

Figure 10c.

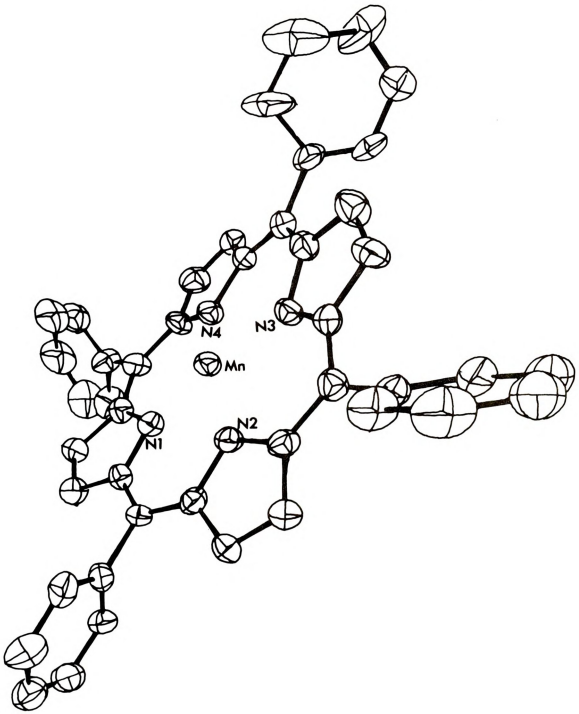


Figure 11. A diagram in perspective of the MnTPP molecule (ORTEP).

Figure 12. Crystal structure of ClMnTPP as viewed in the projection along $\vec{a}$. The solid bar represents the approximate least squares plane of the porphine core.

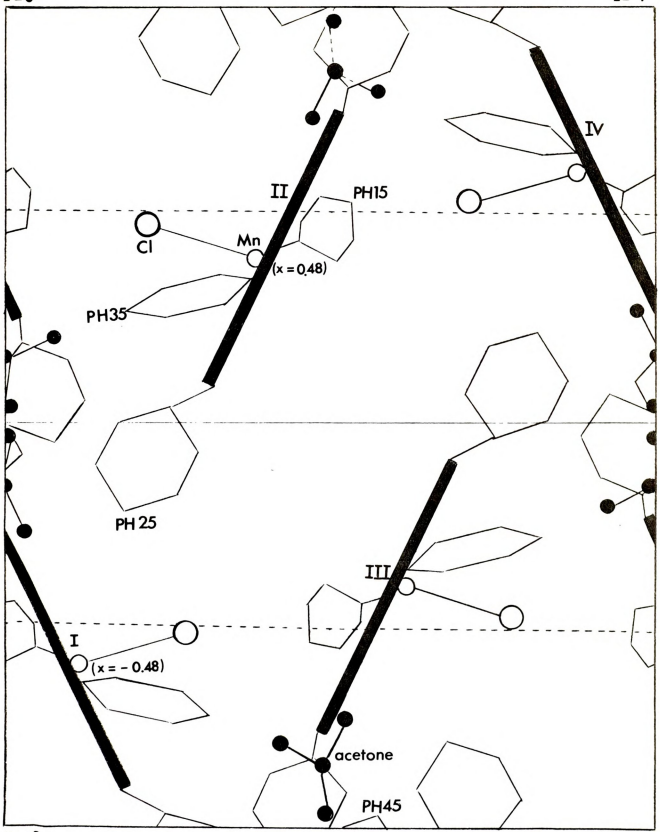

y = 1
z = 0
y = 1
z = 1
IV
II
PH15
Cl
Mn
(x = 0.48)
PH35
PH 25
III
I
(x = - 0.48)
acetone
PH45
y = 0
z = 0
y = 0
z = 1

Figure 12.

V. DISCUSSION

The data presented in Table 5 indicate that the anisotropic temperature factors of the carbon atoms generally increase as the distance of the atoms increases from the center of the molecule. Hence the peripheral carbon atoms have decreased peak heights and increased standard deviations in atomic coordinates. Such characteristics have also been observed in the $Mg(H_2O)$TPP and free base tri-TPP structures. These observations are assumed to be due to the contribution of quasi-rigid body angular oscillations.

An acetone molecule of crystallization was found between adjacent ClMnTPP molecules. The closest approach of the molecule to the porphyrin is through the central carbon atom of the acetone to the chlorine atom of ClMnTPP; the interatomic distance of 3.58Å does not indicate that any particularly significant interaction is occurring (see Fig. 13). As is typical of solvent molecules trapped in a crystal lattice, the large temperature factors of the acetone molecule indicate that it is either disordered with respect to the acetone molecules in neighboring unit cells or that the acetone lattice site is only partially occupied. A somewhat related case in which a solvent molecule of pyridine was included in the phthalocyanine complex of manganese(III)[27] was observed. Two planar and parallel manganese phthalocyanine-ring systems which are joined by an oxygen atom midway between the two

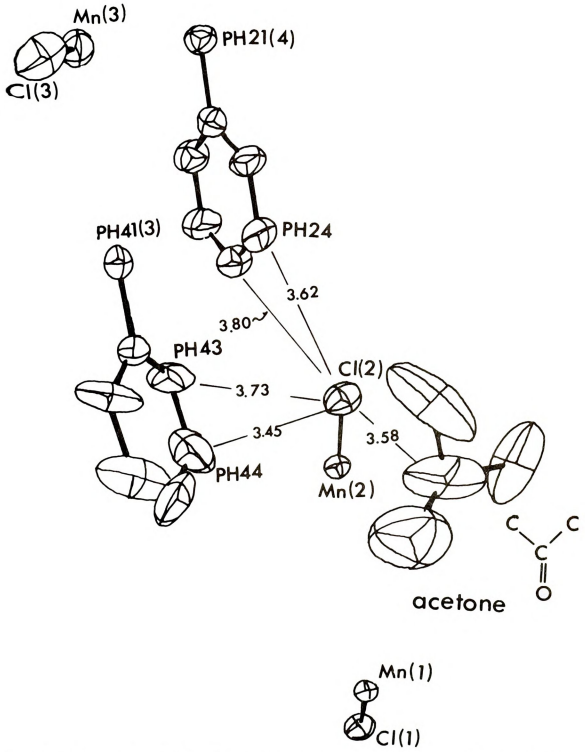


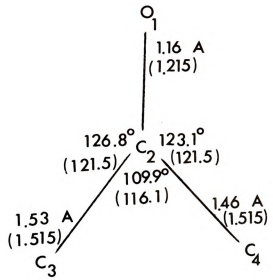
Figure 13. Intermolecular distances from the chlorine atom.

manganese atoms have two pyridine molecules coordinated to the manganese atoms on either side of Mn-O-Mn bridge (see Fig. 2).

The bond distances and bond angles of the acetone of crystallization are shown in Figure 14. The numbers in parentheses are those reported for an acetone molecule in the gas phase.[28] Although large discrepancies exist between the two, there is sufficient correlation between the bond lengths, angles and planarity of the molecule to state confidently that it is an acetone molecule of crystallization.

The residual densities in the final difference electron density map were in the range of 0.11 to 0.18 $e/\AA^3$ in the region of the ClMnTpp molecule. Due to the large thermal motion of the atoms in the acetone molecule, the peak heights of its carbon atoms were much lower than those in the ClMnTPP molecule. Either thermal motion or disorder prevented location of the hydrogen atoms in the acetone molecule. The random residual electron density in the vicinity of the acetone molecule was of the order of 0.65 $e/\AA^3$, somewhat greater than the average peak height for the hydrogen atoms of the ClMnTPP molecule.

The bond distances of the porphyrin skeleton as listed in Figure 10a have an average C-N bond distance of 1.384 ± 0.009 Å, an average C_a-C_m bond distance of 1.394 ± 0.009 Å (where C_a is the carbon atom adjacent to the pyrrole nitrogen, and C_m is the methine carbon atom), and an average C-H bond distance of 1.07 ± 0.09 Å. The reported values of bond distances in an aromatic system (such as benzene) listed in Volume III of the International Tables for X-ray Crystallography are C-C bond of



ACETONE

Figure 14. Bond distances and bond angles of the acetone molecule of crystallization.

1.395 ± 0.003 Å, and C-H bond of 1.084 ± 0.006 Å. The comparison of the bond distances reported in literature with those determined in this structure analysis shows that the average C_a-C_m and C-H is close to the expected value.

From Figure 10a, the average bond distance on the basis of different groups of atoms in ClMnTPP has a somewhat different meaning. The average C_a-C_b bond distance is 1.433 ± 0.007 Å and the average C_b-$C_{b'}$ is 1.356 ± 0.008 Å (where C_b is the carbon atom adjacent to C_a). The former bond length is shorter than the σ bond length of 1.49 Å between sp^2 hybridized carbon atoms, while the latter is longer than the expected double bond value of 1.33 Å. This behavior is commonly observed in most of the porphyrins. The other C-C bond distance joining the bridge carbon atom and the terminal carbon atom of the phenyl group has an average value of 1.493 Å, typical of a σ bond in trigonally hybridized carbon atoms. Because of possible steric interference between phenyl hydrogen atoms and pyrrole hydrogen atoms if the phenyl groups were coplanar to the porphyrin core, the phenyl groups are rotated out of the NLS plane. Thus, the π electron systems of the phenyl rings are isolated from the corresponding system in the porphyrin core by pseudo-single bonds. As is indicated in Table 10, the phenyl and pyrrole rings are essentially planar as individual entities. The dihedral angles between the individual rotated phenyl groups and the

NLS plane are 54.2^0, 123.5^0, 49.7^0, and 77.4^0. The large variation in the angles shows indirectly the crystal packing forces.

The standard deviations of the molecular parameters are in the range between 0.007 and 0.009 Å for C_a-C_b, C_b-C_b, C_a-C_m and C-N bonds. The standard deviations of the crystallographic structure parameters from the last cycle of the least squares structure factor calculation based on the errors of carbon and nitrogen coordinates are in the range between 0.006 and 0.013 Å for C-C and C-N bonds. According to Cruickshank's statistical significance tests[52,53] comparing the errors of the molecular parameters to those of the crystallographic structure parameters, the errors in the molecular parameters are insignificant, since they fall within the value of three standard deviations of the crystallographic structure parameters.

The atomic deviations from the least squares plane based on the inner sixteen atoms of the porphine core are given in Figure 9. Although the atomic deviations of the nitrogen atoms, which range from 0.04 to 0.07 Å, are probably not significant, every other pyrrole atom (i.e., C14, C24, C34, and C41) shows an appreciable atomic deviation of approximately 0.25 Å, alternating above and below the least squares plane. The bridge carbon atoms, PH11, PH21, PH31, and PH41, deviate approximately 0.1 Å from the mean plane. One can conclude from these atomic deviations

that the inner sixteen-membered ring is decidedly nonplanar, in contrast to the sixteen-membered ring found in tri-TPP whose carbon atoms are approximately within the plane.

From the many porphyrins whose structures have been determined, it is obvious that deviations from the planarity of the NLS plane vary uniquely from one porphyrin to another, depending on the particular molecular structure and various crystallographic packing forces. In the present case of ClMnTPP, the atomic deviations from the individual planes of each pyrrole and phenyl group are within the error of the determination (see Table 10). However, considering the whole porphyrin skeleton, one pair of diagonally opposite nitrogen atoms, N1 and N3, is displaced about 0.05 Å slightly above the mean plane of the nitrogen quartet, while the other pair is displaced about the same distance below the plane (see Table 11). The peripheral carbons of the pyrroles have an apparent (0.3-0.5 Å) deviation from the NLS plane in the same direction as their corresponding nitrogen atoms (see Fig. 8). Because of this alternating arrangement, the porphine core of ClMnTPP is ruffled in a puckered way. Furthermore, the atomic deviations show approximate $\bar{4}$ symmetry.

In the structure of free base tri-TPP, each individual pyrrole was found to be planar, but the departure from the planarity of the porphine core differs in a significant way from ClMnTPP. In tri-TPP, one pair of pyrroles carrying

the central hydrogen atoms is inclined away from NLS plane, while the other pair is approximately in the plane. In addition, the atomic deviations from the NLS plane of ClMnTPP are substantially more pronounced than those observed in tri-TPP.

Figure 15 shows the details of the central part of the ClMnTPP molecule. It can be seen that the four nitrogen-nitrogen distances are similar, and the nitrogen-chlorine distances are not equivalent. The difference of 0.22 Å between N2-Cl and N3-Cl corresponds to a difference of 7.9° between the angles ∠N2, Mn, Cl and ∠N3, Mn, Cl. In other words, the apical chlorine atom is slightly inclined toward the N3 atom. Calculations show that the chlorine atom is inclined about 4.7° from the normal of the plane of basal nitrogen atoms. Thus, the square pyramid coordination of the manganese by the four nitrogens and one chlorine is somewhat distorted. Examination of the geometry around the chlorine atom shows an acetone molecule and two phenyl groups belonging to two different adjacent molecules to be the close neighbors (see Fig. 13). If the chlorine atom were at the apical position of the square pyramid, the contact between Cl atom and PH44 atom of the other ClMnTPP molecule would be much shorter than 3.45 Å, about the minimum van der Waals contact distance. Therefore, the chlorine atom, by tipping itself away from the apical of the square pyramid, is able to keep a reasonable

Figure 15. The geometry and the dimensions of square pyramidal coordination in ClMnTPP molecule.

N1-Cl	3.346 Å	Mn-N1	1.999 Å	∠N1,Mn,Cl =	99.98°
N2-Cl	3.392	Mn-N2	2.021	∠ N2,Mn,Cl =	101.04
N3-Cl	3.171	Mn-N3	1.992	∠ N3,Mn,Cl =	93.12
N4-Cl	3.297	Mn-N4	2.022	∠ N4,Mn,Cl =	97.21

Average Mn-N distance 2.008 Å

Average center-nitrogen, Ct-N, 1.989

Out-of-plane displacement, Mn-Ct, 0.273

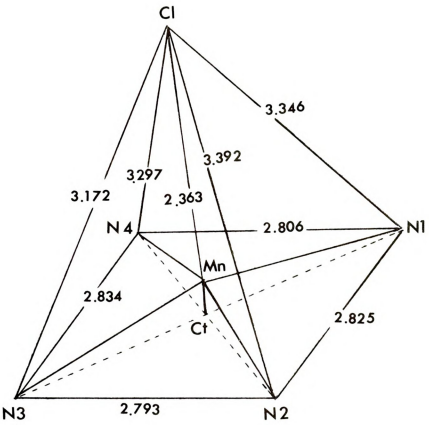

Cl
3.346
3.392
3.297
3.172
2.363
N4
2.806
N1
Mn
2.834
Ct
2.825
N3
2.793
N2

Figure 15.

contact distance to the surrounding atoms. In a similar manner, the phenyl group with the PH44 atom has also adjusted its angular rotation so as to avoid other close constraints and contacts with adjacent molecules due to the crystal packing arrangement.

Of other interest is the fact that the Mn atom is displaced 0.27 Å from the mean nitrogen plane, and the bond length of Mn-Cl of 2.363 Å is somewhat shorter than expected. Although there are no other convincing axial bond length data available for five coordinate compounds, general references to Mn-Cl bond distances in a variety of compounds can be found for comparison. The Mn-Cl bond distance in manganous chloride dihydrate[29] ($MnCl_2 \cdot 2H_2O$) is 2.57 Å, while Mn-Cl distance in the complex of hexamethylenetetramine with manganous chloride[30] (abbreviated HMT, $MnCl_2 \cdot 2(CH_2)_6N_4 \cdot 2H_2O$) is approximately 2.47 Å. It can be said that the longer bond distance in $MnCl_2 \cdot 2H_2O$ is expected due to the ionic character, while the shorter length in HMT corresponds to some covalent bond character. Consequently, the Mn-Cl distance of 2.363 Å in ClMnTPP suggests that there is significant covalent bond character. In addition, the average Mn-N distance of 2.008 Å is also somewhat shorter than that expected by covalent radii estimates (2.04 Å). The shortening of both the Mn-Cl and Mn-N distances might be responsible for the relative high stability of this unique porphyrin.

The shortening of axial ligand distance of square pyramid geometry is also found in ClFeTPP. A qualitative consideration by molecular orbital studies suggested[10] that the $3\ d_{z^2}$ orbital of the metal combined with an appropriate σ-type orbital of axial ligand to give a strong bonding and a weakly antibonding orbital. Also, the 4s and $4\ p_z$ orbitals of the metal can further contribute to the bonding.

The structural parameters of some five-coordinate metallotetraphenylporphyrins are listed in Table 12. Because $Mg(H_2O)TPP$, ClFeTPP, and $(H_2O)ZnTPP$[31] crystallize in the same disordered structure type, the precision of parameter determination is not so good as desired. However, it can be seen that the radius of the central hole of the porphine core Ct-N of ClMnTPP is the shortest of all these tetraphenylporphyrins. There appears to be a contraction of about 0.05 Å in going from the Ct-N value of 2.043 Å of porphine to that of 1.989 Å of ClMnTPP. This contraction might be the cause of the ruffling of the porphyrin core upon metal and side-chain substitutions. In addition to the shortening of Ct-N distance, the Mn-N bond distance of 2.008 Å is somewhat shorter than that of 2.04 Å estimated from covalent radii. The other bond length C_a-N, C_a-C_b and C_b-$C_{b'}$ are approximately the same as those of other tetraphenylporphyrins. A comparison of the bond lengths of ClMnTPP and porphine indicates a slight expansion of the C_a-N bond, and a slight contraction of the C_a-C_b

Table 12. Average Stereochemical Parameters of the Porphine Skeleton in Some Five Coordination Metallotetraphenylporphyrins (two free base molecules are given for comparison).

	ClMnTPP	$Mg(H_2O)TPP$	ClFeTPP	$(H_2O)ZnTPP$	tri-TPP	Porphine*
[a] $M-N$	2.008	2.072	2.049	2.05	--	--
[b] $Ct-N$	1.989	2.054	2.012	2.04	2.065	2.043
[c] C_a-N	1.384	1.376	1.384	1.38	1.369	1.379
C_a-C_b	1.433	1.431	1.446	1.430	1.442	1.442
[d] $C_b-C_{b'}$	1.356	1.360	1.380	1.37	1.351	1.355
C_a-C_m [e]	1.394	1.415	1.395	1.42	1.398	1.382
[f] Δ	0.273	0.27	0.383	0.20	--	--

[a] Metal-nitrogen distance.

[b] Center-nitrogen distance.

[c] C_a is the carbon atom adjacent to pyrrole nitrogen.

[d] C_b is the carbon atom adjacent to C_a.

[e] C_m is the methine carbon atom.

[f] Δ is the out-of-plane displacement of the central metal atom.

* From the structure determination in Part II.

bond, but the C_b-$C_{b'}$ bond, as in general, is relatively insensitive to metal substitution.

PART II

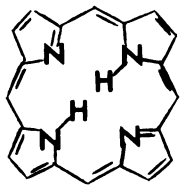
THE REDETERMINATION OF THE STRUCTURE OF PORPHINE

VI. INTRODUCTION

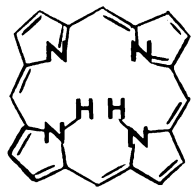
1. General

Porphine (Fig. 1b) is the parent compound of all the porphyrins. The bond distances, the bond angles and the planarity of this molecule form the basis of all comparisons among the porphyrins. Porphine crystallizes with a monoclinic space group in which each asymmetric unit contains one complete molecule. With such an arrangement, the structure of porphine can be expected to be relatively free from any crystalline imposed symmetry or distortion and to approximate the molecule in its free state. Therefore, accurate structural parameters, which are important for the discussion of the general characteristics of porphyrins, are particularly important for this molecule.

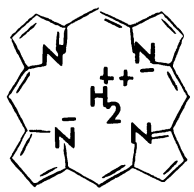
Since porphine is a conjugated system, its carbon-nitrogen skeleton can be represented in terms of several resonance forms. The usual structural assignments to the free base of porphine lead to several possible configurations for the center imino hydrogen atoms:[32] 1) hydrogen atoms on opposite nitrogen atoms (Fig. 16, I), 2) hydrogen atoms on adjacent nitrogen atoms, (II), 3) hydrogens in an ionic form, (III), and 4) hydrogen atoms occupying



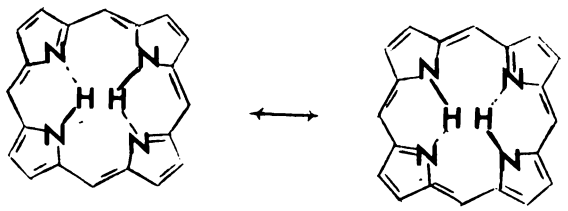
I



II



III



IV (Resonance structures)

Figure 16. Possible central hydrogen models (from Dorough & Shen (1950))[32]

equivalent bridging positions between two nitrogen atoms, (IV). In early studies, neither isomer I nor isomer II could be conclusively isolated, even though a great number of free base porphyrin compounds had been investigated. It was thus concluded that the structure of porphine was that of either an inseparable equilibrium mixture of isomers I and II or some other species (III or IV), in which the hydrogen atoms were bonded in an entirely different manner. The inner-hydrogen structure of the free base porphine and other porphyrins has been studied by infrared and visible spectroscopy, nuclear magnetic resonance, and X-ray diffraction. These studies will be discussed briefly.

2. Visible Spectroscopy

Studies of the visible absorption spectra of porphine and some derivatives of it were carried out by Erdman and Corwin.[33] They observed that the absorption spectrum of a porphine in which one of the two inner hydrogens had been replaced by a methyl group was identical with the absorption spectrum of the corresponding unmethylated free base. These results were interpreted to mean that the replaced hydrogen was bonded covalently since the methyl group was certainly bonded covalently, and the ionic and the resonance hydrogen bridge structures (see Fig. 16, III and IV) were precluded. However, the covalent character of inner hydrogens implied that porphine could exist as structural isomers.

Subsequently, the visible spectrum of the free base of a tetraphenyl porphyrin (TPP) was studied by Dorough et al.[32] The free base dissolved in E.P.A. (which is a mixture of ether, isopentane and alcohol) forms a clear glass without crystallizing at low temperature. The absorption spectrum of the solution was observed at room temperature and the glass at liquid-air temperature. The low temperature spectrum exhibited a blue shift for the long wavelength absorption band, and a red shift for the short wavelength band, the relative heights of these bands were interchanged, and at the low temperature the fine structure of some small bands was resolved. However, the spectra of the metalloporphyrins of Sn(II) and Ag(II) showed no shifting of bands at the two different temperatures. Since divalent metals are presumably bonded equivalently to all nitrogens, the metallo-spectra led to the interpretation that isomeric metallo-structures were impossible. Hence, the behavior of the free base suggested that more than one species was present.

Emission spectra provide an experimental method for obtaining information concerning whether or not a given set of absorption bands is due to one or more absorbing species. A fluorescence spectrum is physically and absolutely characteristic of a given substance and results from an electronic transition from the lowest vibrational level of the first excited state to the ground state. If a sample contains two different species it will exhibit two absorption

bands which can be excited by a particular wavelength of light and thus two different fluorescence spectra will be obtained. Fluorescence spectra which could corroborate the conclusions drawn from visible absorption spectra have been carried out[32], but they contained so many overlapping bands they could not be interpreted easily. However, they appeared to support the proposition that the free base existed as an equilibrium mixture which resulted from the tautomerism of the imino hydrogen atoms.

Theories have been developed which attempt to predict the structural properties of some free base porphyrins and metalloporphyrins. Molecular orbital calculations of porphine by Gouterman[34] predicted that the spectrum of the structure with the two central hydrogens on adjacent nitrogens would resemble closely that of the "opposite" tautomer, since the energy of each of four B and Q bands was predicated to fall within 500 cm^{-1} of its counterpart. Thus the calculation suggested that any "adjacent" tautomer present in solution would be very difficult to detect spectroscopically.

3. Infrared Studies

In the first systematic study of the infrared spectra of porphyrins (in Nujol), Falk and Willis[35] found that the N-H stretching vibration appeared as a weak band at 3280-3300 cm^{-1}. In dilute carbon tetrachloride solution, porphyrins gave N-H stretching bands around 3320 cm^{-1}.

A comparison of the N-H stretching bands of pyrrole and indole in dilute solution led to the conclusion that intermolecular hydrogen bonding had to be present, but, the exact nature of this bonding was not suggested.

Subsequently, from solid state infrared spectroscopic studies of porphine and many of its derivatives, Mason[36] concluded that the nitrogen atoms of the porphine nucleus were extensively hydrogen bonded. To account for the observations he proposed three possible intramolecular hydrogen-bonding schemes for the free base porphyrin (see Fig. 17). In the first model, the hydrogen atoms were attached to adjacent nitrogen atoms and hydrogen bonded to the remaining nitrogen atoms (Fig. 17a). In the second, the hydrogen atoms were bonded to opposite nitrogen atoms and were hydrogen bonded to the adjacent nitrogen atoms (Fig. 17b). In the third, the hydrogen atoms were symmetrically located between each pair of nitrogen atoms (Fig. 17c). At the time the dimensions of the porphine nucleus were not known, so these models were examined on the assumption that the dimensions of the porphine core were very close to those of phthalocyanine[37] (an azaporphine), whose approximate structural parameters were available. From the latter, Mason concluded that the first model would be less stable than the others due to the penetration of each hydrogen atom into the van der Waals sphere of the other. Using similar assumptions and scale models of the porphine core, Badger, et al.,[38] excluded the third

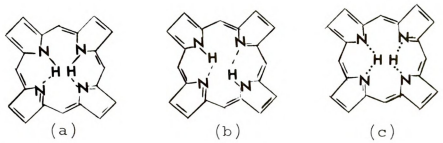


Figure 17. Mason's intramolecular hydrogen-bonded models for porphine.

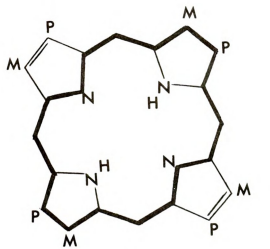


Figure 18. Coproporphyrin.

model, which had symmetrical hydrogen bonds, because the N...N distances of 2.65 and 2.76 Å found for phthalocyanine would clearly cause the N...H bonds to be unsymmetrical. Thus through the process of elimination, the second model was considered the most reasonable.

4. Nuclear Magnetic Resonance

High resolution proton nuclear magnetic resonance spectra of free base porphyrins have been reported by Becker, Bradley, and Watson.[39] The spectra were interpreted in terms of a "ring current" in the π conjugated system as indicated by the heavy line in the porphine skeleton of coproporphyrin I (as shown in Fig. 18). In coproporphyrin I, the methyl groups attached to the two types of pyrrole rings are at different distances from the π electron distribution and should thus experience a different local electrical field. However, the single sharp CH_3 line observed in the nmr spectrum indicated the methyl groups were magnetically equivalent. Furthermore, at the freezing temperature of solvent, $CDCl_3$ (-63^0C), no broadening of the CH_3 line was observed. Thus rapid tautomerism, which would average the properties of the pyrrole rings, was suggested as the only possible interpretation of the CH_3 magnetic equivalence. Calculations showed that the rate of the tautomerism of NH proton should be much greater than 200 sec^{-1}.

5. X-ray Studies

Several conflicting models of the inner hydrogen atom structure of porphine emerged from the visible, infrared and nuclear magnetic resonance spectroscopic studies. However, the X-ray diffraction crystal structure studies of tri-TPP[40], tetragonal TPP[41] and porphine[42] suggest that the central hydrogen atoms are bonded to diagonal nitrogen atoms.

The structure determination of tri-TPP shows two independent pyrroles and phenyl groups. Although the individual pyrrole and phenyl groups are planar, the porphyrin core is nonplanar, as indicated by the fact that one pair of the centrosymmetrical pyrroles is essentially coplanar to the nuclear least squares plane (NLS) of the porphyrin ring, while the other pair, carrying the central hydrogen atoms, is inclined approximately $\pm 6.6^0$ to this plane. The slight deviation of the two central hydrogen atoms from the NLS plane gives H-H contact greater than the in-plane distance. The four bonds which connect the methine carbon atoms to the terminal carbon atoms of the phenyl groups are abnormally long (1.5 Å), and separate the phenyl rings electronically from the porphyrin ring .

The crystal and molecular structure of tetragonal TPP were determined by Hoard, *et al*. They found that in each molecule the central hydrogen atoms are bonded to opposite nitrogens. The crystal structure achieves the space group symmetry requirement (S_4-$\bar{4}$) statistically by using a stereochemical species in which hydrogen atoms are attached to a

diagonal pair of nitrogen atoms which in turn are in orientations differing by a 90^0 rotation. The H-H separation is about 2.1 Å.

The bond parameters of the pyrrole of tetragonal TPP are almost identical to the average of the two pairs of crystallographically independent pyrroles of tri-TPP. Since tetragonal TPP has the molecular symmetry of a fourfold inversion axis, the four pyrroles are crystallographically equivalent. For this reason, the pyrrole with a central hydrogen is indistinguishable from that without a hydrogen atom. Therefore, a precise determination of the inner hydrogen atom structure in tetragonal TPP is limited.

The structure of porphine was originally determined by Webb and Fleischer.[42] They reported the porphine molecule to be planar, with approximate D_{4h} (4/mmm) symmetry, with four half-hydrogens bonded to the nitrogen atoms. The latter was explained as due to the interconversion of N-H tautomers first suggested by Becker on the basis of nuclear magnetic resonance work.[39] During the structure refinement of the porphine, a peak corresponding to 2-3 electrons was observed at the center of the ring, and it was assumed to be due to a 5-10% impurity of copper porphine. When this electron density at the center of the molecule was removed with a calculated contribution, the four peaks which appeared in the vicinity of the nitrogen atoms were assumed to be half-hydrogen atoms. Since peak heights of the half-hydrogen atoms, 0.31, 0.42, 0.29 and 0.44 e $Å^{-3}$, were only slightly

greater than the background of ± 0.2 e Å^{-3}. Their structure determination of the central hydrogens of porphine was at best unreliable. Furthermore, even though the N-H bond distances were reported, the exact nature of the half-hydrogen atoms in relationship to van der Waal's hydrogen contacts was not considered.

VII. EXPERIMENTAL

1. The Problem of the Hydrogen Atoms

The atomic resolution usually obtainable with $CuK\alpha$ radiation, approximately 0.8 Å, is sufficient to resolve hydrogen atoms bonded to carbon or nitrogen atoms. Since hydrogen atoms appear only as weak features on the observed electron density of heavier atoms, they are commonly found from a difference synthesis which provides a means for finding hydrogen atoms by subtracting from the observed electron density the density due to the heavier atoms. Since a difference synthesis is used, the observed structure amplitudes ($|F_o|$), the calculated structure amplitudes ($|F_c|$), the phases, and the scale constant between $|F_o|$ and $|F_c|$ are important factors in determining the hydrogen locations. To locate hydrogen atoms with certainty, accurate structural parameters of the nonhydrogen atoms, which relate to the $|F_c|$'s , and accurate intensity data, which relate to $|F_o|$'s , are required.

Since the hydrogen atom structure of the porphine molecule, particularly the central hydrogens, was the principal interest in redetermining the structure, it was desirable to know which reflections had a substantial hydrogen atom contribution before intensity data collection

was undertaken. In addition to collecting a complete set of intensities for all independent reflections, additional and more elaborate counting techniques could be applied to those reflections with an expected significantly measurable hydrogen atom contribution, thus minimizing counting errors, and adding more significance to the hydrogen atom locations as revealed in a difference synthesis. The reflections which were to be examined in greater detail were ascertained *via* a structure factor calculation in which were required the approximate atomic parameters of the hydrogen atoms and the cell parameters of porphine. The necessary structural parameters were obtained from the structure determination of porphine by Webb and Fleischer.[42]

The numbering scheme for the carbon and nitrogen atoms in porphine is given in Figure 19. The hydrogen atoms are numbered corresponding to the atoms to which they are bonded. The hydrogen atom structure factor calculations included the methine and central hydrogen atoms, the latter in three different combinations. These combinations arise from the fact that the central hydrogen atoms might be associated with different sets of pyrrole nitrogen atoms. The four structure factor calculations which were computed were based on the following structures:

(1) H22, H24 structure

(2) H21, H23 structure

(3) Four one-half hydrogen structure

(4) Four methine hydrogen structure (H5,H10,H15, and H20).

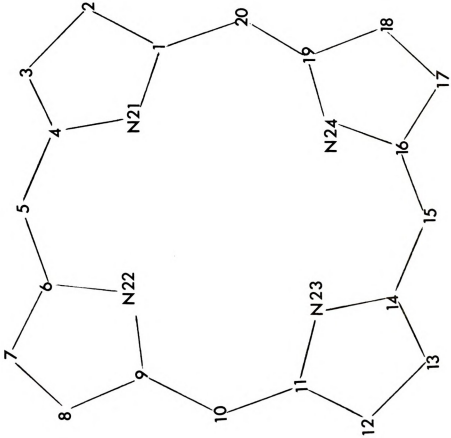


Figure 19. Porphine numbering scheme.

In (1), a structure factor calculation was based on a set of two opposite inner central hydrogen atoms bonded to two pyrrole nitrogen atoms. The second calculation (2) was computed using the other set of two opposite central hydrogen atoms. In (3), half weights were applied to each of four central hydrogen atoms, H21, H22, H23, and H24. This central hydrogen atom structure was the one reported by Webb and Fleischer, which is said to be due to rapid exchange between N-H tautomers. Structure calculation (4) included those hydrogen atoms which are bonded to the bridge carbon atoms of porphine, since these hydrogens were considered important for certain crystal packing properties which might be associated with tri-TPP. All structure factor calculations were confined to the scattering angle of 2θ less than or equal to 50^0, since the mean scattering factor for a hydrogen atom is less than 0.2 electron beyond this region.

The magnitudes of the four sets of structure factors based on the different models of hydrogen locations were compared. Reflections which might contain significant hydrogen atom contributions were then grouped according to the following scheme: (1) $|F_c| > 2.0$ in any of the structure factor calculations, and (2) $1.0 < |F_c| \leq 2.0$ in all the different calculations ($|F_{c(max)}| = 8.0$ for central and 16.0 for methine hydrogen atom calculations). The former included about 10% of all the reflections considered and the latter

about 20%. The calculated F_c for two reflections ($\bar{5}23$) and ($\bar{5}00$) are given as examples.

Reflections	Four 1/2H Structure	H21, H23 Structure	H22, H24 Structure	Four Methine H Structure
($\bar{5}23$)	< 1.0	< 1.0	< 1.0	2.3
($\bar{5}00$)	1.2	1.1	1.3	1.6

After such a process of elimination, eighty reflections considered to be most sensitive to the atomic parameters of the hydrogen atoms were chosen for measurement with more elaborate counting techniques to minimize counting errors. The details of these techniques will be discussed in a later section.

The distribution of structure factors of the central and methine hydrogen atoms of porphine in relationship to the scattering angle (2θ) was also investigated using the four sets of structure factor calculations. A graph of the number of reflections whose calculated structure amplitudes had a value $|F_c| \geq 1.0$ is shown as a function of the scattering angle in Figure 20. Hence, the reflections which occur at medium scattering angles (30^0 to 45^0 of 2θ) may contain significant hydrogen atom contributions and are important for an accurate determination of the hydrogen atom structure.

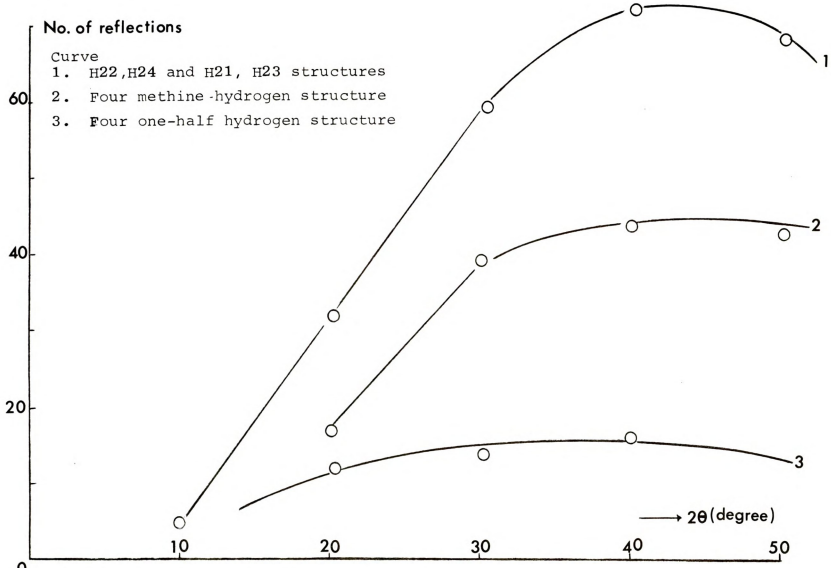


Figure 20. Number of reflections ($|F_c| \geq 1.0$) vs scattering angle (2θ).

2. Preliminary X-ray Examination

Single crystals of porphine in the form of dark-red square platelets were grown by slow evaporation from a benzene solution. The space group was known to be $P2_1/c$ with the unique b axis located along one of the diagonals of the plate. If the b axis is mounted precisely along the spindle axis of the Weissenberg camera, mirror symmetry perpendicular to the spindle will be seen in an oscillation photograph. Therefore, oscillation photographs were used to find the b axis of the crystal and for preliminary alignment of the crystal.

A crystal with the approximate dimensions of 0.2 x 0.275 x 0.05 mm (shown in Fig. 21) was used for the X-ray ($CuK\alpha$) data collection which was carried out on a General Electric XRD-5 Diffractometer equipped with a quarter circle single crystal orienter. The porphine crystal was mounted with the unique b axis along the Φ axis with the a*c* plane in the equatorial plane of the diffractometer when the angular χ setting of the diffractometer is at zero degrees. The angular settings of twelve reflections, which were well-distributed in reciprocal space were carefully measured and subjected to a least squares analysis from which the best orientation and the unit cell dimensions were obtained. The unit cell dimensions and their estimated standard deviations are:

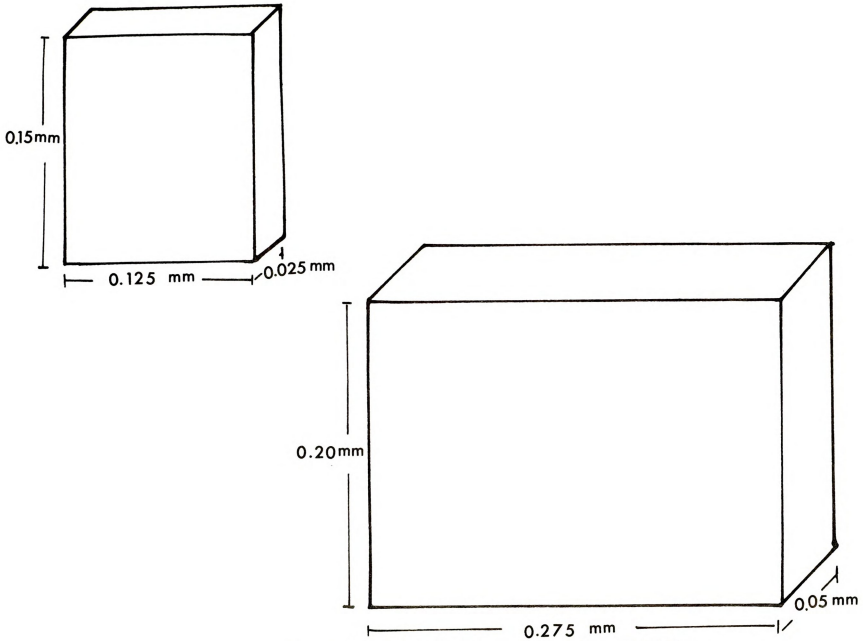


Figure 21. Dimensions of porphine crystals.

a 10.271 ± 0.003 Å

b 12.089 ± 0.003

c 12.362 ± 0.004

β 102.17 ± 0.02° .

Mosaic spreads, which among other things are used for determining the quality of a crystal, were measured on certain reflections by offsetting the azimuthal angle of the reflection to background level and then recording the intensity in 0.05° steps across the peak until the background was encountered again. Since the peak shapes of these mosaic spreads were symmetrical with a maximum peak width of about 0.3° close to the base of the peak, the crystal was judged to be of sufficient quality to allow intensity data to be collected in any quadrant. For convenience, data were collected in the quadrant which was bounded by ±a* through +c*.

The reflections (040) and (0,12,0) were the only observable reflections along the b* axis. However, (0,12,0) was weak and not suitable for accurate measurements. Therefore, an absorption correction was based on the (040) reflection and was measured before and after data collection with the average of the two measurements serving as the correction. The maximum absorption occurred at the Φ values corresponding to the -a* axis with a value of 1.07 ($A_{max}(-a^*)$), and the a* axis ($A_{max}(a^*)$) with a value of 1.14. The ratio $A_{max}(a^*)/A_{max}(-a^*)$ = 1.06 indicates the discrepancy in the intensity measurements along the a* and -a* directions. Anomalous absorption effects by a crystal can cause such disagreement between the intensities of equivalent reflections along the a*

direction, namely I(hk0), and those along -a* direction, $I(\bar{h}k0)$. The average ratio obtained between the reflections of these two zones (hk0, $\bar{h}k0$) was 1.03, obtained from the expression

$$\left\langle \frac{I(\bar{h}k0)}{I(hk0)} \right\rangle_{n=53} = 1.03 \pm 0.02$$

n is number of unique reflections.

The average ratio of 1.03 based on 53 measurements was considered more reliable than the ratio of 1.06 obtained from the absorption curve. Therefore, the absorption curve was adjusted slightly in the regions of the -a* and a* directions to have the ratio of 1.03 instead of 1.06. This adjustment gave the maximum absorption correction of 1.09 at the -a* and 1.12 at the a* direction.

The empirical absorption curve was used with Phillips' method (see Part I) to correct for the absorption of X-rays by the crystal. Basically, the procedure for evaluating the absorption factor as given by Phillips is: (1) calculate the azimuthal angles of incident and diffracted beams,

$$\Phi_{inc} = (\Phi_{hk\ell} - \epsilon_{hk\ell}) \; ; \quad \Phi_{ref} = (\Phi_{hk\ell} + \delta_{hk\ell})$$

where

$$\epsilon_{hk\ell} = \delta_{hk\ell} = \sin^{-1}(\sin\theta \cos\chi),$$

$\Phi_{hk\ell}$ is the Φ value of the reflection,

and (2) obtain the absorption factors $A(\Phi_{inc})$ and $A(\Phi_{ref})$

from the absorption curve. Then, the absorption factor is given by

$$A(hk\ell) = 1/T(hk\ell) = \frac{1}{(T(\Phi_{inc}) + T(\Phi_{ref}))/2}$$

$$= \frac{2}{1/A(\Phi_{inc}) + 1/A(\Phi_{ref})}$$

3. Techniques for Measuring Intensities

In a crystal structure determination, the intensities of all the reflections obtained from intensity-data measurements form a set of relative integrated intensities; from these intensities a set of structure amplitudes can be derived by applying various geometrical and other correction factors. The integrated intensity, I, can be expressed as (see Appendix 1)

$$I = \frac{E\,\omega_v}{I_0}$$

where I_0 is the uniform intensity of the incident beam, ω_v is the angular velocity of the crystal, and E is the total energy of the diffracted beam. The equation indicates that the integrated intensity of a reflection is proportional to the total energy reflected by the crystal at a reflecting position. The measurement of the integrated intensity of a reflection is made by recording the number of quanta entering the detector as the crystal rotates a small angular range about the Bragg position. During this

measuring process, the detector (or a counter) can be either kept stationary or given a small movement relative to that of the crystal. Accordingly, some of the various techniques used for measuring intensities are: (1) stationary crystal - stationary counter, (2) moving crystal - stationary counter, and (3) moving crystal - moving counter.

(1) Stationary Crystal-Stationary Counter Technique*

This technique, as its name implies, involves no mechanical motions whatsoever during the measurement of the intensity. It depends on the apparatus and optics of the experimental arrangement. The conditions required in order to achieve a valid integrated intensity measurement[43] are:

1) The intensity distribution across the width of the X-ray source must be uniform.
2) The apparent width of the source must exceed; a) the width of the reflection taken at the base of the mosaic spread curve, b) the dispersion of the spectra range to be measured, and c) the size of the crystal as it must be completely bathed in the X-ray beam.
3) The width of the aperture at the counter must be greater than the apparent width of the source.
4) The response of the counter must be uniform across the entire aperture used, and
5) If the source intensity varies with time, monitor reflections measured at definite intervals must be used to record the fluctuation of X-ray intensity.

*Hereafter, referred to as SX.

The SX technique offers speed and simplicity in data collection, but cannot be used to measure high-order reflections whose spectral components, $K\alpha_1$ and $K\alpha_2$, have angular separations greater than the width of the counter.

In this work, the SX technique was used to measure the intensities of all reflections within a limiting sphere defined by $2\theta \leq 100^0$. A crystal of appropriate size was chosen so that it was totally immersed in the X-ray beam. Before the intensity of each reflection was measured, the angular settings of the reflection were adjusted so that the diffracted intensity was maximized. The intensity was measured at the adjusted angular settings for a ten second period with a nickel filter and then with a cobalt filter (see balanced filter discussion in Appendix 1). The integrated intensity of a reflection was taken to be the difference between the intensity recorded with the nickel filter and that recorded with the cobalt filter.

(2) Moving Crystal - Stationary Counter Technique*

In this measuring technique, the detector is fixed at the Bragg angle, 2θ, of the reflection and the crystal is rotated with respect to the omega, ω, angle (see Appendix 1). The conditions for a valid integrated-intensity measurement are:

1) The crystal must be rotated through an angle large enough to cause every volume element to diffract

*Hereafter referred to as MX.

from the full width of the source.

2) The counter aperture must be large enough to accept all the radiation of the desired spectral range which is diffracted during the rotation of the crystal.

3) The response of the counter must be uniform across the full aperture.

4) Each and every increment of the angular position of the crystal rotation carries the same weight in the summation of the diffracted intensity.

The MX technique can be executed either by a continuous scanning motion in angular rotation or by a step-by-step motion. In the present work, a manual step-scan method was used in the intensity collection of the eighty reflections which had been considered to have an important contribution to the structure of the inner and methine hydrogen atoms of the porphine molecule.

The step scan of the MX technique consisted basically of using a count-six-drop-two omega (ω) scan procedure (Wyckoff, 1967).[44] The intensity is measured at each of six steps of the most sensitive angular position (ω) and the four largest measurements are used to compute the intensity of the reflection. The reasons for applying this procedure to this work are: (1) to increase the tolerance of the most sensitive angular setting (ω), and (2) to have the best efficiency of total counting time.

Two methods, constant-count timing and constant-time

counting can be used to record the intensity at each step in the ω scan procedure. The counting rate in the constant-time-counting procedure consists of accumulating counts during a predetermined time τ, and dividing the count accumulation, N_j, by τ. The other method, constant-count, is to measure the time t_j required to accumulate the predetermined number of counts, c. The expressions for the counting rate, I_j, in each method are:

$$I_j = N_j/\tau \quad \text{for constant-time counting}$$

and

$$I_j = c/t_j \quad \text{for constant-count timing.}$$

The corresponding estimated variances of these methods as derived by A. J. C. Wilson[45] are:

$$\sigma^2_{ct}(I_j) = I_j/\tau$$

$$\sigma^2_{cc}(I_j) \sim I_j^2/c$$

where the subscripts ct and cc denote constant-time and constant-count, respectively. The variance of the intensity for a reflection can be minimized by proper adjustment of the time of measurement for the constant-time method, or by a careful choice of the predetermined count for the constant-count method. The variance of intensities in the constant-time count is directly proportional to the intensity, I_j, while that in constant-count method is proportional to the square of the intensity. Therefore, the magnitude of the intensity of the reflection should also be taken into the consideration to choose which of the measuring techniques should be used for that reflection. In this work, the constant-time step scan technique was used for the intensity measurement of low intensity reflections, i.e., integrated intensity of a reflection less than 200 counts/10 seconds

as determined from SX measurements, and the constant-count step scan technique was used for medium and high intensity reflections. Details of the application of these measuring techniques will be discussed later.

a. The X-ray Detector.

The electronic circuitry in the detection and counting unit of G.E. XRD-5 Diffractometer consists of two main parts, the Electronic Time Register and the Scaler. The Electronic Time Register consists of six glow transfer counter tubes from which time information can be obtained by observing the relative position of the small glow discharge in each of six glow tubes.

The scaler circuits standardize and accumulate the pulses received from the X-ray detector. In addition, various control circuits are available to provide for manual, preset counts and preset time counting. The pulses accumulated by the scaler in one counting cycle, defined as the time necessary to accumulate a specified number of pulses or a specified time interval, are displayed by eight Decimal Counting Units.

b. Constant-time Step Scan Technique*

This method requires the number count, N_j, for each step to be accumulated for a predetermined time interval, τ. The predetermined time, τ, is selected by a switch on the XRD-5 scaler units, and N_j is indicated by visual read-out scalers. The counting rate, N_j/τ, is recorded and calculated.

*Hereafter referred to as CTST.

The step-scan was performed with respect to the most sensitive angular position (ω). The scan extended approximately $\pm 0.1^0$ from the calculated position and the step scan was carried out in 0.04^0 increments. The intensity was measured for a preset time of 100 seconds at each of the steps and the four largest measurements were totalled to give the intensity of the reflection (count-six-drop-two, Wyckoff, 1967).[44] The crystal was then moved to the ω-position displaying the highest intensity and the background was recorded at this position for 100 seconds with a balanced cobalt filter. Intensities measured for the (241) reflection are given as an example of this measuring technique, along with the corresponding SX values (see Table 13). The intensities of the (241) reflection obtained from the two measurement techniques, can be compared on the basis of relative error, ϵ, (Parish, 1965)[46] to see which measurement has the least error. The relative error in the constant-time measurement is inversely proportional to the square root of the total number of counts accumulated at the Bragg position, i.e., $\epsilon \propto 1/\sqrt{N}$. The number of counts accumulated by the SX technique is 97, and that by the CTST technique is 3774. Thus the ratio between the two relative errors can be written as,

$$\frac{\epsilon_{CTST}}{\epsilon_{SX}} = \frac{\sqrt{97}}{\sqrt{3774}} \sim \frac{1}{6} \quad .$$

Table 13. Intensities of $(\bar{2}41)$ Reflection Measured by CTST and SX Techniques.

Intensity	CTST		SX
	ϕ Settings (degree)	Time (sec)	Accumulating counts
	278.30	100	917
	278.34	100	939
	278.38	100	948
	278.42	100	960
	278.46	100	927
	278.50	100	894
	background at		
	278.42	100	139
I_{Ni}	94 c/10 sec*		97 c/10 sec
I_{Co}	14		13
I_{net}	80		84

*$(I_{Ni})_{CTST}$ = (939 + 948 + 960 + 927)/400 = 3774/400 = 94 c/10 s

$(I_{Co})_{CTST}$ = 139/100 = 14 c/10 s.

This calculation indicates that the relative error of (241) reflection obtained from CTST technique is much smaller than that from the SX technique. In addition, the step scan technique across the peak position eliminates slight variations in peak shapes resulting in a better integrated intensity. Therefore, intensities derived by the SX technique were removed by the CTST procedure before conversion to the corresponding structure factors.

c. Constant-Count Step Scan Technique*

This measuring technique is essentially the same as that of CTST technique except that the time, t_j, to accumulate a constant number of counts, c, is recorded. The number of counts to be used at each step was determined according to the intensity scheme listed in Table 14. The reflection ($\bar{4}12$) is used to compare this measuring technique to the SX technique (see Table 15). Based on Wilson's estimated variance, the SX method gives

$$\sigma^2_{SX} = I_j/\tau = (237 \text{ c}/10\text{s})/10\text{s} = 2.4 \text{ c/s}^2$$

and CCST has a variance of

$$\sigma^2_{CCST} = I_j^2/c = \frac{24 \times 24 \text{ (c/s)}^2}{4000} = 0.2 \text{ c/s}^2$$

This estimated variance indicates that the intensity of this reflection as determined by the CCST technique is about an

*Abbreviated as CCST.

Table 14. Step Scan Measurement.

Intensity Range (c/10s) of SX	Counting Technique	Count at Each Step	Time at Each Step (seconds)	Background at Peak
$I < 200$	const. time	--	100	100 s.
$200 \leq I < 2000$	const. count	1000	---	100 c.
$2000 \geq I < 10,000$	const. count	10,000	---	1000 c.
$I \geq 10,000$	const. count	100,000	---	10,000 c.

Table 15. Intensities of Reflection ($\bar{4}12$) Measured by SX and CCST Techniques

Intensity	CCST		SX
	ϕ Settings (degree)	No. Count for Each Step	Time (sec)
	278.24	1000	40.62
	278.28	1000	38.31
	278.32	1000	35.97
	278.36	1000	34.71
	278.40	1000	35.55
	278.44	1000	39.22
	background at 278.36	100	25.92
I_{Ni}	277 counts/10 sec*		274 counts/10 sec
I_{Co}	39		37
I_{net}	238		237

*$(I_{Ni})_{CCST} = 4000/(38.31 + 35.97 + 34.71 + 35.55) = 277$ c/10s

$(I_{Co})_{CCST} = 100/25.92 = 39$ c/10s

order of magnitude better than that measured by the SX technique. Therefore, the latter procedure was replaced by the former for the hydrogen structure determination of porphine.

(3) Moving Crystal-Moving Counter Technique (2θ-scan)*

In the MX-MC intensity measurement technique, the counter moves at twice the angular displacement of the crystal. The conditions necessary to obtain a valid integrated intensity are very similar to those for the MX measurement.

4. Data Collection

With the scattering angle limit of 100^0 a total of 1725 reflection intensities were measured using the SX technique. In order to estimate the intensity limit for unobserved reflections, the systematically absent reflections of the (h0ℓ) zone and the (0k0) reflections were measured. For these 88 reflections, the average intensity was 5 counts/10 seconds. Therefore, reflections with intensities greater than 5 counts/10 seconds were taken to be observed reflections. After rejecting the unobserved and redundant reflections ($\pm$hk0), 1206 independent reflections remained to compute structure amplitudes.

During the course of the intensity data collection, the reflections ($\bar{5}00$), (040) at a ϕ value of c^*-axis and (040) at a ϕ value of $\bar{a}^*$-axis were used to monitor any intensity fluctuation of the X-ray source and/or the

*Abreviated as MX-MC.

alignment of the crystal during each interval of measurement. A total of 32 monitor measurements were taken throughout the data collection. The standard deviations of the intensities of these monitor reflections were 1.2% for the $(\bar{5}00)$, 1.8% for the (040) reflection along the c*-axis, and 1.1% for the (040) along $\bar{a}^*$ direction. These deviations indicate that the intensity fluctuation of X-ray source was insignificant and the crystal remained well-aligned throughout the data collection.

In space group $P2_1/c$ the intensities of the (hk0) and $(\bar{h}k0)$ reflections are equivalent. A comparison of these equivalent reflections was made in terms of a residual index R_e expressed as

$$R_e = \frac{\sum^{67} |I(\bar{h}k0) - kI(hk0)|}{\sum^{67} (I(\bar{h}k0) + kI(hk0))/2}$$

where k is the scale constant of 1.03 obtained from the average ratio of the intensity of $(\bar{h}k0)$ to that of (hk0). Theoretically, the intensity of an (hk0) reflection should be equal to that of an $(\bar{h}k0)$, but discrepancies which are due to absorption and other such experimental causes are found in practice. The R-value obtained with 67 equivalent reflections was 3.8%. The residual index is an indication of the reliability of the data and is certainly acceptable, especially when considered in terms of the $|F|$'s.

5. Calibration Between Measuring Techniques

Since various intensity measuring techniques were used, systematic errors could arise between different sets of data due to possible scaling errors. Calibration constants between the sets were evaluated by comparing the average ratio of the intensity measured by the SX technique to that measured by the CTST technique, and by comparing the average ratio of intensity measured by the SX method to that determined by the CCST method. They are

$$\left\langle \frac{I_{SX}}{I_{CTST}} \right\rangle_{n=24} = 0.99 \pm 0.06$$

$$\left\langle \frac{I_{SX}}{I_{CCST}} \right\rangle_{n=54} = 1.00 \pm 0.04$$

where n is the number of the reflections used in the averaging. Since these average ratios were very close to unity, it was not necessary to correct the intensities of the same reflection measured by different techniques, and the intensity measured by the SX technique was directly replaced by that measured by the step-scan method for use in the structure amplitude calculations.

VIII. STRUCTURE DETERMINATION

1. Isotropic Refinement

A trial structure based on the coordinates reported by Webb and Fleischer (abbreviated W&F)[42] and isotropic temperature factors for the four nitrogen and twenty carbon atoms (see Table 16) were used to compute a set of initial structure factors. The R-factor for this calculation was 0.142, and decreased to 0.139 after one cycle of least squares refinement of all the parameters (with unit weight). After some small calculated structure factors were eliminated, 1177 (out of 1206) reflections were used to compute the first observed electron density, ρ_{o1}, and the first difference electron density, $\Delta\rho_1$. All the hydrogen atoms were located from $\Delta\rho_1$ at approximately the expected positions in the difference density map. The most striking difference from the W&F structure was the presence of only two central hydrogen atoms which were attached to two opposite nitrogen atoms. The peak heights of the two central hydrogen atoms were approximately 0.3 e/Å^3 for H22, and 0.4 e/Å^3 for H24; these peak heights were somewhat lower than the average peak height (0.5 e/Å^3) of the remaining hydrogen atoms. In addition to these features, residual electron

Table 16. Atomic Coordinates and Isotropic Temperature Factors for Porphine (from Webb & Fleischer)[b].

Atom	(Coordinate ± std. dev.)[a] x 10^4 $x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	B ($Å^2$)
Cl_α	1978 ± 2	4489 ± 2	3114 ± 2	4.2
$C2_\beta$	2661 ± 2	5349 ± 2	3825 ± 3	5.1
$C3_\beta$	2884 ± 2	6059 ± 2	2912 ± 3	5.7
$C4_\alpha$	2351 ± 2	5645 ± 2	1614 ± 2	4.2
$C5_m$	2396 ± 2	6123 ± 3	405 ± 3	4.6
$C6_\alpha$	1903 ± 2	5735 ± 2	-848 ± 2	4.3
$C7_\beta$	1966 ± 2	6234 ± 2	-2098 ± 3	5.3
$C8_\beta$	1393 ± 2	5596 ± 2	-3069 ± 3	5.3
$C9_\alpha$	949 ± 2	4684 ± 2	-2449 ± 2	4.2
$C10_m$	292 ± 2	3836 ± 2	-3099 ± 2	4.6
$C11_\alpha$	-154 ± 2	2962 ± 2	-2520 ± 2	4.3
$C12_\beta$	-850 ± 2	2097 ± 2	-3221 ± 3	5.6
$C13_\beta$	-1105 ± 2	1407 ± 2	-2309 ± 3	5.4
$C14_\alpha$	-566 ± 2	1829 ± 2	-1016 ± 2	4.5
$C15_m$	-621 ± 2	1362 ± 2	199 ± 3	4.8
$C16_\alpha$	-126 ± 2	1756 ± 2	1444 ± 3	4.4
$C17_\beta$	-182 ± 2	1253 ± 2	2697 ± 3	5.3
$C18_\beta$	418 ± 2	1870 ± 2	3669 ± 3	5.1
$C19_\alpha$	862 ± 2	2780 ± 2	3046 ± 2	4.0
$C20_m$	1549 ± 2	3604 ± 2	3702 ± 2	4.4
N21	1811 ± 2	4682 ± 2	1782 ± 2	3.9
N22	1283 ± 1	4794 ± 2	-1108 ± 2	3.9
N23	7 ± 1	2770 ± 2	-1188 ± 2	3.9
N24	517 ± 1	2686 ± 2	1698 ± 2	3.8

[a] Standard deviations estimated by least squares analysis.

[b] The coordinates x, z are equivalent to z, x of the present work. This Table was taken from L. E. Webb, Ph.D. Thesis, Department of Chemistry, University of Chicago, Chicago, Illinois, 1965.

densities found in the vicinity of the outer pyrrole carbon atoms in $\Delta\rho_1$ suggested anisotropic thermal motion for the outer carbon atoms of the porphine molecule. Thus, the individual isotropic temperature factors were converted into the corresponding anisotropic temperature factor form for carbon and nitrogen atoms and the least squares refinement was continued.

2. Anisotropic Refinement

One cycle of least squares refinement in which the coordinates and anisotropic temperature factors of the inner 12 atoms were allowed to vary, followed with another cycle in which the atomic parameters of the outer 12 carbon atoms were allowed to vary, decreased the R-factor about 1% for the first cycle and another 2% in the second cycle to 0.109. Examination of the observed and calculated structure factors indicated the largest discrepancies to be concentrated in some large, low-order reflections, such as (022), $|F_o| = 137.5$ and $|F_c| = 161.4$. This observation is characteristic of secondary extinction, and an attempt to correct for extinction was made before proceeding with further refinement.

3. Extinction Correction

Secondary extinction is related to the amount of mosaic character of crystals. When the X-ray beam must penetrate deeply into the mosaic crystal before it reaches mosaic

blocks which have parallel reflecting planes as those blocks near the surface, there is an attenuation of the beam reaching the deeper mosaic blocks. This effect is known as secondary extinction and is most pronounced for reflections at low ($\sin \theta/\lambda$) where the intensities are generally large. As a result, the observed values for intense reflections are systematically less than their calculated values. There are several methods by which secondary extinction can be detected and corrected. The extinction correction for the intensity data of porphine was made by remeasuring the low order reflections with a small crystal. The small crystal has fewer planes in the reflecting position at the given time, and thus the attenuation of X-ray beam is less than that for a large crystal.

A small crystal with the dimensions of 0.15 x 0.125 x 0.025 mm (see Fig. 21) was used for intensity measurements of reflections which might be affected by secondary extinction. The volume ratio between the large crystal and the small crystal is 5.88. All reflections distributed in the hemisphere with $\pm h \leq 4$, $k \leq 4$ and $\ell \leq 4$ were measured by the use of a Picker 4-Circle Automatic Diffractometer. Proper scaling between different instruments as well as crystals was made by using reflections not affected by extinction. The average ratio obtained between structure amplitudes of the small crystal, $|F_{small}|$, and the structure amplitudes of large crystal, $|F_{large}|$, was

$$\left\langle \frac{|F_{large}|}{|F_{small}|} \right\rangle_{n=30} = 1.61 \pm 0.06$$

where n is the number of reflections.

The residual index in terms of $|F_{small}|$ and $|F_{large}|$, over extinction-unaffected reflections, was assessed by

$$R_E = \frac{\Sigma\,||F_{large}| - 1.6|F_{small}||}{\Sigma\,(|F_{large}| + 1.6|F_{small}|)/2|} = 3.3\%$$

This number indicated that the two sets of structure amplitudes, based on two different sized crystals, measured by different diffractometers and methods were in good agreement. It is of note that the thirty reflections which were used to determine the average ratio of the structure amplitudes had amplitudes ($|F_o|$) ranging from 3 to 74 (absolute scale). The average intensity ratio can be written as the square of average ratio of structure amplitude. The average ratio of intensities had a value of 2.6 which does not correspond to the volume ratio of 5.88. This is probably due to the fact that the automatic diffractometer is more sensitive for X-ray detection.

The structure factor calculation (excluding hydrogen atoms) computed after six strong low-order reflections from the large crystal which showed pronounced secondary extinction were replaced by the new structure amplitudes (see Table 17) and an R-factor of 0.10. A difference electon density was then calculated and examined, from which all the hydrogen coordinates were obtained. Individual

Table 17. The Reflections Corrected for Extinction.

Reflection	$\|F_c\|$	$\|F_{o\ large}\|$	$\|F_{o\ small}\|$
(022)	161.4	137.5	160.6
($\bar{1}$22)	108.8	95.5	111.1
(013)	100.1	89.7	99.8
(023)	122.7	116.3	129.7
($\bar{1}$13)	121.4	107.0	122.3
($\bar{1}$23)	166.3	155.2	172.8

isotropic temperature factor for each hydrogen atom was approximated to be 20% greater than that of its adjacent carbon and nitrogen atom in the porphine molecule. These isotropic values were then converted to anisotropic temperature factor form. The structure factor calculation (hydrogens included) of the porphine molecule had an R-factor of 0.086, and after one cycle of least squares refinement of all coordinates of carbon and nitrogen atoms, the R-factor decreased to 0.078. With one cycle of least squares refinement of anisotropic temperature factors of the 12 outer atoms followed by another cycle of refining the 12 inner atoms, the R-value went to 0.072 for the former and to 0.068 for the latter. Performing one cycle of least squares on all the hydrogen coordinates, the R-factor improved to 0.067. At this point the refinement by least squares was altered by basing it on a different weighting scheme.

4. Weighting Scheme

As it has been mentioned in Part I, the method of least squares applied to the structure refinement consists in systematically varying the atomic parameters so as to minimize the quantity

$$R = \sum_{i=1}^{n} w_i (|F_o| - |F_c|)^2$$

where the sum is taken over all independent structure amplitudes and w_i is the weight of an observation. Each

weight w_i is to be taken as the inverse of the square of the standard deviation of the corresponding observation, and may be estimated from the agreement of independent measurements or from considerations of the way the measurement was made. Factors which were taken into consideration for the weighting scheme for the porphine intensity data were counting statistics, the instrumental instability, and the reliability of the measurement. Three different weighting functions were used according to the intensity of the reflection. They were as follows

a) $12{,}000 \geq I \geq 400$ (Intensity, I, is counts per 10 sec)

$\sigma = 0.04 \times |F_o|$ where $\sigma = 1/\sqrt{w}$

or $w = 1/\sigma^2 = \frac{1}{(0.04)^2} |F_o|^{-2}$

Since the weight is inversely proportional to $|F_o|^2$, this weighting scheme is similar to that of Hughes .[47] The constant of 0.04 (4%) is the error estimated for unit weight observations. Generally, data in this intensity range were very reliable, as evidenced by the small fluctuation observed for the monitors (~2%) throughout the data collection. In addition, the counting statistics, $\sqrt{I}$, can be expressed in terms of the percentage counting error, $\sqrt{I}/I$, which is small in this intensity range. The two extreme conditions can be illustrated. For an intensity, I, equal to 12000 counts/10 sec, the counting error is less than 1%; for I equal to 400 counts/10 sec, the counting error is 5%. The latter value corresponds to

approximately 3% error on structure amplitude, since the standard deviation of $|F|$, σ_F, is approximately one-half the standard deviation of intensity, σ_I. Thus the average error for an observation in this intensity range was assumed to be slightly greater than 3%, or 4%.

b) $I > 12{,}000$

$$\sigma = 0.04 \times I/12000 \times |F_0| .$$

In this intensity range, the error of the observation is assumed to be linearly dependent on the magnitude of the intensity. Because extinction and crystal mis-setting problems are more pronounced for very intense reflections, the errors increase to account for these effects.

c) $400 > I > 5$

The error for an observation in this range was obtained from a curve derived from plotting the error (%) as a function of the intensities (shown in Fig. 22). The boundary conditions, $I = 5$ and $I = 400$, were selected so that the relative error was 100% for the former and 4% for the latter. This curve was then constructed by fitting three selected points, determined as follows:

(1) when $I = 68$, the error is 15%. This error was the maximum counting error for the (306) reflection which was one of the seven reflections selected in the intensity range between 5 and 200 count/10 sec and was measured repeatedly.

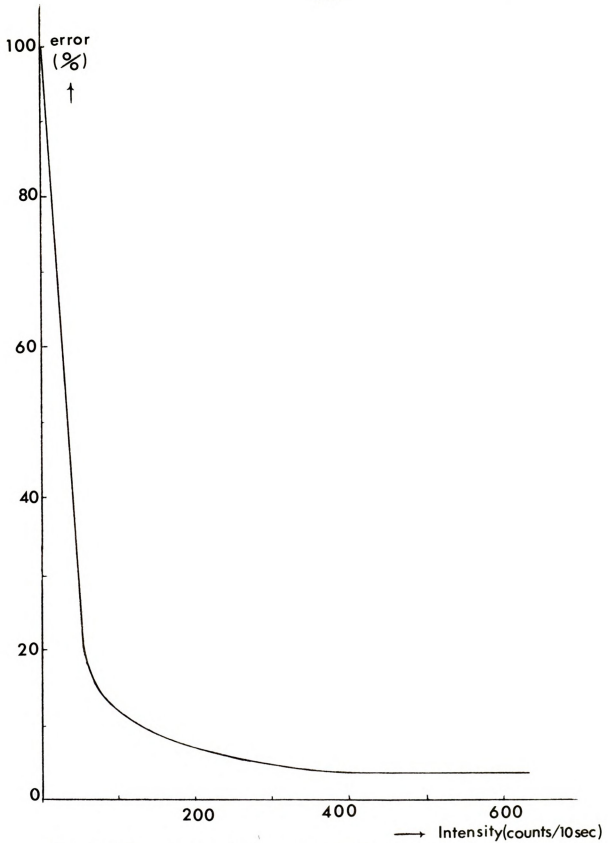


Figure 22. Error (%) vs intensity (I).

(2) The second point is that when I = 234, the error is 8%. This point was determined from the reflection ($\bar{1}10$) whose counting error of 8% was the largest among five selected reflections in the intensity range from 200 to 300 counts/10 sec.

(3) The third point is that when I = 300, the error is 5%. This point was obtained from the ($\bar{4}25$) reflection, as one of the five reflections whose intensities were in the range of 300 to 400 counts/10 sec.

In order to make the calculation of weight easier in this region, the curve was divided into 10 regions and the errors for estimating the standard deviation of a reflection are shown in Table 18.

The weighting scheme was applied to all the reflections except the ($\bar{1}00$) and ($\bar{2}00$) reflections. These reflections were not improved by the extinction correction, since the size of the second crystal used was not small enough to correct completely their secondary extinction effects. Zero weight (w = 0) was then applied to these two reflections to exclude them from the refinement.

When the new weights were applied and two cycles of least squares refinement of coordinates and anisotropic temperature factors of all the carbon and nitrogen atoms were performed, the R-factor lowered to 0.059 and the weighted R-factor to 0.041. The difference between the R-factor and the weighted R-factor is

Table 18. Error for Intensity Less than 400.

Intensity Range	Error
$300 \leq I < 400$	0.05
$250 \leq I < 300$	0.06
$200 \leq I < 250$	0.07
$150 \leq I < 200$	0.08
$125 \leq I < 150$	0.09
$100 \leq I < 125$	0.11
$75 \leq I < 100$	0.14
$50 \leq I < 75$	0.23
$25 \leq I < 50$	0.53
$5 \leq I < 25$	1.00

$$R = \frac{\Sigma \left| |F_o| - k|F_c| \right|}{\Sigma |F_o|}$$

$$\text{weighted } R = \frac{[\Sigma w(|F_o| - k|F_c|)^2]^{1/2}}{[\Sigma w |F_o|^2]^{1/2}}$$

where k is the scale constant between $|F_o|$ and $|F_c|$. Since one additional cycle of least squares on all the hydrogen coordinates had no apparent effect, the refinement of the porphine structure by least squares was terminated with a final R-factor of 0.059 and weighted R-factor of 0.041.

IX. RESULTS

The final coordinates, anisotropic temperature factors, the mean square atomic displacement ($\bar{u}^2$) in the direction of each principal axis, and peak heights of all the carbon and nitrogen atoms are listed in Table 19. The final coordinates, isotropic temperature factors and the peak heights of the hydrogen atoms are shown in Table 20. The isotropic temperature factors of the peripheral pyrrole hydrogens were approximated to be 20% greater than the average isotropic temperature factors of their adjacent pyrrole carbons (B = 5.6 Å); the isotropic temperature factors of the remaining hydrogen atoms were estimated to be 20% greater than the average isotropic temperature factors of their adjacent atoms (B = 4.6 Å).

The atomic deviations from different least squares planes based on the individual pyrrole rings, the plane defined by the four nitrogen atoms, and the plane based on the eight inner pyrrole carbon and nitrogen atoms are given in Table 21. The atomic deviations from the nuclear least squares plane (NLS) of the porphine molecule are shown in Figure 23; the standard deviation (excluding hydrogens) is 0.02 Å. The porphine bond distances and angles are shown in Figure 24 and Figure 25, respectively. The standard

Table 19. Final Atomic Parameters and Peak Heights of

Atom	Coordinates in Fractions			Anisotropic Temperature		
	x	y	z	β_{11}	β_{22}	β_{33}
N21	0.1757	0.4670	0.1809	0.0121	0.0066	0.0063
C1A	0.3113	0.4476	0.1978	0.0112	0.0086	0.0071
C2B	0.3825	0.5359	0.2657	0.0148	0.0102	0.0072
C3B	0.2904	0.6068	0.2877	0.0177	0.0092	0.0071
C4A	0.1613	0.5628	0.2353	0.0142	0.0076	0.0061
C5M	0.0418	0.6121	0.2388	0.0160	0.0067	0.0058
N22	-0.1116	0.4801	0.1282	0.0113	0.0077	0.0065
C6A	-0.0846	0.5743	0.1918	0.0151	0.0075	0.0057
C7B	-0.2088	0.6244	0.1970	0.0186	0.0090	0.0077
C8B	-0.3077	0.5598	0.1391	0.0135	0.0109	0.0076
C9A	-0.2475	0.4672	0.0955	0.0091	0.0105	0.0066
C10M	-0.3120	0.3826	0.0292	0.0102	0.0114	0.0070
N23	-0.1183	0.2775	0.0014	0.0102	0.0075	0.0069
C11A	-0.2527	0.2953	-0.0146	0.0133	0.0084	0.0064
C12B	-0.3260	0.2092	-0.0855	0.0151	0.0097	0.0079
C13B	-0.2330	0.1407	-0.1097	0.0169	0.0092	0.0082
C14A	-0.1038	0.1823	-0.0579	0.0151	0.0069	0.0067
C15M	0.0171	0.1358	-0.0623	0.0154	0.0075	0.0073
N24	0.1682	0.2671	0.0520	0.0103	0.0065	0.0071
C16A	0.1425	0.1741	-0.0141	0.0150	0.0149	0.0056
C17B	0.2661	0.1232	-0.0198	0.0185	0.0083	0.0087
C18B	0.3661	0.1863	0.0412	0.0157	0.0079	0.0085
C19A	0.3046	0.2768	0.0861	0.0112	0.0074	0.0068
C20M	0.3699	0.3598	0.1559	0.0099	0.0092	0.0073
$\sigma x 10^4$	0.1- 4	0.1- 4	0.1- 3	0.1- 4	0.1- 2	0.03-2

*In the direction of each principal axis.

Carbon and Nitrogen Atoms of Porphine.

Parameters			Mean Square Atomic Displacements* ($\AA^2$)			Peak Height ($e/\AA^3$)
β_{12}	β_{13}	β_{23}	$8\pi^2\bar{u}_1^2$	$8\pi^2\bar{u}_2^2$	$8\pi^2\bar{u}_3^2$	ρ_0
0.0008	0.0023	-0.0001	3.48	3.82	4.92	7.6
-0.0006	0.0026	0.0014	3.31	4.66	5.54	6.2
-0.0044	0.0015	-0.0002	3.75	4.28	8.23	5.9
-0.0041	0.0019	-0.0014	3.48	4.81	8.43	5.5
-0.0009	0.0017	0.0003	3.48	4.36	5.92	6.0
0.0007	0.0020	0.0006	3.22	4.03	6.54	6.0
0.0026	0.0025	0.0005	3.22	3.65	5.75	7.2
0.0030	0.0029	0.0003	3.06	3.61	6.91	5.9
0.0053	0.0038	0.0012	3.58	4.21	9.17	5.3
0.0047	0.0041	0.0021	3.45	3.89	8.49	5.4
0.0029	0.0021	0.0017	3.00	3.58	6.96	6.2
-0.0004	0.0011	0.0013	3.75	4.32	6.91	5.8
-0.0001	0.0017	0.0013	3.41	4.14	5.09	7.4
-0.0008	0.0022	0.0013	3.25	5.09	5.50	5.9
-0.0037	0.0009	0.0004	4.06	4.54	8.08	5.5
-0.0052	-0.0001	-0.0000	3.51	4.85	9.17	5.2
-0.0023	0.0015	0.0005	3.41	3.99	6.82	5.9
-0.0014	0.0022	-0.0009	3.82	4.70	6.27	5.9
0.0020	0.0025	0.0005	2.97	3.89	5.01	7.9
0.0069	0.0021	0.0034	2.79	3.78	6.45	6.0
0.0053	0.0040	0.0011	3.25	4.89	9.01	5.7
0.0050	0.0043	0.0020	2.91	4.32	8.28	5.6
0.0022	0.0029	0.0024	2.73	3.78	6.01	6.1
0.0001	0.0021	0.0016	3.68	4.03	5.84	5.9
0.1- 3	0.1- 5	0.1- 2				

Table 20. Final Coordinates, Isotropic Temperature Factors, and Peak Heights of Hydrogen Atoms of Porphine.

Atom	Coordinates			Isotropic Temperature Factors	Peak Heights
	x*	y	z	B ($\AA^2$)	ρ (e $\AA^{-3}$)
H22	-0.0458	0.4358	0.1183	5.5	0.5
H24	0.1042	0.3167	0.0633	5.5	0.5
H2B	0.5058	0.0367	0.2067	6.5	0.5
H3B	0.7033	0.1750	0.1650	6.5	0.5
H5M	0.9575	0.1842	0.2117	5.5	0.5
H7B	0.2242	0.1958	0.2700	6.5	0.5
H8B	0.4133	0.0533	0.3783	6.5	0.6
H10M	0.5850	0.3808	0.0192	5.5	0.5
H12B	0.5650	0.2825	0.3958	6.5	0.4
H13B	0.7433	0.4325	0.3400	6.5	0.5
H15M	0.0125	0.4300	0.3875	5.5	0.5
H17B	0.2750	0.4458	0.4342	6.5	0.5
H18B	0.4685	0.1742	0.0542	6.5	0.5
H20M	0.4758	0.3533	0.1708	5.5	0.6

*Coordinates of hydrogen atoms were obtained from difference density map.

Table 21. Atomic Deviations from the Least Squares Planes of Individual Pyrrole, Inner Eight Atoms, and Four Nitrogen Atoms.

Atom	d(Å)	Atom	d(Å)	Atom	d(Å)
Pyrrole N21		Pyrrole N22		Pyrrole N23	
N21	-0.02	N22	-0.01	N23	0.04
C1	-0.02	C6	0.01	C11	0.00
C2	-0.00	C7	-0.03	C12	-0.01
C3	-0.01	C8	-0.00	C13	0.01
C4	0.00	C9	0.01	C14	-0.01
s.d.*	0.01	s.d.	0.02	s.d.	0.02
Pyrrole N14		Four Nitrogen		Eight Inner Atoms	
N24	0.01	N21	0.01	C1	0.03
C16	-0.01	N22	-0.01	C4	-0.02
C17	0.00	N23	0.01	C6	-0.03
C18	-0.00	N24	-0.01	C9	0.02
C19	0.00	s.d.	0.01	C11	0.02
s.d.	0.01			C14	-0.01
				C16	-0.02
				C19	0.01
				s.d.	0.02

*Standard deviation

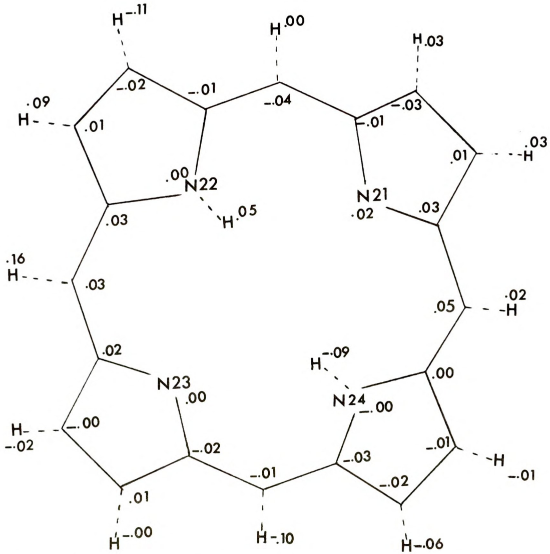


Figure 23. Atomic deviations (Å) from nuclear least squares plane.

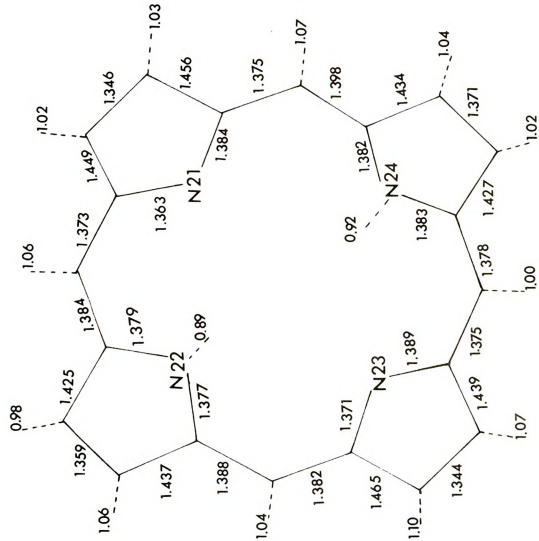


Figure 24. Porphine bond distances (Å).

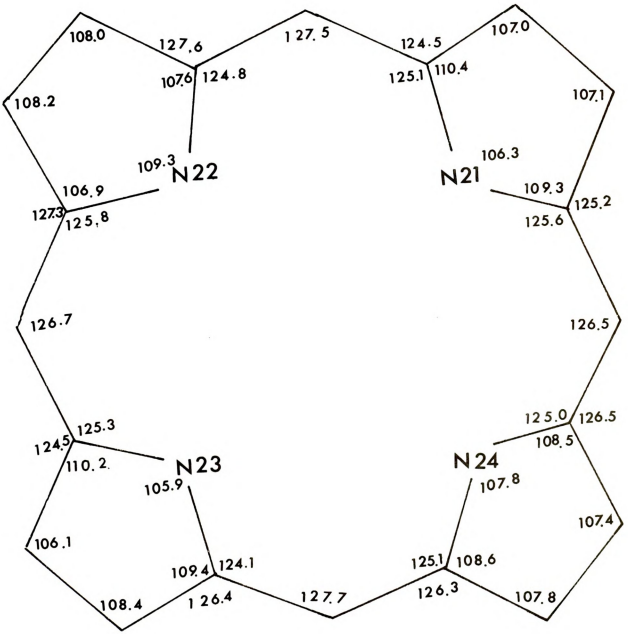


Figure 25. Porphine bond angles (degrees).

deviation of the lengths and angles of carbon-carbon and carbon-nitrogen bonds are approximately 0.004-0.007 Å and 0.3-0.5° respectively, based on the standard errors of coordinates of carbon and nitrogen atoms in the last cycle of least squares refinement.

The composite difference electron density (based on the structure factor calculation excluding all hydrogen atoms) projected onto the ac plane is shown in Figure 26. The first contour is drawn at a level of 0.12 e $Å^{-3}$ with each additional contour occurring at 0.12 e $Å^{-3}$. In addition, the difference electron-density in the vicinity of four nitrogen atoms is given in Figure 27; the electron densities of hydrogen atoms as well as the residual densities ($\sim$ 0.1 e $Å^{-3}$) due to background fluctuation in this region are indicated. Figure 28 shows the interatomic distances and angles of the two central hydrogen atoms with respect to the four nitrogen atoms in porphine molecule.

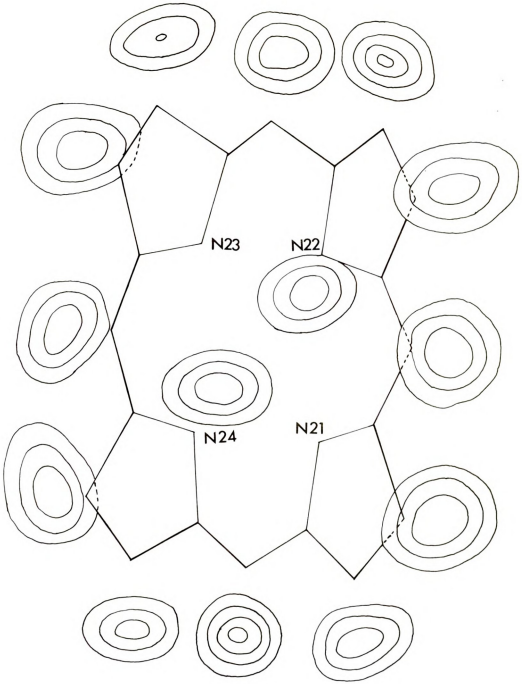


Figure 26. Composite electron density of the hydrogen atoms perpendicular to the ac plane.

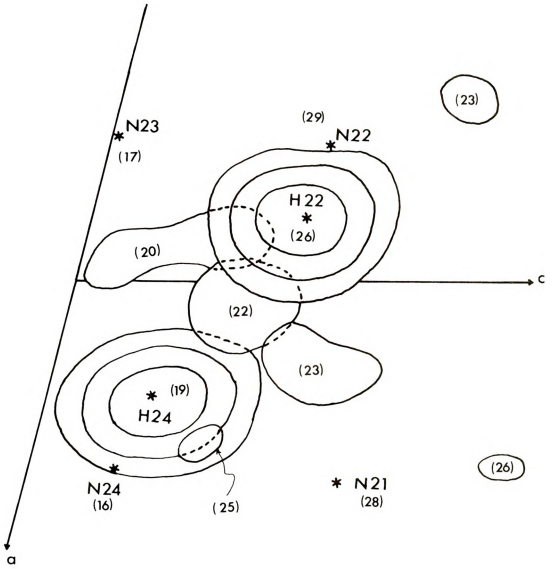


Figure 27. The difference electron density in the vicinity of the four nitrogen atoms. The length of b axis is divided into 60 sections, and the numbers in parenthesis are the section number corresponding to the y-coordinate of the atoms or the residual density (greater than 0.1 e A^{-3}) along the b axis.

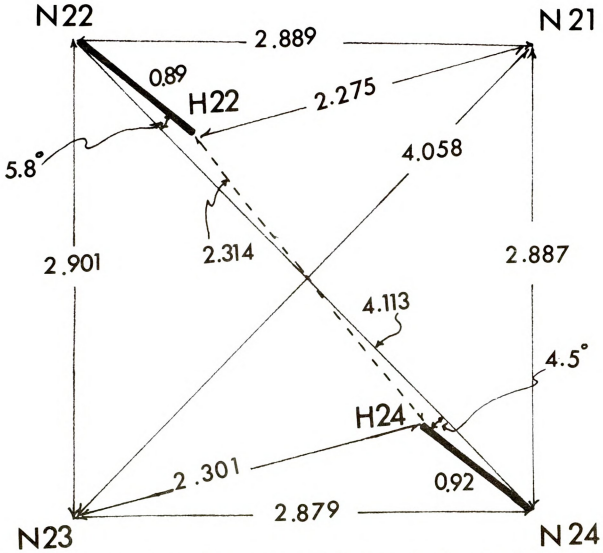


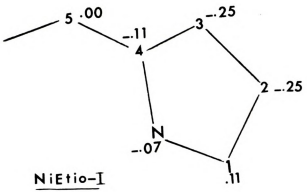
Figure 28. The interatomic distances and angles of the nitrogen and hydrogen atoms. Heavy lines indicate N-H bonds.

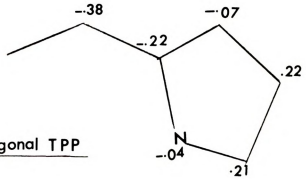
X. DISCUSSION

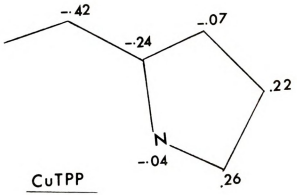
The deviations of the atoms from the least squares plane of each pyrrole indicate that the individual pyrroles (see Table 21) are essentially planar within the error of the structure determination ($\sim$ 0.01-0.02 Å). In addition, from the small atomic deviations from the least squares plane formed by the inner eight atoms, the plane of four nitrogen atoms, and the NLS plane, one can conclude that the porphine molecule is also essentially planar. In contrast to this planarity of the porphine molecule, the porphyrin skeletons of some free base porphyrins and some metalloporphyrins are found to be very ruffled. Factors which might influence the observed departure from planarity could be either metal or side-chain substitution, and/or forces arising from crystal packing. Examples of nonplanar porphyrin skeletons are illustrated in Figure 29. The NiEtio-I, CuTPP, and tetragonal TPP crystallize in tetragonal forms and the independent structural parameters determined are restricted to one quarter of the molecule due to the space group symmetry relations. From Figure 29 it can be seen that the nonplanarity of NiEtio-I manifests itself in pronounced deviations of peripheral pyrrole carbon atoms

Figure 29. Deviations of porphyrin skeleton from planarity.

In NiEtio-I position 2 and 3, position 1 and 4, and Ni atoms are fixed by symmetry; the atomic deviations indicated are the the perpendicular distances from (008) plane. The atomic deviations of CuTPP and tetragonal TPP are the perpendicular distances from (001) plane. The atomic deviations of tri-TPP are with respect to the nuclear least squares plane.


5 .00
-.11
4
3 -.25
2 -.25
N
-.07
1
.11
NiEtio-I


-.38
-.07
-.22
.22
N
-.04
.21
Tetragonal TPP


-.42
-.24
-.07
.22
N
-.04
.26
CuTPP

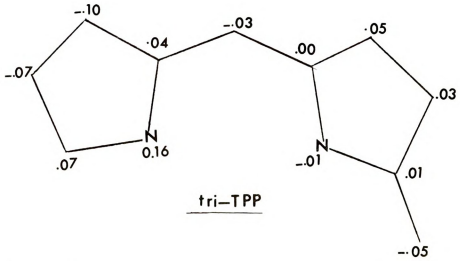

-.10
.04
-.03
.00
.05
-.07
.03
N
0.16
.07
N
-.01
.01
-.05
tri-TPP

Figure 29.

($\sim$ 0.3 Å) from the plane fitting the methine and pyrrole atoms, while CuTPP is nonplanar in a different way: the bridge carbon and some of the pyrrole carbon atoms ($\sim$ 0.2-0.4 Å) show the largest deviations. In the case of tri-TPP, the maximum deviation is found to be the pyrrole nitrogen atom which carries the central hydrogen atom ($\sim$ 0.2 Å); in addition, the pyrrole group is inclined with respect to the NLS plane ($\pm$ 6.6°). The nonplanarity of ClMnTPP is different from all the cases mentioned above. The atomic deviations for ClMnTPP (see Fig. 8, Part I) are found to fall into the following groups of decreasing atomic deviations:

$$d(C_b) > d(C_m) > d(N)$$

where C_b, C_m, and N denote the peripheral pyrrole carbon, the methine carbon and the nitrogen atoms, respectively. Furthermore, the atomic deviations have approximately $\bar{4}$ symmetry. All these different types of nonplanarity found in porphyrin systems suggest that the porphyrin skeleton is indeed very flexible.

The bond distances shown in Figure 24 have average bond lengths of 1.379 $\pm$ 0.008 Å for C-N, 1.381 $\pm$ 0.008 Å for C_a-C_m, and 1.04 $\pm$ 0.03 Å for C-H. The corresponding bond distances given in Volume III of International Tables for X-ray Crystallography are, C-C of 1.395 $\pm$ 0.003 Å in aromatic systems, and C-H of 1.084 $\pm$ 0.006 Å in benzene. A comparison of the reported values with those of this

determination shows that the bond distances of C-C and C-H are very close to the expected values.

Also of interest are the average distances within the pyrrole rings. The average C_a-N, C_a-C_b and C_b-$C_{b'}$ distances of tri-TPP, tetragonal TPP, porphine from W&F, and from this structure determination are listed in Table 22; the average of these bond distances on the basis of pyrrole with and without central hydrogen in tri-TPP and porphine are also included. A comparison of the average bond distances of the pyrrole with the hydrogen atom to those of the pyrrole without the hydrogen atom in porphine, indicates the differences: +0.004 Å for N-C_a, -0.021 Å for C_a-C_b, and +0.020 Å for C_b-$C_{b'}$. The corresponding values found in tri-TPP are +0.01 Å for N-C_a, -0.028 Å for C_a-C_b, and +0.008 Å for C_b-$C_{b'}$. Even though the magnitudes of the bond-length differences are different in the two cases, the pyrrole with hydrogen attached seems to have larger N-C_a and C_b-$C_{b'}$ bond lengths, and a contracted C_a-C_b bond length. In addition, comparison of the average pyrrole bond angles of the pyrrole with a hydrogen atom to the average pyrrole bond angles of that without a hydrogen atom in the porphine structure is +2.5° for $\angle$ C_a,N,C_a, -1.9° for $\angle$ N,C_a,C_b, and 0.7° for $\angle$ C_a,C_b,C_b (see Table 23). The corresponding values found in tri-TPP are 3.0° for $\angle$ C_a,N,C_a, -3.0° for $\angle$ N,C_a,C_b, and 1.3° for $\angle$ C_a,C_b,C_b. Such comparisons could not be extended to the tetragonal TPP since its pyrrole rings are similar.

Table 22. Average Pyrrole Bond Lengths in Some Free Base Porphyrins and Porphine.

	tri-TPP			Tetrag-		Porphine[g]		
	Pyrrole N-H[a]	Pyrrole[b]	Av.[c]	onal[d] TPP	Porphine[e] (W&F)	Pyrrole N-H	Pyrrole	Av.
$N-C_a$	1.374	1.364	1.369	1.350	1.366	1.381±0.003	1.377±0.012	1.379
C_a-C_b	1.428	1.455	1.442	1.438	1.442	1.431±0.006	1.452±0.011	1.442
C_b-C_b'	1.355	1.347	1.351	1.362	1.342	1.365±0.006	1.345±0.001	1.355

[a]The pyrrole with central hydrogen.

[b]The pyrrole without central hydrogen.

[c]The average of pyrrole N-H and pyrrole bond lengths.

[d]Only one set of crystallographically independent pyrrole.

[e]The structure parameters from W&F porphine. The average is based on four crystallographically indpendent pyrrole groups.

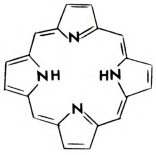
[g]The porphine from this work.

Table 23. Average Pyrrole Bond Angles in tri-TPP and the Porphine of this Work.

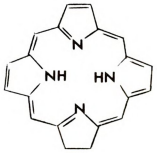
	tri-TPP		Porphine (present work)	
	Pyrrole N-H	Pyrrole	Pyrrole N-H	Pyrrole
$\angle C_a,N,C_a$	109.2	106.2	108.6	106.1
$\angle N,C_a,C_b$	107.3	110.3	107.9	109.8
$\angle C_a,C_b,C_b$	108.1	106.8	107.9	107.2

It is interesting to note that porphine and the porphyrin nucleus of tri-TPP can be described as corresponding to a structure of hybrids of the two predominant classical resonance forms of the porphine molecule. These two forms are shown in Figure 30(a) and (b); Figure 30(c) is an attempt to represent the expected nature of the hybrid. The average pyrrole bond distances of porphine and tri-TPP are shown; the bond distances of tri-TPP are indicated in parentheses. In the hybrid form, the C_b-C_b distance in pyrrole 1 should show increased double bond character (shorter bond length) compared to the equivalent distance in pyrrole 2. Likewise, the C-N distance in pyrrole 2 should show decreased double bond character compared to that in pyrrole 1. Trends towards these proposed results have been observed in the porphine and tri-TPP structures.

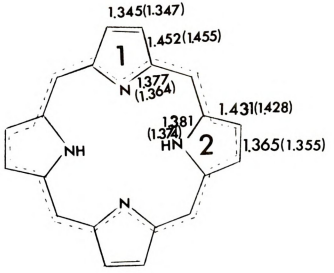
The most striking difference between this structure determination and that of W&F is the existence of two central hydrogen atoms bonded to two opposite pyrrole nitrogen atoms. These hydrogen atoms, H22 and H24, have peak heights of about 0.5 e Å^{-3} (background level $\sim$ 0.1 e Å^{-3}) as indicated in Figure 27. The N22-H22 and N24-H24 bond distances are 0.89 Å and 0.92 Å, respectively. The locations of the imino hydrogen atoms are slightly off the line joining their opposite nitrogen atoms; a deviation of 5.8^0 toward N21 is found for H22 and of 4.5^0 toward N23 with respect to N22-N24 for H24. These departures make the central hydrogen van der Waals contact (2.31 Å) slightly larger (0.01 Å)



(a)



(b)



(c)

Figure 30. Porphine resonance forms.

than the contact between two hydrogen atoms lying on the line of N22-N24. It is noteworthy that the central hydrogen atoms are essentially coplanar to the porphine molecule, as shown by their small atomic deviations from the NLS plane (see Fig. 23, 0.05 Å for H22 and -0.09 Å for H24). The central hydrogen structure of the porphine is different from that of tri-TPP. In tri-TPP case the central hydrogen atoms are slightly inclined from the NLS plane, presumably in order to keep a reasonable contact distance.

It is of additional interest that the distance between the pair of pyrrole nitrogen atoms which carry the central hydrogen atoms is 0.06 Å longer than the corresponding distance of the other pair of nitrogen atoms. A similar value of 0.14 Å is found in tri-TPP. This slight elongation of the N-N distance tends to increase the distance between the central hydrogens.

A comparison between the central region of the porphine molecule as reported by W&F and this work was made. It can be seen from the difference electron density in the vicinity of the nitrogen atoms projected on the ac plane (see Fig. 27) that only small residual electron densities other than the hydrogen atoms (about 0.1 e $Å^{-3}$) can be found. This observation suggests strongly that: (1) the sample of porphine used for this work does not contain a metal impurity at the center of the porphine molecule, and (2) only one pair of diagonal central hydrogen atoms is bonded to diagonal nitrogen atoms. The coordinates and peak heights of the

central hydrogen atoms of the two structures are listed in Table 24. The pair of alleged "half-hydrogen atoms", H21 and H23 are of peak heights of about 0.3 e $\AA^{-3}$; the corresponding locations are found to lie in negative regions in the present difference electron density. By comparing these peak heights (0.3 e $\AA^{-3}$) with the background level of 0.2 e $\AA^{-3}$ in the structure reported by W&F, one can see that hydrogen atoms, H21 and H23 could be error fluctuations of the background.

Final Remarks

A comparison of the observed structure amplitues of this work with those of W&F gave an R_d-factor, indicating the discrepancy between the two sets of data, which was 0.13, where

$$R_d = \sum^{n} ||F_o| - |F_o|_{W\&F}| / \sum^{n} |F_o|$$

and n is the total number of reflections of the present structure determination (n = 1206). This R_d-value indicates a substantial disagreement between the two sets of data. Factors which may have contributed to this disagreement are as follows.

1) Extinction Correction

A secondary extinction correction was made in this work. The crystal used for the main intensity measurement had a size of 0.20 x 0.275 x 0.05 mm, while the crystal

Table 24. Fractional Coordinates and Peak Heights of Central Hydrogen Atoms from Two Porphine Structure Analyses.

Atom	x[a]	y	z	Peak Height ($e\ A^{-3}$)	Present Work
H21	0.142	0.433	0.125	0.3	(negative)
H22	0.100 (0.118)[b]	0.433 (0.436)	-0.058 (-0.046)	0.4	(0.5)
H23	0.033	0.321	-0.058	0.3	(negative)
H24	0.067 (0.063)	0.308 (0.317)	0.108 (0.104)	0.4	(0.5)

[a]Coordinates x, z from W&F work are equivalent to z, x of this work.

[b]The numbers in the parentheses are obtained from this work.

used by W&F work was 0.36 x 0.36 x 0.20 mm (reported as 0.50 mm along the diagonal of one face). The latter is approximately eight times larger than the former. It is well known that secondary extinction effects are much more pronounced for larger crystals. Thus, strong low-order reflections can contribute to the large discrepancy between two sets of data due to extinction.

2) Counting Error

The counting error of 7% of intensity data (80 out of 1206 reflections) from this work was minimized by using ω (omega) step-scan measuring techniques. Thus the set of $|F_o|$'s of the present data is probably affected by more favorable counting statistics and this could contribute to the discrepancies with W&F data.

REFERENCES

REFERENCES

1. J. L. Hoard, J. Amer. Chem. Soc., 87, 2305 (1965).

2. E. B. Fleischer, Accounts of Chemical Research, 3, 105 (1970).

3. E. B. Fleischer, C. Miller, and L. E. Webb, J. Amer. Chem. Soc., 86, 2342 (1964).

4. E. B. Fleischer, J. Amer. Chem. Soc., 85, 146 (1963).

5. J. L. Hoard, G. H. Cohen, and M. D. Glick, J. Amer. Chem. Soc., 89, 1992 (1967).

6. R. C. Petterson, Acta. Cryst., B25, 2527 (1969).

7. R. Timkovich, and A. Tulinsky, J. Amer. Chem. Soc., 91, 4430 (1969)

8. W. E. Bennett, D. E. Broberg, and N. C. Baenziger, Inorg. Chem., in press.

9. E. B. Fleischer, and T. S. Srivastava, J. Amer. Chem. Soc., 91, 2403 (1969).

10. J. H. Hoard in "Structural Chemistry and Molecular Biology," A. Rich, and N. Davidson Ed., W. H. Freeman and Company, San Francisco, Calif., (1968), pp 573-594.

11. R. Countryman, D. M. Collins, and J. L. Hoard, J. Amer. Chem. Soc., 91, 5166 (1969).

12. P. A. Loach, and M. Calvin, Biochemistry, 2, 361 (1963).

13. P. A. Loach, and M. Calvin, Nature, 202, 343 (1964).

14. M. Calvin, Rev. Pure Appl. Chem., 15, 1 (1965).

15. L. J. Boucher, J. Amer. Chem. Soc., 90, 6640 (1968)

16. L. J. Boucher, and J. J. Katz, J. Amer. Chem. Soc., 89, 134 (1967).

17. D. Harker, J. Chem. Phys., 4, 381 (1936).

18. R. W. James, "The Optical Principles of the Diffraction of X-rays," Cornell University Press, New York (1965)

19. A. D. Adler, J. Inorg. Nucl. Chem., 32, 2443 (1970).

20. H. Lipson and W. Cochran, "The Determination of Crystal Structures," Cornell University Press, New York (1966), pp 73-76.

21. J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press, Long Island City, New York (1965), pp 133-139.

22. G. H. Stout, and L. H. Jensen, "X-ray Structure Determination," The Macmillan Company, New York (1968), pp 242.

23. W. R. Bushing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-squares Program," Report ORNL-TM-305, Oak Ridge, Tennessee (1962).

24. C. T. North, D. C. Phillips, and F. S. Mathews, Acta. Cryst., A24, 351 (1968).

25. D. J. Wehe, and W. R. Bushing, "A Fortran Program for Calculating Single Crystal Absorption Correction," Oak Ridge National Laboratory, Report ORNL-TM-229 (1962).

26. C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

27. L. H. Vogt, A. Zalkin, and D. H. Templeton, Inorg. Chem., 6, 1725 (1967).

28. L. E. Sulton, et al., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Burlington House, London (1965), pp 99.

29. A. J. C. Wilson, Structure Report, 16, 184 (1952).

30. Y. C. Tang, and J. H. Sturdivant, Acta. Cryst., 5, 74 (1952).

31. M. D. Glick, G. H. Cohen, and J. H. Hoard, J. Amer. Chem. Soc., 89, 1966 (1967).

32. G. D. Dorough, and K. T. Shen, J. Amer. Chem. Soc., 72, 3939 (1950).

33. J. Erdman, and A. H. Corwin, J. Amer. Chem. Soc., 68, 1885 (1946).

34. M. Gouterman, G. Wagniere, and L. C. Snyder, J. Mol. Spectroscopy, 11, 108 (1963).

35. J. Falk, and E. Willis, Austral. J. Sci. Res., 4, 579 (1951).

36. S. F. Mason, J. Chem. Soc., 976 (1958).

37. J. M. Robertson, J. Chem. Soc., 1195 (1936).

38. G. M. Badger, R. T. Harris, R. A. Jones, and J. Sasses, J. Chem. Soc., 4329 (1962).

39. E. D. Becker, R. B. Bradly, and C. J. Watson, J. Amer. Chem. Soc., 83, 3743 (1961).

40. S. Silvers, and A. Tulinsky, J. Amer. Chem. Soc., 89, 3331 (1967).

41. M. J. Hamor, T. A. Hamor, and J. L. Hoard, J. Amer. Chem. Soc., 86, 1938 (1964).

42. L. Webb, and E. Fleischer, J. Chem. Phys., 43, 3100 (1965).

43. T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Company, Milwaukee (1957).

44. H. W. Wyckoff, M. Doscher, D. Tsernoglou, T. Inagami, L. N. Johnson, K. D. Hardman, N. M. Allewell, D. M. Kelly, and F. M. Richards, J. Mol. Biol., 27, 563 (1967).

45. A. J. C. Wilson, Acta. Cryst., A23, 888 (1967).

46. W. Parrish, Phillips Technical Review, 17, 206 (1965).

47. E. W. Hughes, J. Amer. Chem. Soc., 63, 1737 (1941).

48. U. W. Arndt, and B. T. Willis, "Single Crystal Diffractometry," University Press, Cambridge (1966), pp 15-30, 234-236.

49. M. J. Buerger, "Crystal-Structure Analysis," John Wiley & Sons, Inc., New York (1960).

50. C. G. Darwin, Phil. Mag., 43, 800 (1922).

51. V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, Acta. Cryst., 12, 600 (1959).

52. D. W. J. Cruickshank, Acta. Cryst., 2, 65 (1949).

53. D. W. J. Cruickshank, and A. Robertson, Acta. Cryst., 6, 198 (1953).

54. International Tables for X-ray Crystallography (1962), Vol. III, pp 202-207. Birmingham: Kynoch Press.

APPENDICES

APPENDIX 1

GENERAL REVIEW OF X-RAY DIFFRACTION[48,49]

1. Bragg's Law and its Application

Diffraction, considered as the reflection of X-rays from planes ($hk\ell$) of a crystal lattice, can be expressed in a simple form

$$2\, d(hk\ell) \sin\theta = n\lambda$$

where h, k, ℓ, and n are integers, θ is the angle at which the incident and reflected beam intersect the planes ($hk\ell$) and $d(hk\ell)$ is the spacing of lattice planes which are parallel and intersect the unit cell edges $\vec{a}$, $\vec{b}$, $\vec{c}$, at $n(a/h)$, $n(b/k)$, and $n(c/\ell)$. Mathematically, these conditions can lead to equations with different forms. The most common expression is in terms of the reciprocal lattice with corresponding reciprocal cell parameters a*, b*, and c*. The parameters, a*, b*, and c* can be considered as vectors with the following properties

$$\vec{a}^* \cdot \vec{a} = \vec{b} \cdot \vec{b}^* = \vec{c}^* \cdot \vec{c} = 1$$

and

$$\vec{a}^* \cdot \vec{b} = \vec{a}^* \cdot \vec{c} = \vec{b}^* \cdot \vec{c} = \vec{b}^* \cdot \vec{a} = \vec{c}^* \cdot \vec{a} = \vec{c}^* \cdot \vec{b} = 0$$

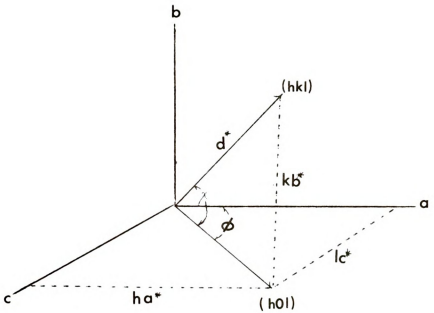
Consider, in the reciprocal lattice, a vector $\vec{r}$ = $h\vec{a}^* + k\vec{b}^* + \ell\vec{c}^*$ constructed between the lattice point $hk\ell$ and the origin, with a magnitude of $1/d(hk\ell)$, and perpendicular to the lattice plane $hk\ell$ in direct space. The reciprocal lattice vector $\vec{r}$ can then be interpreted in terms of certain angular settings by the use of polar coordinates. An example based on the orthorhombic crystal system is shown in Figure 31.

2. Mosaic Crystal

Most crystals possess irregulatities in their atomic arrangement, in the form of dislocations, point defects, and the like. These irregularities tend to destroy the coherence between the components of the incident beam scattered by different parts of the crystal. The crystal can be divided, effectively, into small regions, about 10,000 Å across, which are sufficiently perfect to reflect the X-ray beam coherently, but between which there is loss of coherence. These perfect regions are known as "mosaic block". A crystal possessing mosaic blocks is known as a mosaic crystal.

3. Integrated Intensity

When a crystal is rotated with uniform angular velocity, ω_v, through the $hk\ell$ plane in an incident X-ray beam whose uniform intensity is I_0, the integrated intensity, I, of the diffracted beam, whose total energy is E_0, can be



$$d^* = \left((h a^*)^2 + (k b^*)^2 + (l c^*)^2\right)^{1/2}$$

$$\sin\chi = k b^* / d^*$$

$$2\theta = 2 \sin^{-1} (\lambda / 2d)$$

$$\tan\phi = l c^* / h a^*$$

$$a^* = 1 / a$$

$$b^* = 1 / b$$

$$c^* = 1 / c$$

Figure 31. Polar coordinates of a reciprocal lattice point (hkℓ) for orthorhombic crystal system.

expressed as

$$I = \frac{E_0 \, (1)_V}{I_0} \quad .$$

The integrated intensity should be corrected for effects of systematic errors. These types of errors generally arise from absorption and extinction effects and if they are significant, affect the precision of the structure determination.

4. Absorption

The absorption of the incident X-ray beam is dependent on the length of the path of the X-ray beam through the crystal. As a result, in a typical, nonspherical, crystal, the amount of absorption is a function of the angular orientation. The absorption correction procedure for a single crystal may be simplified by grinding the crystal into the shape of a sphere to make the X-ray path through the crystal equal in all directions. However, this grinding process is only applicable for those crystals, which neither fragment nor cleave during shaping.

An absorption correction procedure has been suggested by Furnas (1957)[43] for the unshaped crystal. The method makes use of the fact that the azimuthal angle, Φ , of some reflection planes can be changed without destroying the Bragg reflecting conditions. To apply this method to the ClMnTPP crystal, whose unique b axis was at $\chi = 90^0$,

the (0k0) reflections were chosen for the absorption measurement because diffraction from these planes is independent of the azimuthal setting. The variation of the intensity of an axial reflection with respect to Φ at $\chi = 90^0$ will be an indication of the absorption of X-rays as a function of crystal orientation.

The intensities of the (0k0) reflections of the ClMnTPP crystal were measured in increments of 10^0 over the Φ range in which the X-ray intensity data were taken. The absorption factor, by which each reflection, $hk\ell$, was multiplied depending upon its Φ value, was

$$A_k(\Phi) = I_{max} (\Phi_0)/I(\Phi)$$

and can be obtained by plotting the quantities $A_k(\Phi)$ as a function of the Φ angle. For the ClMnTPP crystal the maximum absorption factor from each absorption curve was observed to be linearly dependent on the 2θ angle (Fig. 32). The absorption for each independent reflection was then computed as a function of its Φ angle and its scattering angle, 2θ.

Other ways to correct for absorption include the method of Bushing and Wehe (1962)[25] of absorption factor based on the shape of the crystal and the semi-empirical method developed by Phillips et al.,[24] and have been discussed in Part I.

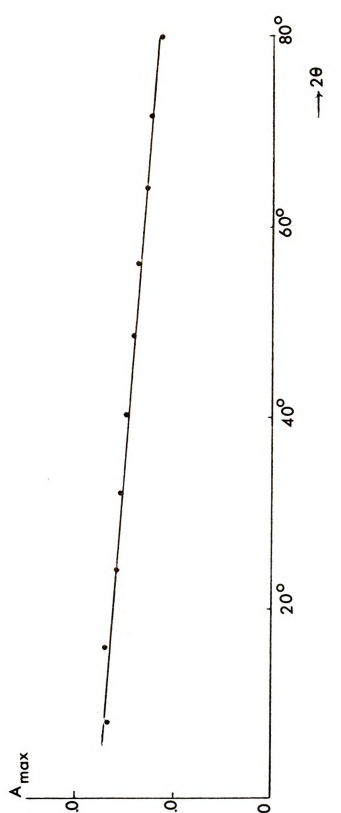


Figure 32. Maximum absorption factors vs 2θ.

5. Extinction

The effect of absorption is to attenuate the X-ray beam as it passes through the crystal. An additional attenuating effect is extinction which is known to be of two different kinds, classified as primary and secondary extinction.

Primary extinction relates to an interference process which reduces the intensity of a beam as it passes through a crystal. Given a set of planes in the position to reflect the incident beam, the reflected beam can be at the proper angle for further reflection by another set of planes (second time or more). Thus, this interference effect will cause part of reflected beam to be out of phase and decrease its intensity. The primary extinction effects are more serious in perfect crystals than in mosaic crystals In the latter case, the perfect planes cannot extend over appreciable ranges for multiple reflections with the mosaic blocks.

Secondary extinction is commonly encountered in single crystal work and its effect can be very serious for structure refinement. For a given set of planes at the reflecting position, the deeper planes will receive less incident intensity and therefore reflect less power than the upper planes. This interference effect is usually more pronounced for reflections at low sin θ/λ values and a correction can be made for it. Methods for correcting for

secondary extinction are: (1) an empirical method derived by Darwin (1922),[50] (2) the use of a small crystal to re-measure those reflections which are most seriously affected by extinction, and (3) quenching the crystal in liquid nitrogen to break up the mosaic blocks into even smaller blocks.

6. Conversion of Intensities to Structure Amplitudes

The structure amplitude of a reflection is related to the intensity as

$$|F(hk\ell)| = \sqrt{\frac{KI(hk\ell)}{LP}}, \text{ where } \quad L = 1/\sin 2\theta, \quad P = (1 + \cos^2 2\theta)/2,$$

and K is a constant which depends on the crystal size, incident beam intensity and a number of other fundamental constants. The polarization factor, P, arises because the degree of polarization of the X-ray beam varies with the reflection angle. The Lorentz factor, L, arises because the time required for a reciprocal lattice point to pass through the sphere of reflection varies both with its position in reciprocal space and the direction in which it approaches the reflecting sphere.

7. Diffractometer

In a four-circle diffractometer the crystal has three rotational degrees of freedom, a number sufficient to give any vector, any arbitrary orientation in space referred to

axes in the crystal. The three circles (see Figure 33) are the ω-circle, the χ-circle which is carried on the ω-circle and whose axis is normal to the ω-axis, and the Φ-circle which is mounted on the χ-circle and carries the goniometer head supporting the crystal.

The X-ray source is set in a fixed position with respect to the crystal orienter and the detector is mounted on the 2θ circle. The angle between the detector and the direct beam can be set to any desired value within the range of the instrument.

In addition to the four-circle elements described, the diffractometer includes a regulated power supply for the X-ray tube, scalers for counting the pulses produced by the detector, a rate meter for displaying on a chart recorder the rate at which pulses are being received, and a pulse-height analyzer for discriminating against pulses which are either much weaker or much stronger than those expected for the characteristic energy being used.

8. Unwanted X-ray Radiation

The radiation emitted from an X-ray tube is not monochromatic. The desired $k\alpha$ radiation is always accompanied by a $K\beta$ component of somewhat shorter wavelength and both $K\alpha$ and $K\beta$ are superposed on the background. Unwanted radiation can be removed by use of balanced filters which are made with a pair of metallic foils, one foil of which

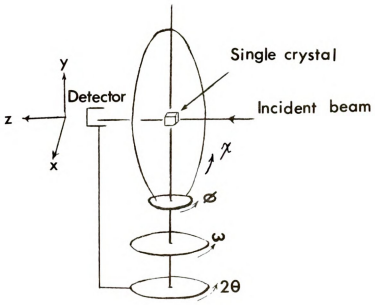


Figure 33. Schematic representation of a four-circle diffractometer.

has an absorption edge just covering the $K\alpha$ radiation and the other an edge covering $K\beta$. The intensity of each reflection is measured once with each filter, and the difference is taken to be the intensity.

APPENDIX 2

1. Observed and Calculated Structure Amplitudes of ClMnTPP.

2. Observed and Calculated Structure Amplitudes of Porphine.

1. Observed and Calculated Structure Amplitudes of ClMnTPP

H	K	L	Y(OBS)	Y(CALC)
0	2	0	53,2340	56.3110
0	4	0	130,1040	120.2495
0	6	0	31,7360	32.6717
0	8	0	37,6000	35.2419
0	10	0	18,0270	17.1564
0	12	0	25,4830	23.6723
0	14	0	33,6950	34.1770
0	16	0	13,5340	12.8343
0	18	0	9,4790	8.9222
0	20	0	17,9250	17.5340
1	0	0	149,3140	196.5233-
1	1	0	12,4790	7.8388
1	2	0	41,0110	39.9819
1	3	0	4,6060	10.5917
1	4	0	22,6150	21.4906
1	5	0	76,0900	77.3227
1	6	0	73,6010	78.7968
1	7	0	11,2150	8.2221
1	8	0	50,4190	55.6604
1	10	0	7,7500	5.5246
1	11	0	3,6350	3.4594
1	12	0	6,7500	1.4790
1	13	0	10,5040	11.1471
1	14	0	39,6620	43.2462
1	15	0	4,7170	4.0267
1	16	0	25,5610	26.8027
1	17	0	19,0860	19.4436
1	18	0	37,9410	40.1784
1	19	0	13,0800	14.3133
1	20	0	16,5620	17.4439
2	0	0	107,7700	104.4572
2	1	0	10,8960	.9933
2	2	0	10,2410	4.7202
2	3	0	26,2360	18.8120
2	4	0	119,2060	116.4816
2	5	0	26,4640	29.2104
2	6	0	32,9730	37.6495
2	7	0	31,3250	28.1222
2	8	0	24,6240	26.5711
2	9	0	59,8750	59.7010
2	10	0	67,3060	68.8391
2	11	0	16,2680	17.1035
2	12	0	12,5120	14.8406
2	13	0	24,0130	23.7006
2	14	0	15,7240	16.1641
2	15	0	15,3560	16.7933
2	16	0	33,2020	31.9172
2	17	0	24,8020	22.2601
2	18	0	12,2690	11.4807
2	19	0	20,1360	20.4308
2	20	0	12,3170	12.0302
3	0	0	78,9200	82.6974
3	1	0	59,3280	52.6068
3	2	0	14,9230	14.5584
3	3	0	68,4270	61.6408
3	4	0	49,7190	53.8431
3	5	0	27,9210	23.6820
3	6	0	42,2780	40.7368
3	7	0	21,7650	20.1510
3	8	0	44,6200	47.5247
3	10	0	23,7870	22.9896
3	11	0	3,9810	2.6680
3	12	0	56,4680	58.2627
3	13	0	4,0370	3.4447
3	14	0	20,5680	19.8104
3	15	0	7,5980	6.4726
3	16	0	30,1140	30.6687
3	17	0	19,8830	20.4997
3	18	0	7,2850	6.9100
3	19	0	17,2880	16.9934
3	20	0	13,8780	13.4715
4	0	0	46,0440	43.7749
4	1	0	15,8520	17.4170
4	2	0	11,2620	9.9487
4	3	0	25,6950	26.8745
4	4	0	49,8440	47.7999
4	5	0	59,9790	58.8293
4	6	0	53,7360	52.5064
4	7	0	29,8660	28.8069
4	8	0	46,9580	50.5250
4	9	0	7,9260	5.7344
4	10	0	5,8110	7.2306
4	11	0	4,2870	4.5550
4	12	0	34,5890	37.8768
4	13	0	18,7980	18.9526
4	14	0	29,9010	30.3858
4	15	0	12,6390	11.1569
4	16	0	29,1800	29.5400
4	17	0	4,9430	3.4461
4	18	0	17,6540	18.2089
5	0	0	5,5170	7.2638
5	1	0	3,5830	2.1359
5	2	0	4,9290	4.5741
5	3	0	17,4410	18.2943
5	4	0	43,6090	45.5698
5	5	0	6,6250	6.0547
5	6	0	36,5280	34.6746
5	7	0	65,6440	63.0242
5	8	0	40,5840	39.9252
5	10	0	13,0470	12.7200
5	11	0	25,5240	25.6025
5	12	0	13,4840	14.6386
5	13	0	23,6460	23.1611
5	14	0	17,6990	16.0218
5	15	0	5,1170	3.2502
5	16	0	23,1370	21.1860
5	17	0	9,1740	8.3203
5	18	0	6,5440	6.3830

H	K	L	Y(OBS)	Y(CALC)
6	0	0	19,2260	21.6164
6	1	0	10,3400	10.2534
6	2	0	4,6920	6.0085
6	3	0	13,1740	14.8322
6	4	0	26,9520	28.3316
6	6	0	6,2990	3.7147
6	7	0	32,6190	33.6626
6	8	0	23,6830	24.3326
6	9	0	19,9530	19.3246
6	10	0	18,7130	19.2887
6	11	0	30,6870	32.7722
6	12	0	10,3350	11.4620
6	13	0	20,7370	22.4916
6	14	0	20,7150	20.7575
6	15	0	26,0760	29.2340
6	16	0	8,1590	9.7152
6	17	0	21,2210	23.3972
7	0	0	66,5120	69.3819
7	1	0	14,8760	13.5398
7	2	0	13,2580	11.7953
7	3	0	24,6660	24.3417
7	4	0	29,1290	30.6347
7	5	0	5,8640	4.6180
7	6	0	21,5720	21.7052
7	7	0	28,2990	30.0566
7	8	0	4,4710	5.2272
7	9	0	7,7370	8.7541
7	10	0	5,0760	4.3433
7	11	0	18,6940	20.6812
7	14	0	16,1930	16.4965
7	15	0	21,2500	22.1430
8	0	0	28,3370	26.5513
8	1	0	21,9010	21.8976
8	2	0	24,0860	23.1037
8	3	0	33,9940	32.7444
8	5	0	8,1300	7.6621
8	6	0	23,2700	22.8893
8	7	0	4,9290	1.5051
8	9	0	10,5230	9.0922
8	10	0	20,9690	22.1604
8	11	0	5,0420	3.2733
8	13	0	18,6430	19.5771
9	0	0	47,8830	50.4912
9	1	0	22,7620	22.9068
9	2	0	19,6390	19.5181
9	3	0	34,6470	33.5554
9	4	0	9,8780	8.4075
9	5	0	23,2840	21.8667
9	6	0	12,9180	12.9859
9	7	0	14,5770	13.5723
9	8	0	15,0510	15.9771
9	9	0	17,3720	16.6290
10	0	0	14,7950	14.3995
10	1	0	19,9130	19.1066
10	2	0	17,6830	15.7717
10	3	0	16,7070	16.0620
0	1	1	105,6390	147.2905
0	2	1	63,5960	66.8647
0	3	1	47,0530	66.5157
0	4	1	65,6070	63.5224
0	5	1	36,5430	26.8660
0	6	1	11,5690	5.7835
0	7	1	6,0760	9.2154
0	8	1	4,3510	4.8976
0	9	1	55,2670	55.9235
0	10	1	49,4910	48.9007
0	11	1	5,4160	3.8312
0	12	1	21,6310	18.4947
0	13	1	19,4840	20.5957
0	14	1	6,0210	5.8575
0	15	1	10,0860	9.4441
0	16	1	35,7650	40.5696
0	17	1	18,0300	18.6977
0	20	1	24,1380	21.3016
0	21	1	15,3430	15.5553
1	1	1	26,7920	42.4992
-1	1	1	92,6460	88.7701
1	2	1	31,7670	30.7397
-1	2	1	44,7740	29.6803
1	3	1	81,8180	89.7151
-1	3	1	6,1370	10.5479
1	4	1	94,2270	88.2246
-1	4	1	36,5870	36.0009
1	5	1	47,3010	44.3957
-1	5	1	19,6580	20.3065
1	6	1	65,6890	67.4167
-1	6	1	35,5890	34.0170
1	7	1	33,1670	28.3427
-1	7	1	52,3260	46.9551
1	8	1	14,6000	14.1494
-1	8	1	38,5660	40.4014
1	9	1	47,0790	50.7068
-1	9	1	19,0140	21.6492
1	10	1	26,4710	26.3990
-1	10	1	13,9660	14.8707
-1	11	1	27,2140	25.1728
1	11	1	28,3480	28.1950
1	12	1	8,7300	9.0001
-1	12	1	14,9080	14.4835
1	13	1	20,5700	21.7532
-1	13	1	24,1290	26.9815
1	15	1	14,7660	12.5138
-1	15	1	41,6570	40.3790
1	16	1	42,9390	44.9120
-1	16	1	40,7620	44.4559
1	17	1	43,3230	44.9625
-1	17	1	23,0750	23.7120
1	18	1	17,2880	17.5096

H	K	L	Y(OBS)	Y(CALC)
-1	18	1	20,2920	20.8551
1	19	1	17,5650	19.5783
-1	19	1	15,5330	18.1259
1	20	1	30,9990	30.7768
-1	20	1	35,5090	27.4473
1	21	1	19,7470	16.7714
-1	21	1	31,2140	25.6886
2	1	1	102,3610	94.3300
-2	1	1	39,2260	46.8235
2	2	1	62,0730	57.5733
-2	2	1	14,6360	2.1821
2	3	1	50,5980	44.5309
-2	3	1	50,9280	56.3045
2	4	1	11,6000	10.7461
-2	4	1	61,2770	60.0318
2	5	1	28,5580	31.3168
-2	5	1	43,1010	42.3206
2	6	1	67,9950	66.7649
-2	6	1	6,7290	7.4433
2	7	1	7,4510	8.3413
-2	7	1	4,6980	5.4706
2	8	1	4,5810	2.3364
-2	8	1	30,3850	29.3147
2	9	1	94,0830	97.3954
-2	9	1	18,7950	18.9153
2	10	1	41,9950	41.3669
-2	10	1	49,7710	46.6640
-2	11	1	9,0210	8.5945
2	12	1	6,6440	9.1019
-2	12	1	8,7970	8.0093
2	13	1	22,2760	24.3790
-2	13	1	30,5470	32.3361
2	14	1	4,7220	3.0916
-2	14	1	4,9710	3.9960
2	15	1	29,0440	29.4703
-2	15	1	29,9290	30.1791
2	16	1	24,0330	23.9404
-2	16	1	14,8680	15.6458
2	17	1	6,4350	7.3430
-2	17	1	21,2910	22.9529
-2	18	1	21,9770	25.3015
-2	19	1	26,4900	30.7241
2	20	1	33,8440	31.5129
-2	20	1	40,5580	35.6039
-2	21	1	21,1700	19.6416
3	1	1	15,1990	14.7462
-3	1	1	31,7210	32.4492
3	2	1	5,5350	2.5424
-3	2	1	22,9020	13.5553
3	3	1	5,9160	3.2817
-3	3	1	60,0590	60.5834
3	4	1	19,6870	19.5120
-3	4	1	59,7670	60.2780
3	5	1	51,2980	50.0091
-3	5	1	42,9300	46.0205
3	6	1	30,6710	32.2409
-3	6	1	11,9810	8.4953
3	7	1	35,5240	30.1562
-3	7	1	37,9730	36.4660
3	8	1	53,3000	51.7200
-3	8	1	26,3070	28.1140
3	9	1	50,7640	48.1251
-3	9	1	64,4930	65.9881
3	10	1	16,0090	18.7692
-3	10	1	4,3190	3.7705
3	11	1	24,7580	22.0747
3	12	1	37,3300	38.2157
-3	12	1	6,7490	6.7748
3	13	1	38,5870	37.3061
-3	13	1	29,1910	31.1202
3	14	1	29,8040	31.1373
-3	14	1	8,1350	7.9862
3	15	1	19,2470	19.6411
-3	15	1	18,1240	18.4950
3	16	1	11,8550	13.2628
-3	16	1	15,1390	14.2737
3	17	1	5,1370	2.8009
-3	17	1	5,6990	3.2803
-3	18	1	10,9390	10.2288
3	19	1	12,6280	12.5500
-3	19	1	4,9430	5.2061
3	20	1	25,9480	25.4421
4	1	1	11,9960	12.6599
-4	1	1	13,1750	14.1261
4	2	1	18,6420	19.5643
-4	2	1	22,9780	19.9248
-4	3	1	29,1060	23.3439
4	4	1	8,4560	6.2458
-4	4	1	58,6280	56.6729
4	5	1	57,7660	51.7489
-4	5	1	55,9950	53.1056
4	6	1	50,5830	51.4999
-4	6	1	8,4320	7.3437
4	7	1	29,2430	29.2442
-4	7	1	4,4120	3.9048
4	8	1	50,4990	50.4698
-4	8	1	22,6550	21.3501
4	9	1	7,7170	5.9575
-4	9	1	59,5630	62.2216
4	10	1	40,0370	38.9390
-4	10	1	51,8690	50.3080
-4	11	1	11,6330	9.6375
4	12	1	29,9290	31.5675
4	13	1	24,7780	24.5068
-4	13	1	54,1100	57.0271
4	14	1	20,6720	20.6633
-4	14	1	14,0120	12.1992
4	15	1	7,1520	8.1620

H	K	L	Y(OBS)	Y(CALC)
-4	15	1	5,9860	5.9357
-4	16	1	10,9810	11.4714
-4	17	1	14,1290	12.7570
-4	18	1	6,3770	4.7393
4	19	1	5,4430	4.3305
-4	19	1	6,6770	5.4011
5	1	1	30,6490	29.9751
-5	1	1	16,3120	13.7325
5	2	1	10,6700	5.4219
-5	2	1	3,9390	2.8323
-5	3	1	37,4960	37.5999
5	3	1	5,9090	6.1196
5	4	1	3,6250	2.3771
-5	4	1	30,4140	28.6720
5	5	1	8,6300	9.6803
-5	5	1	77,7940	77.6685
5	6	1	32,3510	33.1159
-5	6	1	4,5450	4.9742
5	7	1	17,7450	16.5887
-5	7	1	6,8180	3.3755
5	8	1	42,6740	42.6694
-5	8	1	6,4510	6.0711
5	9	1	11,3640	11.3964
-5	9	1	34,6490	38.4150
5	10	1	44,3600	45.8752
5	11	1	12,1770	12.6113
5	12	1	18,2930	21.1502
-5	12	1	9,9060	9.4246
5	13	1	9,8310	10.9137
-5	13	1	43,0370	44.5357
5	14	1	6,5690	6.8227
-5	14	1	11,2520	13.0338
5	15	1	4,9530	3.4781
-5	15	1	17,1420	17.2491
5	16	1	17,0180	18.2167
-5	16	1	14,4410	14.7149
5	17	1	6,9960	8.0257
-5	19	1	5,1390	5.4211
6	1	1	4,5800	4.6183
-6	1	1	28,6680	25.7424
6	2	1	21,1580	23.0723
-6	2	1	17,3820	15.5622
6	3	1	22,5180	21.4733
-6	3	1	32,8270	29.8279
6	4	1	19,0530	18.5141
-6	4	1	27,0680	25.0292
6	5	1	20,1430	19.6889
-6	5	1	60,9060	59.4768
6	6	1	29,3140	29.8831
-6	6	1	31,9990	29.8497
6	7	1	19,9330	20.0867
-6	7	1	8,5590	7.2165
6	8	1	5,8600	4.7690
-6	8	1	6,1530	3.5447
6	9	1	16,9630	16.9602
-6	9	1	50,6210	50.5176
6	10	1	16,4460	16.6572
-6	10	1	34,6500	32.5742
6	11	1	16,9300	16.9052
-6	11	1	11,0850	11.0042
6	12	1	14,6240	16.3758
-6	12	1	12,6920	11.9816
-6	13	1	33,0300	31.7637
6	14	1	30,8030	32.7126
-6	14	1	8,1490	9.1494
6	15	1	9,4240	10.3687
-6	15	1	8,6620	7.4587
6	16	1	27,6290	30.8070
-6	16	1	8,6580	8.3171
-6	17	1	11,7590	11.1686
-6	18	1	20,1180	20.1510
7	1	1	24,4100	26.0358
-7	1	1	16,6840	15.9683
7	2	1	60,2780	59.9341
-7	2	1	6,9430	5.9373
7	3	1	22,2750	21.3834
-7	3	1	10,2240	8.8769
7	4	1	19,9730	20.1160
-7	4	1	4,6650	2.2301
7	5	1	14,4650	14.0546
-7	5	1	22,2370	22.3342
7	6	1	20,8740	19.1787
-7	6	1	10,4400	10.3973
7	7	1	15,9980	16.0105
7	8	1	12,6850	13.4150
7	9	1	19,2210	20.4034
-7	9	1	45,5100	44.5774
7	10	1	17,6270	19.4590
-7	10	1	18,2970	18.6999
7	11	1	6,9830	7.5726
-7	11	1	6,3440	7.4787
7	12	1	16,4260	16.3687
-7	12	1	14,4970	14.5934
-7	13	1	27,9990	28.2041
-7	14	1	14,8640	15.0083
8	1	1	17,8460	17.2324
-8	1	1	44,0660	41.3326
8	2	1	29,4230	28.7435
8	3	1	8,9750	8.9547
8	4	1	10,1170	11.1522
-8	4	1	25,9570	26.0033
8	5	1	16,2960	17.4116
-8	5	1	29,9410	28.6675
8	6	1	15,5980	15.8256
8	7	1	6,9570	7.3727
-8	7	1	3,7550	3.2488
8	8	1	9,8320	9.7045
-8	8	1	33,8270	33.7108

H	K	L	Y(OBS)	Y(CALC)
8	9	1	7,6600	8.0671
-8	9	1	6,6800	8.9385
8	10	1	15,0300	14.2518
-8	10	1	8,6490	7.6393
8	11	1	5,2050	5.1625
-8	11	1	8,2910	9.5356
-8	12	1	15,4220	15.8202
-8	13	1	14,6330	13.3461
-8	14	1	21,2120	21.5367
-9	1	1	22,7270	24.8260
9	2	1	32,4090	31.7402
-9	3	1	20,7150	21.1640
9	3	1	10,7120	10.2481
-9	4	1	6,6830	5.5787
9	4	1	20,5280	19.3800
-9	5	1	6,0050	5.3689
9	5	1	10,8090	10.4710
-9	6	1	26,0280	23.9412
9	6	1	21,0620	21.2718
-9	9	1	5,8400	4.6385
-9	10	1	35,1490	34.7289
-9	12	1	4,7330	2.6648
-10	1	1	15,3140	15.3148
-10	1	1	15,3140	15.3148
-10	2	1	14,6230	12.9829
-10	4	1	1,5460	1.3867
-10	5	1	5,9760	6.6539
-10	6	1	6,7720	5.6481
0	0	2	60,1130	47.8029
0	1	2	5,4340	.7990
0	2	2	90,3750	91.6340
0	3	2	67,9270	90.2832
0	4	2	32,9760	23.4511
0	5	2	13,1350	8.3853
0	6	2	22,5260	28.3948
0	7	2	48,9830	53.2139
0	8	2	50,1950	50.6316
0	9	2	15,1980	15.6840
0	10	2	12,6250	8.9712
0	11	2	22,9700	25.8837
0	12	2	19,0330	22.1346
0	13	2	7,8020	9.0874
0	15	2	9,1730	9.3218
0	16	2	20,0980	20.2406
0	17	2	9,8940	10.4880
0	19	2	12,1890	11.7603
0	20	2	9,8610	6.9660
0	21	2	8,0810	7.4193
1	0	2	78,9570	66.3902
-1	0	2	103,1690	145.9540
1	1	2	10,6360	14.6812
-1	1	2	66,8260	91.1437
1	2	2	42,6770	40.7672
-1	2	2	37,7070	38.0113
1	3	2	37,6330	34.0777
-1	3	2	14,0550	19.0824
1	4	2	24,7290	29.4987
-1	4	2	47,5490	35.2697
1	5	2	58,2040	48.9027
-1	5	2	67,8200	95.2557
-1	6	2	97,1670	99.5930
1	6	2	51,0640	50.7240
1	7	2	51,0010	50.4863
-1	7	2	6,1560	2.1891
1	8	2	4,3800	5.3079
-1	8	2	15,1870	14.8467
1	9	2	23,5330	24.0956
-1	9	2	16,0620	16.8828
1	10	2	10,3660	10.8601
-1	10	2	58,3790	55.0354
1	11	2	53,3330	54.1070
-1	11	2	16,3700	17.6486
1	12	2	13,4800	11.7274
-1	12	2	16,1290	17.5223
1	13	2	37,6300	40.3077
-1	13	2	12,8960	12.7016
1	14	2	19,2880	19.4999
-1	14	2	8,1070	6.6677
1	15	2	24,8010	25.9915
-1	15	2	40,4350	41.5891
1	16	2	16,4070	18.3593
-1	16	2	16,8180	18.7675
-1	17	2	22,2470	21.7689
1	18	2	16,5180	16.7837
-1	18	2	13,1260	13.1514
1	19	2	10,3550	12.0973
-1	19	2	19,5780	21.3171
-1	20	2	14,0090	12.5689
2	0	2	76,0620	70.5225
-2	0	2	12,5390	5.9659
2	1	2	35,5420	34.4018
-2	1	2	10,7550	4.2638
2	2	2	24,8160	21.7464
-2	2	2	24,6490	27.2518
2	3	2	7,0340	4.0552
-2	3	2	8,3960	3.6649
2	4	2	12,8930	7.7834
-2	4	2	13,1550	13.6457
2	5	2	22,0870	21.3752
-2	5	2	5,8890	2.7151
2	6	2	21,0130	19.3047
-2	6	2	7,7230	6.5724
2	7	2	94,1910	100.4506
-2	7	2	8,0980	1.6243
2	8	2	3,9930	3.9061
-2	8	2	33,1810	37.3239
2	9	2	7,6220	7.3392
-2	9	2	4,4350	.5838

H	K	L	Y(OBS)	Y(CALC)
2	10	2	6,1470	7.1284
-2	10	2	16,9190	15.2979
2	11	2	53,6780	55.5261
-2	11	2	13,6130	10.6186
2	12	2	3,9460	2.7388
-2	12	2	24,4600	24.9262
2	13	2	10,9350	11.6342
-2	13	2	14,0950	13.5264
2	14	2	20,6560	20.1893
-2	14	2	43,0740	42.1223
2	15	2	6,7610	6.4416
-2	15	2	36,7250	35.1317
2	16	2	22,2840	21.7334
2	17	2	7,0440	7.8674
-2	17	2	13,5260	14.1843
-2	18	2	26,7980	27.7361
2	19	2	23,9490	25.3682
-2	19	2	53,1060	54.6056
2	20	2	12,4920	12.3586
-2	21	2	9,1230	8.4389
3	0	2	23,9400	25.5071
-3	0	2	15,8600	11.4063
3	1	2	16,2850	13.6976
-3	1	2	61,6870	48.6752
3	2	2	4,8720	3.7639
-3	2	2	38,9460	39.6425
3	3	2	50,6340	48.3187
-3	3	2	80,0430	72.8254
3	4	2	18,7300	16.7278
-3	4	2	62,9230	65.1872
3	5	2	5,5470	4.6993
-3	5	2	39,9960	43.6567
3	6	2	4,6650	2.9992
-3	6	2	12,2090	10.3155
3	7	2	52,9270	54.7035
-3	7	2	24,5780	23.0233
3	8	2	4,5000	3.5261
-3	8	2	35,9370	38.7660
3	9	2	8,1810	6.6658
-3	9	2	9,1460	8.2811
3	10	2	10,7480	8.3739
-3	10	2	14,5100	14.1311
3	11	2	64,2000	64.3606
-3	11	2	28,4560	29.2030
3	12	2	10,8440	9.6426
-3	12	2	20,1320	20.1492
3	13	2	4,9870	4.0472
-3	13	2	6,2790	4.9035
3	14	2	7,5050	5.5087
-3	14	2	24,4780	24.8723
3	15	2	6,7630	6.1230
-3	15	2	37,3390	38.6385
3	16	2	18,7470	20.5160
3	17	2	10,5790	9.6936
-3	17	2	6,1910	8.6908
3	18	2	5,2470	4.0390
-3	18	2	24,0930	24.2793
3	19	2	14,0450	12.0866
-3	19	2	25,0360	27.7254
-3	20	2	19,0300	15.3541
-3	21	2	21,7220	20.3130
-4	0	2	94,3740	97.9732
4	1	2	9,1590	8.7239
-4	1	2	26,5260	27.6662
4	2	2	5,3570	4.2933
-4	2	2	18,7990	15.7066
4	3	2	34,1980	32.7965
-4	3	2	20,6350	21.0574
4	4	2	7,7750	6.7761
-4	4	2	57,3540	61.2311
4	5	2	8,4980	8.2531
-4	5	2	34,1720	34.4424
4	6	2	22,5800	21.1333
-4	6	2	3,2520	4.7757
4	7	2	21,7910	21.3068
-4	7	2	55,5870	59.1871
-4	8	2	39,2590	36.7950
4	9	2	15,6000	16.6353
-4	9	2	41,4080	37.4663
4	10	2	24,8630	22.6810
-4	10	2	38,2590	39.2759
4	11	2	35,6440	36.1175
-4	11	2	30,0170	30.6208
4	12	2	22,2330	22.8058
-4	12	2	9,4270	8.0896
-4	13	2	5,9690	5.2881
-4	14	2	32,9090	34.1364
4	15	2	6,2230	3.0761
-4	15	2	14,9880	13.7044
4	16	2	14,9670	15.0193
-4	17	2	5,5740	4.7706
-4	18	2	13,6600	14.1224
-4	19	2	7,7850	6.0801
-4	20	2	16,1600	15.6642
-5	0	2	107,0110	114.4046
5	1	2	27,7750	30.3302
-5	1	2	29,2320	25.7782
5	2	2	14,9410	13.5166
-5	2	2	9,0940	7.9288
5	3	2	33,1550	32.3350
-5	3	2	13,6440	11.6404
5	4	2	21,2800	19.5566
-5	4	2	65,7610	69.2902
5	5	2	20,4780	21.2715
-5	6	2	8,1800	4.6460
5	7	2	43,1730	43.4950
-5	7	2	43,4120	43.3810
5	8	2	16,0110	15.2571

H	K	L	Y(OBS)	Y(CALC)
-5	8	2	43,5020	43.4647
5	9	2	14,0600	13.4725
-5	9	2	26,1080	27.9544
-5	10	2	5,1140	4.0406
5	11	2	11,6550	9.2846
-5	11	2	22,9510	24.1741
5	12	2	14,7720	14.4541
-5	12	2	18,1940	17.2292
5	13	2	12,2920	13.9978
5	14	2	8,6790	7.0760
-5	14	2	30,9460	30.8546
5	15	2	17,3640	14.5339
5	16	2	8,6950	9.6919
-5	16	2	14,1840	11.9851
-5	17	2	6,2130	6.8636
-5	18	2	6,7170	.8534
-5	19	2	5,1760	4.5926
-6	0	2	38,9010	29.4729
6	1	2	28,1910	27.9386
-6	1	2	54,5940	53.5214
-6	2	2	7,0680	7.0101
6	3	2	15,5850	14.5196
-6	3	2	44,2490	39.8703
6	4	2	13,9270	13.2428
-6	4	2	28,2010	31.7090
6	5	2	29,1980	30.7329
-6	5	2	16,5370	15.1667
6	6	2	5,6630	5.3245
-6	6	2	29,4620	25.3814
6	7	2	14,8480	15.5378
-6	7	2	37,7520	37.5006
6	8	2	6,9730	6.2453
-6	8	2	38,6640	39.9529
-6	9	2	5,7410	3.7844
6	10	2	6,9830	7.2105
-6	10	2	10,6090	12.7321
6	11	2	7,6790	4.9653
-6	11	2	27,9010	26.6254
6	12	2	7,1970	8.2028
-6	12	2	23,1800	23.3914
6	13	2	6,2590	8.2427
-6	13	2	12,7920	11.7649
6	14	2	11,8270	12.7981
-6	14	2	35,4590	35.5245
-6	15	2	5,8160	5.8680
-6	16	2	18,4930	18.7470
-6	18	2	14,0420	14.7179
7	0	2	4,5180	1.3708
-7	0	2	25,4950	25.4328
7	1	2	16,0460	15.2056
-7	1	2	14,0650	16.1609
7	2	2	13,3180	12.5327
-7	2	2	4,5970	4.7569
7	3	2	40,0910	39.1449
-7	3	2	7,6760	5.9087
-7	4	2	32,6200	29.4125
7	5	2	6,5820	4.9836
-7	5	2	4,1220	3.1531
7	6	2	6,5470	5.9781
-7	6	2	26,5950	24.4574
7	7	2	5,2300	3.2788
-7	7	2	33,9400	32.4969
7	8	2	13,5440	13.2173
-7	8	2	9,7010	9.4130
7	9	2	6,2940	4.5807
-7	9	2	16,0670	14.6626
7	10	2	11,7650	11.6319
-7	10	2	25,7220	25.4555
7	11	2	5,5410	3.9185
-7	11	2	12,4340	12.2556
7	12	2	7,6280	8.7958
-7	12	2	46,5420	46.3683
-7	13	2	7,9590	7.5284
-7	14	2	20,8040	22.0817
-7	16	2	22,7000	24.0756
-7	17	2	10,6970	11.3897
-8	0	2	58,1620	56.4806
8	2	2	6,9560	4.1874
-8	2	2	16,4790	15.9426
8	3	2	18,6020	18.1902
-8	3	2	10,2260	10.7373
8	4	2	26,0970	25.8064
-8	4	2	32,5160	34.2341
8	5	2	5,1110	7.0307
8	6	2	11,4450	13.1821
-8	6	2	26,7060	27.2403
8	7	2	7,3000	6.3447
-8	7	2	22,8840	22.5596
8	8	2	10,6100	10.1187
-8	8	2	17,6210	17.2865
-8	9	2	34,0300	33.6047
-8	10	2	14,8710	15.0871
-8	12	2	10,1180	8.3848
-8	13	2	28,5540	29.4852
-8	14	2	17,0320	16.9836
-9	0	2	44,5230	46.2259
-9	1	2	7,7160	4.9174
-9	2	2	10,0180	12.5987
-9	3	2	12,1470	13.2687
-9	4	2	5,9230	.6135
-9	5	2	4,8280	4.6534
-9	6	2	4,5810	2.3102
-9	7	2	13,0720	13.2200
-9	8	2	25,2690	24.5684
-9	9	2	14,2810	14.9954
-9	11	2	5,2140	4.6122
-9	12	2	11,7530	11.4618
-9	13	2	22.4460	22.3060

H	K	L	Y(OBS)	Y(CALC)
-10	0	2	69,9870	72.6303
-10	1	2	16,0190	16.4349
-10	2	2	12,1380	10.7445
-10	3	2	12,8780	11.4776
-10	4	2	12,2310	9.1836
-10	5	2	9,0060	8.6466
-10	6	2	20,1270	19.0158
-10	7	2	10,1460	9.9958
-10	8	2	23,8500	24.5937
-10	9	2	19,2770	19.8856
-10	10	2	5,6240	2.6245
-11	0	2	22,3510	23.1164
-11	1	2	5,7710	4.9037
-11	2	2	5,2020	5.2518
-11	4	2	6,5170	3.7121
0	1	3	132,8800	136.6405
0	2	3	50,8800	59.7248
0	3	3	67,1090	71.8141
0	4	3	110,4270	108.2439
0	5	3	25,6120	23.9909
0	6	3	8,5550	3.7453
0	7	3	21,8960	18.5479
0	8	3	40,1420	43.7312
0	9	3	29,5450	28.9690
0	10	3	39,5060	42.6868
0	11	3	4,4350	2.5708
0	12	3	33,6670	36.6683
0	14	3	18,0090	20.6396
0	15	3	6,6390	6.0973
0	16	3	13,0380	14.3948
0	17	3	24,5260	26.9814
0	19	3	11,2330	13.0357
0	20	3	11,6970	10.3701
1	1	3	11,2100	9.8367
-1	1	3	2,1000	8.4481
1	2	3	14,6640	9.2749
-1	2	3	221,0800	255.0999
1	3	3	7,9090	11.3419
-1	3	3	143,0820	150.8564
1	4	3	5,0330	3.5445
-1	4	3	51,2910	54.7631
1	5	3	17,8950	15.4604
-1	5	3	59,8440	55.8779
1	6	3	23,5830	21.9989
-1	6	3	11,8870	4.7005
1	7	3	45,6890	45.3761
-1	7	3	52,6300	50.3924
1	8	3	21,7300	24.7211
-1	8	3	26,6040	26.5010
1	9	3	9,9400	12.4574
-1	9	3	25,6350	26.2446
1	10	3	40,2140	43.6574
-1	10	3	7,2990	6.0685
1	11	3	48,0890	48.1907
-1	11	3	19,8130	21.5395
1	12	3	12,1970	12.0605
-1	12	3	14,7390	13.2814
1	13	3	12,5220	14.7415
-1	13	3	18,9710	18.9917
1	14	3	25,8490	28.1694
-1	14	3	48,6790	49.7002
1	15	3	28,4500	29.4966
-1	15	3	21,4680	21.9303
1	16	3	8,2690	7.5371
-1	16	3	10,6500	12.5838
1	17	3	10,8140	10.2294
-1	17	3	13,1560	14.0020
1	18	3	20,1620	20.617
-1	18	3	11,9780	11.6[illegible]
1	19	3	6,1450	6.0[illegible]
1	20	3	35,3940	33.0285
-1	20	3	6,9880	3.9081
2	1	3	4,7280	3.5347
-2	1	3	77,0770	82.0065
2	2	3	71,8070	72.1823
-2	2	3	38,4470	51.0108
2	3	3	23,8880	20.2426
-2	3	3	6,1460	11.0911
2	4	3	28,4520	26.6579
-2	4	3	31,0650	33.2239
2	5	3	41,2560	39.7404
-2	5	3	66,7080	61.0326
2	6	3	44,5220	45.2044
-2	6	3	55,4520	60.1206
-2	7	3	7,3890	6.7381
2	8	3	22,5910	23.8101
-2	8	3	35,0780	36.3671
2	9	3	43,3710	42.3475
-2	9	3	13,5110	13.7896
2	10	3	5,0620	2.9795
-2	10	3	9,5560	7.6469
2	11	3	10,7660	12.1314
-2	11	3	41,5220	39.4731
2	12	3	27,6340	29.8252
-2	12	3	35,2710	38.1147
2	13	3	6,0450	5.0176
-2	13	3	32,6780	31.6537
-2	14	3	18,7150	19.1283
2	15	3	4,7670	3.8941
-2	15	3	19,2480	17.1095
2	16	3	11,3360	12.7951
-2	16	3	40,0120	42.0623
-2	17	3	8,2000	7.4473
2	18	3	12,6840	11.9584
-2	18	3	21,1840	22.6049
2	19	3	18,9480	19.1510
-2	19	3	19,8990	22.1350
-2	20	3	24.0240	18.1825

H	K	L	Y(OBS)	Y(CALC)
3	1	3	21,0070	21.9758
-3	1	3	34,0340	36.5251
3	2	3	50,0610	49.1373
-3	2	3	151,2220	156.3198
3	3	3	32,1200	30.2875
-3	3	3	105,9980	105.1350
3	4	3	25,2900	24.0667
-3	4	3	41,8690	37.3912
3	5	3	4,4910	4.5436
-3	5	3	46,6970	46.0481
3	6	3	21,4260	22.7402
-3	6	3	15,3700	15.7066
3	7	3	16,9090	15.9782
-3	7	3	5,4780	7.4502
3	8	3	14,3380	12.0656
-3	8	3	15,7620	18.0612
3	9	3	26,4870	26.6856
-3	9	3	38,7190	38.5588
3	10	3	21,6550	21.2484
-3	10	3	17,8590	15.2019
3	11	3	18,6120	19.2994
-3	11	3	32,0020	29.1439
3	12	3	37,0830	38.4539
-3	12	3	54,9520	55.3834
3	13	3	14,0030	14.9560
-3	13	3	33,4100	32.5045
3	14	3	9,0730	9.1402
-3	14	3	33,6410	31.7143
3	15	3	9,9380	8.9367
3	16	3	16,0900	14.4620
-3	16	3	30,2050	32.5191
-3	17	3	9,3420	10.9591
3	18	3	4,7480	5.2088
-3	18	3	17,6200	18.4740
-3	19	3	17,9830	17.5509
-3	20	3	16,1060	15.8619
-3	21	3	6,1470	3.9108
4	1	3	13,7310	10.8976
-4	1	3	6,0680	4.1726
4	2	3	49,9470	47.7937
-4	2	3	125,1080	129.8196
4	3	3	46,7420	42.0262
-4	3	3	27,9460	28.1421
4	4	3	8,5050	6.7103
-4	4	3	49,7350	49.2236
4	5	3	9,6740	7.6163
-4	5	3	14,5860	15.1654
4	6	3	4,9200	1.0639
-4	6	3	46,8640	50.6800
4	7	3	8,8080	6.7043
-4	7	3	19,8460	17.0008
4	8	3	8,4240	6.3502
-4	8	3	3,6200	3.4572
-4	9	3	47,0020	45.5878
4	9	3	13,0120	13.1057
4	10	3	15,1560	1[illegible].6620
-4	10	3	10,7710	1[illegible]126
4	11	3	10,9690	1[illegible]617
-4	11	3	9,5100	[illegible]874
4	12	3	21,9590	22.[illegible]647
-4	12	3	9,1710	10.[illegible]723
4	13	3	18,2110	19.[illegible]248
-4	13	3	13,7790	14.1911
4	14	3	15,0680	15.7418
-4	14	3	29,4400	29.1181
-4	15	3	11,2560	9.6380
4	16	3	20,9600	20.023[illegible]
-4	16	3	31,3220	33.11[illegible]
4	17	3	17,6550	16.2903
-4	17	3	19,9030	21.6721
-4	18	3	18,5550	17.8703
-4	19	3	9,5310	9.8133
-4	20	3	7,5910	4.4376
5	1	3	13,1050	14.1521
-5	1	3	7,8860	4.8768
5	2	3	13,5980	13.0207
-5	2	3	77,2960	77.4356
5	3	3	42,6710	40.4752
-5	3	3	18,9040	16.7046
-5	4	3	34,9090	32.1610
5	5	3	5,3540	5.4152
-5	5	3	34,1490	30.6646
5	6	3	7,4750	6.3520
-5	6	3	50,3580	48.0032
5	7	3	23,9270	23.0446
-5	7	3	54,4070	54.4423
5	8	3	6,1080	5.7612
-5	8	3	33,7070	32.8232
5	9	3	5,4710	2.6575
-5	9	3	21,9610	24.4291
-5	10	3	4,0770	3.2501
5	11	3	4,8460	3.3830
-5	11	3	26,7980	26.3049
5	12	3	20,7640	20.7698
-5	12	3	7,3650	7.5631
5	13	3	18,9790	19.4960
-5	13	3	11,0090	13.6878
5	14	3	6,6950	6.3428
-5	14	3	9,2770	10.2566
5	15	3	10,3560	8.9784
-5	15	3	10,2080	9.3618
-5	16	3	28,5240	30.4755
-5	17	3	10,6380	10.1509
-5	18	3	27,0600	29.5118
-5	19	3	13,0660	13.8922
-5	20	3	10,6820	8.6545
6	1	3	12,8940	11.4868
-6	1	3	13.3800	15.7283
6	2	3	17,2100	17.5013
-6	2	3	15,0080	16.4943
6	3	3	20,6300	19.8208
-6	3	3	10,2270	11.5222
6	4	3	10,1450	8.5562
-6	4	3	53,7980	46.9384
-6	5	3	62,7010	59.6160
6	5	3	6,3260	5.9816
-6	6	3	53,6260	51.7463
6	7	3	16,5860	15.6733
-6	7	3	27,2640	25.8735
6	8	3	4,8070	3.7658
-6	8	3	4,7470	2.8191
6	9	3	12,5070	12.3097
-6	9	3	9,5780	8.3426
-6	10	3	23,0590	24.1676
-6	11	3	8,5040	9.4971
6	12	3	21,1540	22.2334
-6	12	3	27,6290	28.0092
6	13	3	13,6330	14.1328
-6	13	3	15,7480	15.9598
-6	14	3	16,9290	15.6524
-6	15	3	8,4740	9.6136
-6	16	3	6,5370	6.4973
-6	17	3	12,1770	11.0825
-6	18	3	14,0500	14.2074
-6	19	3	17,8450	18.2773
7	1	3	29,6260	29.6475
-7	1	3	35,1530	38.3745
7	2	3	12,7960	13.1888
-7	2	3	36,7690	36.2199
-7	3	3	36,4330	34.0014
-7	4	3	27,8730	27.9368
7	5	3	18,9150	19.9280
-7	5	3	39,6730	38.5727
7	6	3	6,7060	5.4967
-7	6	3	39,0790	36.8631
7	7	3	11,0740	11.6756
-7	7	3	6,2440	3.3289
-7	8	3	17,5640	18.6530
7	9	3	5,7130	4.1747
-7	9	3	5,4830	4.5012
-7	10	3	7,2380	7.4153
-7	11	3	10,7120	10.4996
-7	12	3	15,8180	16.7543
-7	13	3	31,0050	31.5552
-7	14	3	21,0500	21.9481
-7	16	3	7,5560	6.6614
-7	17	3	27,2400	30.6009
-7	18	3	6,6470	5.2534
8	1	3	11,1550	10.7101
-8	1	3	34,8830	34.3818
8	2	3	6,4090	6.7514
-8	2	3	27,7400	29.3907
-8	3	3	26,5100	25.5477
-8	4	3	5,2750	3.7675
-8	5	3	37,2400	35.1794
-8	6	3	20,4920	19.7299
-8	7	3	5,6960	4.4184
-8	8	3	4,2340	[illegible].4713
-8	9	3	22,9730	21.9132
-8	10	3	35,4940	35.7189
-8	11	3	13,0530	13.1758
-8	12	3	19,8400	22.2902
-8	13	3	6,4750	3.8114
-8	14	3	26,8820	28.5928
-8	15	3	5,2590	4.0582
-9	1	3	32,2170	31.6158
-9	2	3	24,9650	24.5533
-9	3	3	6,1550	3.0942
-9	4	3	14,0650	14.2727
-9	5	3	11,0660	9.9795
-9	6	3	8,5050	8.1028
-9	9	3	14,7510	14.4579
-9	10	3	17,2040	16.3280
-9	12	3	5,4380	4.2678
-9	13	3	16,2190	16.7256
-9	14	3	7,9250	8.9743
-10	1	3	38,2790	39.4588
-10	2	3	14,5600	14.8316
-10	4	3	10,5620	10.7165
-10	5	3	25,0730	24.0469
-10	6	3	8,1710	5.5914
-10	7	3	9,5970	7.1032
-10	9	3	37,0500	36.7902
-10	10	3	18,9930	18.1953
-10	11	3	16,3670	15.6067
-11	1	3	24,7460	26.5332
-11	2	3	6,0410	6.9468
-11	4	3	12,3240	12.5328
-11	5	3	5,9560	6.2879
-11	6	3	11,2690	11.1774
-11	8	3	10,7720	10.2748
0	0	4	59,8060	69.1615
0	1	4	60,6850	57.6091
0	2	4	23,8610	25.5621
0	3	4	87,1620	89.5426
0	4	4	8,2880	5.9072
0	5	4	4,0090	2.0231
0	6	4	17,9050	18.2229
0	7	4	17,3770	19.0565
0	8	4	55,6540	59.7163
0	9	4	51,4990	52.6240
0	10	4	30,0790	29.6593
0	11	4	19,5620	20.4631
0	12	4	30,8850	33.3607
0	13	4	6,5560	4.9980
0	15	4	8,5920	8.6072
0	17	4	11,1770	12.1535
0	19	4	24,3720	24.6383
0	20	4	26,2070	21.2344
1	0	4	9,4820	1.8478
-1	0	4	10,4810	9.4232
1	1	4	46,0530	50.6683
-1	1	4	56,7110	63.1368
1	2	4	32,0220	31.3129
-1	2	4	183,1030	195.3154
1	3	4	15,7440	14.4829
-1	3	4	92,7880	99.3831
1	4	4	47,1120	46.0718
-1	4	4	56,9750	55.3093
1	5	4	42,0720	44.4577
-1	5	4	43,3430	45.9234
1	6	4	22,6110	19.2587
-1	6	4	23,6240	24.7825
1	7	4	30,5220	30.6578
-1	7	4	22,5180	24.5039
1	8	4	73,8280	69.8311
-1	8	4	6,7700	8.0991
1	9	4	14,6630	15.1878
-1	9	4	11,4510	10.4601
1	10	4	21,9200	22.1117
1	11	4	13,6530	14.9494
-1	11	4	44,7490	45.0646
1	12	4	19,7330	19.5954
-1	12	4	57,9560	59.4951
1	13	4	6,8730	7.1987
-1	13	4	19,5600	20.4962
1	14	4	10,1760	10.0962
-1	15	4	7,4540	8.0100
1	16	4	16,8470	17.8271
-1	16	4	12,1710	11.6120
1	17	4	6,4880	5.1683
-1	17	4	18,8610	21.7662
1	18	4	25,6260	26.3674
-1	18	4	9,3500	9.5223
1	19	4	24,3030	23.9896
-1	19	4	6,6600	6.7675
-1	20	4	6,5370	6.0203
2	0	4	20,6690	25.4797
-2	0	4	44,2630	48.4806
2	1	4	32,1630	29.7608
-2	1	4	36,8480	41.3908
2	2	4	4,4790	4.1841
-2	2	4	113,0400	123.3093
2	3	4	30,4940	28.7166
-2	3	4	79,9880	85.4274
2	4	4	26,1190	27.9076
-2	4	4	88,1790	88.6425
2	5	4	61,2700	58.0094
-2	5	4	12,9050	10.8044
-2	6	4	5,5360	3.7307
2	6	4	10,5560	9.1079
2	7	4	13,0760	9.4020
-2	7	4	70,8830	76.6534
2	8	4	7,5620	10.1132
-2	8	4	21,2300	21.7772
2	9	4	4,7860	3.8312
-2	9	4	38,1110	40.9211
2	10	4	26,5250	26.6947
-2	10	4	28,7160	27.3419
2	11	4	21,1970	21.4194
-2	11	4	60,4190	61.3703
2	12	4	8,3460	10.1576
-2	12	4	25,5510	25.4188
2	13	4	6,3620	4.4213
-2	13	4	13,1600	13.7540
2	14	4	11,0080	10.5558
-2	14	4	5,0320	6.1033
2	15	4	9,5950	10.5993
-2	15	4	34,8260	36.2405
-2	16	4	13,7380	12.2328
2	17	4	12,4420	11.1158
-2	17	4	16,4340	16.2138
2	18	4	29,3030	31.1467
-2	18	4	14,7980	14.1092
-2	19	4	17,4980	15.8473
-2	20	4	7,1400	5.2969
-2	21	4	16,1860	13.3276
3	0	4	41,2460	44.5659
-3	0	4	61,2870	64.4629
3	1	4	29,2170	30.1336
-3	1	4	13,0750	16.3148
3	2	4	35,7060	34.4625
-3	2	4	41,9480	45.5980
3	3	4	40,6890	40.0891
-3	3	4	25,8710	28.1297
3	4	4	42,2300	41.6490
-3	4	4	11,8280	12.0457
3	5	4	16,3000	15.4562
-3	5	4	8,7860	11.6946
-3	6	4	14,7230	16.3138
3	6	4	19,0170	20.5236
-3	7	4	73,7410	72.6614
3	8	4	15,2150	15.8595
-3	8	4	24,8080	23.7192
-3	9	4	10,1470	10.8672
3	9	4	10,2990	8.4232
3	10	4	12,0350	12.4174
-3	10	4	8,0560	7.8523
3	11	4	25,8430	26.6449
-3	11	4	84,4450	82.5115
3	12	4	19,1140	17.4336
-3	12	4	12,2630	12.6733
3	14	4	16,4580	16.8403
-3	14	4	10.3140	11.8708
-3	15	4	45,4710	45.6668
3	16	4	7,7480	9.4972
-3	16	4	13,6620	14.5071
-3	17	4	12,8090	11.3239
-3	18	4	33,7420	34.2652
-3	19	4	5,1040	6.0116
-3	20	4	20,1760	16.8529
4	0	4	38,8390	42.0889
-4	0	4	46,8730	49.7881
-4	1	4	32,8840	35.0690
4	2	4	21,4450	20.0413
-4	2	4	4,7620	7.1362
4	3	4	4,1680	4.9301
-4	3	4	70,9840	75.2780
4	4	4	46,4300	45.7614
-4	4	4	12,3410	12.0693
4	5	4	20,6810	18.1991
-4	5	4	25,0380	27.1334
4	6	4	6,3210	3.7334
-4	6	4	16,2900	13.7715
4	7	4	9,6160	9.0538
-4	7	4	90,4190	95.2632
4	8	4	20,1970	19.5136
-4	8	4	4,9620	4.6059
4	9	4	7,5870	9.6366
-4	9	4	9,9310	10.9252
4	10	4	5,4240	3.0297
-4	10	4	11,9820	13.0383
4	11	4	17,2020	18.3612
-4	11	4	40,0130	44.5920
-4	12	4	30,8730	30.9983
4	13	4	7,9130	8.3480
-4	13	4	8,5700	7.0139
4	14	4	11,2260	11.4567
-4	14	4	33,1000	33.3550
4	15	4	10,6480	11.2196
-4	15	4	26,1260	25.9776
-4	16	4	29,6250	30.5742
-4	17	4	5,8130	6.2197
-4	18	4	11,2380	11.4853
-4	19	4	7,6870	7.2332
-4	20	4	16,1020	12.4412
5	0	4	16,4280	16.2621
-5	0	4	39,2140	33.9221
5	1	4	9,2740	9.2352
-5	1	4	51,0190	52.9451
5	2	4	10,9790	10.7193
-5	2	4	33,5590	28.9322
5	3	4	7,3290	7.9930
-5	3	4	57,1320	54.2798
5	4	4	34,4370	33.8102
-5	4	4	35,3930	31.8474
-5	5	4	55,2120	55.5474
5	6	4	15,1850	15.5973
-5	6	4	3,3020	3.7441
5	7	4	15,5450	16.0176
-5	7	4	86,1130	85.4498
5	8	4	33,4340	33.1758
-5	8	4	13,1130	12.8075
5	9	4	7,1690	7.1095
-5	9	4	6,0040	6.3086
5	10	4	10,4970	9.1889
-5	10	4	18,3090	16.2375
5	11	4	14,0240	15.5653
-5	11	4	37,7410	40.7916
5	12	4	10,0580	9.5274
-5	12	4	14,1730	14.5615
-5	15	4	27,7710	29.4777
-5	16	4	31,1130	31.3400
-5	17	4	13,8690	14.3035
-5	18	4	23,9020	24.7992
-5	19	4	6,1380	5.4373
-5	20	4	15,4690	15.4633
6	0	4	14,7070	15.0533
-6	0	4	3,5590	7.7964
6	1	4	5,5320	4.3421
-6	1	4	43,3280	45.7781
6	2	4	22,9410	23.1569
-6	2	4	15,9320	14.4507
6	3	4	8,9600	8.2693
-6	3	4	34,9310	31.5553
6	4	4	17,0520	14.5269
-6	4	4	26,6290	26.0676
6	5	4	7,4210	6.2114
-6	5	4	53,9230	56.5736
6	6	4	20,9230	22.2812
-6	6	4	13,3440	11.4627
-6	7	4	33,4650	36.1952
6	8	4	14,5090	12.6154
-6	8	4	28,3610	27.4343
-6	9	4	7,3790	6.4933
6	10	4	19,7110	20.3812
-6	10	4	8,9660	6.0334
-6	11	4	24,1390	25.4387
-6	12	4	11,6270	12.3955
-6	13	4	7,4290	8.1160
-6	14	4	10,1340	8.2451
-6	15	4	15,8050	14.9671
-6	16	4	34,5420	35.8062
-6	17	4	8,9240	9.1628
-6	18	4	18,3640	17.9558
-6	19	4	26,6470	28.0203
7	0	4	7,4020	5.2823
-7	0	4	4,9300	2.9130
7	1	4	16,1280	16.6902
-7	1	4	9,0700	2.5982
7	2	4	21,8550	22.3627
-7	2	4	23,9330	23.4117

H	K	L	Y(OBS)	Y(CALC)
7	3	4	9,5540	10.4325
-7	3	4	9,5210	10.0045
7	4	4	20,5490	19.4352
-7	4	4	13,1310	12.4793
7	5	4	8,5840	9.1511
-7	5	4	30,2010	31.8699
-7	6	4	35,2510	33.9576
-7	7	4	16,4140	17.5275
-7	8	4	21,6440	20.5872
-7	9	4	9,1590	11.0478
-7	11	4	38,2530	40.2511
-7	12	4	8,9730	7.6531
-7	13	4	15,9300	16.1888
-7	14	4	21,3200	19.5053
-7	15	4	12,7140	13.4920
-7	16	4	28,6890	28.6934
-7	17	4	4,6950	5.2397
-7	18	4	6,2030	5.9554
-8	0	4	52,3900	53.5151
-8	1	4	32,8840	31.5654
-8	2	4	13,4300	13.6390
-8	3	4	33,2100	32.6675
-8	4	4	41,3100	41.8221
-8	5	4	11,0410	9.3273
-8	6	4	15,7000	16.6815
-8	7	4	35,3200	36.6393
-8	8	4	9,0950	4.6303
-8	9	4	9,2230	8.4832
-8	10	4	4,9400	3.6397
-8	11	4	36,2500	39.5398
-8	12	4	9,2570	9.7665
-8	13	4	11,8600	12.8256
-8	15	4	9,7600	9.2313
-8	16	4	13,3720	19.6612
-9	0	4	45,7490	42.9854
-9	1	4	18,4530	15.7748
-9	2	4	22,9830	21.6169
-9	3	4	45,3120	43.0609
-9	4	4	26,0800	24.4845
-9	5	4	6,8390	7.0894
-9	6	4	17,3100	17.5204
-9	7	4	26,3810	24.7387
-9	8	4	5,2590	1.9399
-9	9	4	17,8410	18.1958
-9	10	4	14,9200	14.7498
-9	11	4	7,5230	5.7360
-9	12	4	22,6920	25.1080
-9	13	4	16,4710	17.1085
-9	14	4	14,0600	11.9413
-9	15	4	16,3020	16.2771
-10	0	4	36,7490	38.4262
-10	1	4	7,6390	8.6018
-10	2	4	24,4420	25.2571
-10	3	4	17,4830	18.7574
-10	4	4	14,6230	14.2462
-10	6	4	12,5930	11.8855
-10	7	4	12,0840	11.2084
-10	8	4	38,9040	41.3844
-10	9	4	6,6830	5.1210
-10	10	4	15,5060	14.6640
-10	11	4	14,8320	14.7109
-10	12	4	10,1770	7.3988
-10	13	4	4,9790	5.9265
-11	0	4	23,4670	21.3706
-11	1	4	3,3890	.4533
-11	2	4	14,4670	14.2229
-11	3	4	12,2310	14.0314
-11	4	4	6,5070	5.7147
-11	5	4	6,3330	6.7363
-11	6	4	12,6370	12.4957
-11	7	4	29,6790	29.9339
-11	8	4	20,2110	20.4034
0	1	5	29,2750	29.9570
0	2	5	5,8350	7.5776
0	3	5	39,0740	41.0132
0	4	5	11,0600	11.0503
0	5	5	36,7940	37.0411
0	6	5	5,0790	4.6285
0	7	5	4,6900	6.1377
0	9	5	27,6820	28.9560
0	10	5	4,2210	2.5080
0	11	5	7,9550	8.9876
0	13	5	19,4530	21.2880
0	14	5	15,0480	14.7489
0	15	5	8,0020	6.2506
0	16	5	15,0760	14.1434
0	17	5	23,9970	26.0701
0	18	5	5,3330	4.3777
0	19	5	15,6100	16.1787
1	1	5	7,9080	9.0572
-1	1	5	19,6900	20.3826
1	2	5	14,4200	10.7189
-1	2	5	66,6050	67.6466
1	3	5	64,6120	63.9460
-1	3	5	37,0400	38.5047
1	4	5	5,6620	6.2468
-1	4	5	40,4770	40.1301
1	5	5	18,7370	19.6215
-1	5	5	77,0480	79.8072
-1	6	5	5,5830	4.6678
1	7	5	52,6360	53.3832
-1	7	5	20,9490	18.3127
1	8	5	5,6830	4.9026
-1	8	5	30,6700	31.3864
1	9	5	25,3280	26.8690
-1	9	5	44,2310	46.2219
1	10	5	9,0640	9.2805
-1	10	5	3,9460	4.9806

H	K	L	Y(OBS)	Y(CALC)
1	11	5	5,8810	4.3297
-1	11	5	10,8350	11.8933
-1	12	5	11,5120	11.4665
1	13	5	5,5170	2.8254
-1	13	5	35,2150	38.2043
1	14	5	15,1130	12.8095
-1	14	5	7,3680	7.5367
1	15	5	13,6480	12.0008
-1	15	5	11,2060	10.5318
1	16	5	5,4990	4.4765
1	17	5	47,0020	50.4162
-1	17	5	5,7520	1.6209
-1	18	5	11,4100	8.2832
-1	19	5	5,0970	4.5479
-1	20	5	14,3270	12.3896
2	1	5	42,6290	45.8807
-2	1	5	57,0900	58.5901
2	2	5	20,9450	20.4825
-2	2	5	71,8530	70.5474
2	3	5	44,7290	45.2022
-2	3	5	40,5290	35.7227
-2	4	5	6,7680	8.8943
2	5	5	19,0540	19.9567
-2	5	5	106,6070	108.1873
2	6	5	14,6460	14.7672
-2	6	5	42,5110	42.6509
2	7	5	12,9020	14.2077
-2	7	5	9,3180	4.3236
2	8	5	5,8230	6.3273
-2	8	5	33,9440	32.6671
2	9	5	30,0210	30.6273
-2	9	5	35,6390	37.9187
2	10	5	16,8820	16.1357
-2	10	5	13,6190	14.5600
2	11	5	4,6360	3.1340
-2	11	5	23,9640	22.2593
2	13	5	8,2000	6.6613
-2	13	5	61,5010	59.6760
2	14	5	22,9980	23.6736
-2	14	5	6,2740	6.5318
2	15	5	16,5550	17.8094
-2	15	5	24,4920	23.2583
-2	16	5	28,0550	28.4683
2	17	5	31,3930	33.0241
-2	17	5	10,0440	10.6942
-2	18	5	6,6880	6.6463
-2	20	5	14,9120	12.3154
3	1	5	34,4690	35.1540
-3	1	5	41,2590	39.9710
3	2	5	21,7930	22.0939
-3	2	5	37,1260	36.9855
3	3	5	28,3600	29.0944
-3	3	5	4,4540	8.4145
3	4	5	9,9620	9.8381
-3	4	5	12,5520	14.1259
3	5	5	17,2200	17.8119
-3	5	5	19,1230	21.5568
3	6	5	12,7510	13.3306
-3	6	5	12,7600	10.6360
-3	7	5	8,6110	8.9234
-3	8	5	7,0640	3.7684
3	9	5	21,1740	21.6017
-3	9	5	33,5950	33.2610
3	10	5	15,3880	15.3312
-3	10	5	33,2700	32.1969
-3	11	5	22,5950	23.5825
3	12	5	29,3700	31.0764
-3	12	5	31,8400	30.7520
3	13	5	5,0190	3.5778
-3	13	5	46,8870	44.2713
3	14	5	20,8600	21.7517
-3	14	5	13,2450	12.4085
3	15	5	10,4980	10.1397
-3	15	5	23,6920	23.2008
-3	16	5	29,4800	30.7981
-3	17	5	30,9830	31.3873
4	1	5	11,6690	10.0135
-4	1	5	4,3700	2.9958
4	2	5	24,0300	24.4021
-4	2	5	41,7130	44.2135
4	3	5	14,2710	13.7829
-4	3	5	36,4640	36.6417
4	4	5	18,0160	17.9460
-4	4	5	83,6780	85.5907
4	5	5	26,7040	28.3827
-4	5	5	16,9360	13.3315
4	6	5	6,1050	5.5457
-4	6	5	35,5280	35.6222
4	7	5	22,6450	23.6515
-4	7	5	3,7070	.6363
4	8	5	15,4500	17.0706
-4	8	5	19,2250	21.3684
4	9	5	30,5490	30.9931
-4	9	5	49,7300	48.4970
-4	10	5	57,1810	59.3054
-4	11	5	10,9490	13.5722
4	12	5	7,4990	4.1805
-4	12	5	24,2340	24.0089
4	13	5	16,2260	17.1470
-4	13	5	29,7380	28.7040
-4	14	5	36,8300	36.9755
-4	17	5	14,7600	15.8703
-4	18	5	10,9740	11.1610
-4	19	5	6,2260	5.7002
-4	20	5	14,2320	10.1282
5	1	5	11,8320	12.8756
-5	1	5	12,8430	11.2415
5	2	5	11,4850	12.6252

H	K	L	Y(OBS)	Y(CALC)
-5	2	5	6,9550	2.9639
-5	3	5	14,3260	17.1771
-5	4	5	61,2130	61.1972
5	5	5	24,0260	26.6820
-5	5	5	19,9870	18.3588
5	6	5	10,6350	9.6660
-5	6	5	52,0590	50.0559
-5	7	5	59,2840	60.7846
5	8	5	8,7990	8.8108
-5	8	5	73,3730	74.2228
5	9	5	36,8770	38.1634
-5	9	5	19,0990	20.6103
5	10	5	8,0220	7.9767
-5	10	5	43,0210	44.8727
-5	11	5	5,7550	5.2065
-5	12	5	22,1320	22.0138
-5	13	5	19,2130	18.1678
-5	14	5	20,5180	21.1101
-5	15	5	21,7180	21.1578
-5	16	5	13,0920	13.0987
-5	17	5	8,6240	6.1008
-5	18	5	8,4530	9.7000
-5	20	5	12,8040	8.8522
-6	1	5	5,4100	6.3265
-6	2	5	75,5640	77.3712
6	3	5	18,6780	18.3004
-6	3	5	53,6820	51.1259
6	4	5	19,1830	18.6025
-6	4	5	46,9500	49.9904
6	5	5	15,7180	15.2074
-6	5	5	5,0840	2.2819
-6	6	5	29,4800	31.9758
6	7	5	10,3030	9.7717
-6	7	5	4,5950	1.6118
-6	8	5	25,9250	25.0816
-6	9	5	5,6400	6.3061
-6	10	5	17,3900	19.1132
-6	12	5	10,6210	10.4095
-6	14	5	5,2270	2.1830
-6	15	5	24,3370	22.8920
-6	16	5	14,4160	15.9016
-6	17	5	23,2720	24.7882
-6	18	5	13,3290	12.6828
-7	1	5	13,7640	11.0131
-7	2	5	6,2300	3.4985
-7	3	5	68,0110	62.9666
-7	4	5	5,4250	3.1017
-7	6	5	26,3840	29.0684
-7	7	5	20,1230	20.1481
-7	8	5	18,0730	15.9579
-7	9	5	10,3370	9.4381
-7	10	5	32,0900	32.4992
-7	12	5	41,0400	41.5481
-7	13	5	12,5300	13.2131
-7	14	5	4,0810	.3028
-7	15	5	29,7380	29.8369
-7	16	5	17,7550	20.6266
-7	17	5	9,9690	9.2249
-7	18	5	7,9120	9.1354
-8	1	5	9,4100	8.6235
-8	2	5	76,9360	75.4161
-8	3	5	6,1400	5.3232
-8	4	5	5,0870	2.3235
-8	5	5	12,3520	13.1178
-8	6	5	24,2680	24.9835
-8	7	5	11,1950	12.8550
-8	8	5	10,5020	10.4651
-8	9	5	4,2600	2.9815
-8	10	5	4,7030	2.1304
-8	11	5	8,2450	9.1000
-8	12	5	32,7020	33.2962
-8	14	5	4,7970	.4055
-8	15	5	28,0810	29.1201
-8	16	5	4,9690	2.7928
-8	17	5	11,6900	14.6839
-9	2	5	49,9400	51.6728
-9	3	5	38,0820	32.0724
-9	4	5	9,2980	7.7041
-9	5	5	5,7060	4.6009
-9	6	5	29,0670	30.3867
-9	7	5	11,5740	13.4942
-9	8	5	5,1600	5.3949
-9	9	5	6,8900	7.4277
-9	10	5	8,8490	7.6940
-9	11	5	36,7060	36.8383
-9	12	5	8,9860	8.2170
-9	13	5	14,1010	13.9706
-9	14	5	5,5510	5.3362
-9	15	5	6,8600	6.9639
-9	16	5	18,2260	19.6109
-10	1	5	4,7790	5.2288
-10	2	5	40,5070	41.2308
-10	3	5	35,6830	35.1239
-10	5	5	5,3140	3.5601
-10	6	5	8,8350	8.4716
-10	7	5	25,3960	24.1429
-10	8	5	4,8750	.7434
-10	9	5	18,3750	18.9186
-10	10	5	7,5230	4.4893
-10	11	5	13,0150	12.8874
-10	12	5	17,5550	17.5228
-10	13	5	6,2730	6.7840
-10	14	5	10,9900	9.8485
-11	1	5	7,8570	7.9933
-11	2	5	26,5120	28.4003
-11	3	5	30,8220	33.2281
-11	4	5	15,5180	15.7804
-11	5	5	7,4150	6.1044

H	K	L	Y(OBS)	Y(CALC)
-11	6	5	12,1070	12.7336
-11	7	5	8,9840	9.8291
-11	8	5	8,1730	7.3505
-11	9	5	6,2550	6.6204
-11	10	5	22,3240	19.6658
-11	11	5	18,2950	18.7978
0	0	6	18,2100	21.0618
0	1	6	48,5280	48.3677
0	2	6	46,4610	45.9280
0	3	6	33,5460	32.7736
0	4	6	52,0950	55.1338
0	5	6	16,2650	17.3059
0	6	6	20,5740	20.2658
0	7	6	27,9620	26.7003
0	8	6	11,7620	12.1766
0	9	6	4,9280	.3117
0	10	6	10,4060	8.8300
0	11	6	13,6980	14.4934
0	12	6	5,0450	4.5383
0	13	6	12,8020	12.3684
0	14	6	16,3940	14.1462
0	15	6	18,4160	17.8779
0	16	6	14,0420	13.1276
0	17	6	6,2100	7.4096
0	18	6	31,9920	32.8049
1	0	6	61,1620	61.2965
-1	0	6	28,3220	33.3844
1	1	6	30,4290	27.6300
-1	1	6	12,8650	7.0892
1	2	6	19,2660	19.0291
-1	2	6	7,9970	9.8057
1	3	6	34,0540	32.4161
-1	3	6	27,8390	29.5206
1	4	6	40,3150	38.2835
-1	4	6	65,7640	66.8463
1	5	6	27,2550	27.7091
-1	5	6	31,9490	33.7952
1	6	6	10,0150	10.1272
-1	6	6	49,1710	50.8632
-1	7	6	7,3190	7.7053
1	8	6	6,4890	2.5688
-1	8	6	10,0920	9.8017
1	9	6	6,0490	5.5770
-1	9	6	13,5680	14.3964
1	10	6	14,4890	15.1162
-1	10	6	4,1780	3.6730
1	11	6	5,8850	6.2677
-1	11	6	9,3030	8.0206
1	12	6	6,8980	7.2868
1	13	6	26,7710	27.7110
-1	13	6	4,6400	4.9778
1	14	6	12,8480	11.9540
-1	14	6	20,2070	20.7507
1	15	6	16,0500	15.8540
-1	15	6	5,2010	6.5062
1	16	6	7,0690	6.2272
-1	16	6	6,5420	5.4576
-1	18	6	24,5100	24.1171
-1	19	6	10,0360	10.3051
2	0	6	32,5990	34.6201
-2	0	6	13,8870	10.0897
2	1	6	37,0590	38.5599
-2	1	6	35,2650	41.7729
-2	2	6	34,0690	35.4638
2	3	6	4,3790	3.8087
-2	3	6	37,9230	41.1545
2	4	6	9,4470	10.4185
-2	4	6	72,3740	76.1787
2	5	6	15,7380	15.3316
-2	5	6	85,1300	87.0404
2	6	6	8,1910	8.9161
-2	6	6	8,6690	10.1706
-2	7	6	38,4890	40.6143
2	8	6	20,3550	22.4137
-2	8	6	11,7950	8.2854
2	10	6	33,3870	33.9692
-2	10	6	8,2680	7.8230
-2	11	6	9,6450	11.7280
2	12	6	12,8220	12.5260
-2	12	6	39,5320	40.4524
2	13	6	36,7190	37.5325
-2	13	6	26,7120	25.2316
2	14	6	7,8070	5.0174
-2	14	6	22,5230	21.9818
2	15	6	11,1050	9.6849
-2	15	6	12,1050	11.6090
-2	16	6	15,7520	14.9170
-2	17	6	13,2810	14.7284
-2	18	6	14,6860	15.2438
-2	19	6	12,5000	12.3363
3	0	6	21,8160	21.3839
-3	0	6	74,0920	73.0522
3	1	6	20,1880	19.7973
-3	1	6	36,6590	38.0983
3	2	6	12,3410	11.3236
-3	2	6	66,5210	62.2101
3	3	6	6,3660	6.8233
-3	3	6	7,3270	5.0204
-3	4	6	44,0480	45.8495
3	5	6	17,0440	17.7497
-3	5	6	38,1620	38.2544
3	6	6	21,0010	21.2898
-3	6	6	29,6940	28.4723
3	7	6	15,9650	15.3390
-3	7	6	66,0370	61.5414
3	8	6	14,1110	13.5160
-3	8	6	8,9170	8.5934
3	9	6	8,4220	7.7393

H	K	L	Y(OBS)	Y(CALC)
-3	9	6	4,5380	3.2725
3	10	6	30,2420	30.9892
-3	10	6	45,3600	46.3653
3	11	6	21,3890	23.2607
-3	11	6	6,1270	4.1757
3	12	6	11,4510	10.6621
-3	12	6	47,0800	46.1787
3	13	6	15,2630	16.5773
-3	13	6	24,3910	23.1481
-3	14	6	38,0230	37.1368
-3	15	6	11,2120	10.3986
-3	16	6	25,1710	26.2111
-3	17	6	40,4900	41.7887
-3	18	6	27,6680	27.0641
-3	19	6	14,3550	13.9833
-4	0	6	43,8050	50.5614
4	1	6	10,3150	9.3856
-4	1	6	15,9880	14.6838
4	2	6	14,6470	14.0527
-4	2	6	4,0570	2.1470
4	3	6	7,7260	7.0700
-4	3	6	13,5890	10.5735
-4	4	6	8,8790	6.1057
4	5	6	13,9710	15.1208
-4	5	6	6,9750	4.4034
4	6	6	5,3720	4.8215
-4	6	6	21,6740	20.9588
4	8	6	16,0130	17.5746
-4	8	6	13,3560	6.4861
4	9	6	13,5320	13.4061
-4	9	6	32,8510	29.4131
4	10	6	18,7580	18.5471
-4	10	6	52,7870	49.7345
4	11	6	20,1340	21.1849
-4	11	6	29,6110	26.7058
-4	12	6	36,6950	36.9912
-4	13	6	11,9990	11.6412
-4	14	6	24,5000	23.5594
-4	15	6	14,1560	14.0970
-4	16	6	27,6880	26.8776
-4	17	6	11,5790	10.8707
-4	18	6	14,3980	14.6013
-4	19	6	9,0120	7.7304
-4	20	6	13,6870	10.4282
5	0	6	12,8990	12.8790
-5	0	6	27,0540	30.2328
5	1	6	5,2660	4.1593
-5	1	6	5,8250	4.2656
5	2	6	4,8890	3.9082
-5	2	6	22,2620	22.6274
-5	3	6	17,4460	17.6508
5	4	6	8,0220	6.5456
-5	4	6	33,6620	35.3047
5	5	6	6,8440	7.0332
-5	5	6	24,7120	24.3023
-5	6	6	10,2500	8.1616
5	7	6	22,6910	21.3848
-5	7	6	32,9410	34.1538
-5	8	6	67,1210	67.2763
-5	9	6	9,6730	10.2694
-5	10	6	35,1290	36.1639
-5	11	6	32,6410	34.7340
-5	12	6	26,0870	29.1834
-5	13	6	7,6390	7.5279
-5	14	6	13,4460	12.6423
-5	15	6	7,4980	7.1719
-5	16	6	13,7370	11.6398
-5	17	6	21,2240	20.4845
-5	18	6	5,6590	1.6138
-5	19	6	5,0410	5.3956
-6	0	6	10,1240	3.4259
-6	1	6	24,9200	24.6540
-6	2	6	26,2390	24.5830
-6	3	6	34,5960	32.6085
-6	4	6	23,9050	25.5458
-6	5	6	32,2370	30.0879
-6	6	6	6,7010	4.9178
-6	7	6	50,3090	50.6358
-6	8	6	10,2130	9.4721
-6	9	6	17,5600	16.8349
-6	10	6	37,4200	37.8056
-6	11	6	32,2930	32.5925
-6	12	6	15,2390	14.8635
-6	13	6	18,8950	19.1770
-6	14	6	5,5690	4.6890
-6	15	6	13,4340	14.3450
-6	16	6	19,4000	20.0665
-6	17	6	5,5690	4.3101
-6	18	6	13,4820	14.5328
-7	0	6	28,6690	29.6384
-7	1	6	52,1420	49.3212
-7	2	6	66,1310	61.7961
-7	3	6	40,5410	37.8051
-7	4	6	41,3930	43.0090
-7	5	6	41,1030	39.7975
-7	6	6	32,4690	32.8477
-7	7	6	18,6850	20.7349
-7	8	6	9,2210	5.8347
-7	9	6	18,7760	19.3435
-7	10	6	22,2730	23.6106
-7	11	6	39,2560	41.2900
-7	12	6	30,8940	31.0690
-7	13	6	19,1820	19.9187
-7	14	6	18,3830	18.9205
-7	15	6	22,0370	24.5567
-7	17	6	14,3780	14.5136
-7	18	6	32,1320	36.0666
-8	0	6	41,3460	40.6872
-8	1	6	24,4590	23.5135
-8	2	6	18,6940	18.9908
-8	3	6	58,0160	59.7967
-8	4	6	29,2360	27.2724
-8	6	6	10,0910	10.1397
-8	7	6	38,9560	39.5691
-8	8	6	21,2480	19.9936
-8	9	6	10,6340	10.2421
-8	10	6	8,7430	7.8805
-8	11	6	39,2700	39.5444
-8	13	6	10,0150	9.5214
-8	14	6	20,6710	20.1714
-8	15	6	7,9720	7.3395
-9	0	6	43,5440	46.9219
-9	1	6	27,1590	26.9168
-9	2	6	4,5180	2.2714
-9	3	6	27,8500	28.4239
-9	4	6	21,8540	22.2103
-9	5	6	30,1520	30.6892
-9	6	6	15,3080	14.2035
-9	7	6	33,9050	33.2497
-9	8	6	28,6290	26.4376
-9	9	6	11,4630	12.5588
-9	10	6	11,4840	11.8236
-9	11	6	6,7070	5.2063
-9	12	6	12,7670	12.6785
-9	14	6	7,3690	5.6718
-9	15	6	10,6450	8.0185
-9	16	6	5,7990	4.4276
-10	0	6	29,2660	30.4274
-10	1	6	46,9210	49.7799
-10	2	6	27,2970	27.5601
-10	3	6	40,1260	42.4692
-10	4	6	10,1950	6.1064
-10	5	6	13,0790	12.9201
-10	7	6	5,5420	1.1697
-10	8	6	7,9460	5.6548
-10	9	6	7,4960	6.0244
-10	10	6	6,1580	6.4867
-10	11	6	7,9780	6.8786
-10	12	6	10,1490	9.7211
-10	13	6	18,4910	18.8017
-10	15	6	15,7570	15.6159
-11	0	6	4,6600	2.1136
-11	1	6	23,7290	22.0905
-11	2	6	32,1490	34.9332
-11	3	6	31,1850	30.3247
-11	5	6	15,4200	14.7080
-11	6	6	10,2610	10.3062
-11	7	6	13,2740	13.5154
-11	8	6	10,7610	11.1034
-11	9	6	24,6730	23.2436
-11	10	6	14,2110	14.8839
-11	11	6	20,8990	19.4672
0	1	7	27,5700	26.7745
0	2	7	52,3800	52.6450
0	3	7	22,1490	21.1656
0	4	7	26,4340	27.6861
0	5	7	25,7760	25.6443
0	6	7	35,5900	32.0645
0	7	7	6,2990	7.1049
0	8	7	19,4080	20.1208
0	9	7	16,3590	17.4514
0	10	7	22,0840	20.4174
0	11	7	8,9720	8.4534
0	12	7	16,6810	17.3605
0	13	7	17,2070	16.9572
0	15	7	7,0100	7.6152
0	16	7	13,2580	12.7016
0	17	7	13,5800	13.6960
1	1	7	19,2960	19.3786
-1	1	7	28,5440	30.4477
1	2	7	15,0530	16.0763
-1	2	7	71,8400	72.6439
-1	3	7	68,7360	69.5413
1	4	7	7,9530	7.7344
-1	4	7	24,4620	24.3394
1	5	7	19,6490	20.4002
-1	5	7	61,4050	63.3702
1	6	7	31,6170	34.2177
-1	6	7	8,3980	2.9419
1	7	7	20,5720	19.7340
-1	7	7	13,2190	10.1536
-1	8	7	32,5340	32.9325
1	9	7	33,3850	34.5599
-1	9	7	7,4410	8.4188
1	10	7	15,1440	14.6034
-1	10	7	18,0910	20.2153
1	11	7	5,1270	6.8994
-1	11	7	5,9530	5.7816
-1	12	7	7,4310	5.9244
1	13	7	11,7180	12.3263
1	14	7	5,9950	4.6308
-1	14	7	7,7280	7.5006
1	15	7	5,7490	4.3965
-1	15	7	9,2090	8.3818
1	16	7	7,0710	5.5424
-1	16	7	13,6230	12.2615
-1	17	7	8,3370	9.2666
-1	18	7	7,3020	7.9904
2	1	7	8,7010	7.8303
-2	1	7	19,7180	21.2244
2	2	7	16,7350	14.2066
-2	2	7	22,6360	23.7954
-2	3	7	80,7280	82.6363
2	4	7	5,8580	1.7231
-2	4	7	66,5660	63.7208
2	5	7	5,7300	2.9080
-2	5	7	50,2910	51.0289
2	6	7	31,5400	30.5966
-2	6	7	14,5600	16.1207
-2	7	7	21,9360	23.6581
-2	8	7	17,6930	16.0080
2	9	7	29,1280	30.0794
-2	9	7	5,0960	3.5651
2	10	7	22,0600	23.0755
-2	10	7	19,8920	19.9743
2	11	7	10,2900	9.7320
-2	11	7	7,1300	8.5101
2	12	7	14,4040	14.9040
2	13	7	9,1620	9.4363
-2	13	7	12,0910	13.1422
2	14	7	6,9490	6.4540
-2	14	7	7,4690	7.4255
-2	15	7	5,5210	5.6506
-2	16	7	13,6940	13.0828
-2	17	7	7,9080	7.9209
3	1	7	10,9690	10.3762
-3	1	7	68,5250	70.8970
3	2	7	25,8450	25.1165
-3	2	7	12,4620	13.4241
3	3	7	6,4340	8.5103
-3	3	7	15,3510	12.8479
3	4	7	19,6870	21.7176
-3	4	7	24,7310	23.3185
3	5	7	5,6030	4.4885
-3	5	7	66,0890	69.0780
3	6	7	20,1000	17.6324
-3	6	7	49,5450	51.3809
3	7	7	4,9530	4.9165
-3	7	7	45,6560	46.2435
3	8	7	5,2210	4.1516
-3	8	7	13,5990	11.1566
3	9	7	6,8670	6.5920
-3	9	7	6,6890	5.2438
3	10	7	24,0760	24.5363
-3	10	7	42,3650	42.0812
3	12	7	6,2050	6.2217
-3	12	7	22,1380	20.8947
-3	13	7	37,4920	38.1725
-3	14	7	29,3990	31.0909
-3	15	7	26,6900	25.3805
-3	16	7	15,5400	16.7797
-3	17	7	24,4500	26.0384
4	1	7	8,1590	6.2439
-4	1	7	30,1310	34.3345
4	2	7	9,8770	7.0849
-4	2	7	10,5110	6.6606
-4	3	7	52,7320	53.9911
4	4	7	5,4810	4.2604
-4	4	7	26,6790	25.7622
4	5	7	4,9970	5.2427
-4	5	7	6,5740	.5447
4	6	7	23,1580	25.7765
-4	6	7	12,7200	13.1542
4	7	7	8,6440	8.3161
-4	7	7	23,9000	23.7700
4	8	7	12,5430	11.0368
-4	8	7	12,7890	13.4427
-4	9	7	31,8670	31.8948
-4	10	7	23,9180	23.8511
-4	11	7	4,0900	4.8979
-4	12	7	21,7570	19.7798
-4	13	7	45,7800	45.7551
-4	14	7	21,0140	20.6208
-4	15	7	12,5990	12.6325
-4	16	7	16,8440	18.8280
-4	17	7	38,9440	39.4074
-4	19	7	6,4230	3.9973
-5	1	7	52,6380	57.7132
-5	2	7	17,0160	17.9296
-5	3	7	34,5880	31.4932
-5	4	7	14,0490	16.0228
-5	5	7	87,3520	91.7722
-5	6	7	23,8110	23.4813
-5	7	7	4,6470	5.0311
-5	9	7	65,8160	63.2666
-5	10	7	29,2130	28.7360
-5	11	7	8,5980	6.5955
-5	12	7	15,0010	14.4785
-5	13	7	12,9660	13.6824
-5	14	7	6,4040	4.9590
-5	15	7	10,2390	10.1928
-5	16	7	12,8290	13.3579
-5	17	7	16,3290	15.6870
-5	18	7	16,7760	16.8473
-6	1	7	43,5090	45.3045
-6	2	7	6,2780	3.7973
-6	3	7	19,6030	18.7219
-6	4	7	18,8500	16.3939
-6	5	7	81,2500	84.1643
-6	6	7	12,7350	12.3892
-6	7	7	28,1740	29.0297
-6	8	7	5,7070	5.8811
-6	9	7	80,0190	82.2890
-6	10	7	17,7520	17.9595
-6	11	7	4,3470	3.3520
-6	12	7	12,3340	11.0124
-6	13	7	27,7000	29.3129
-6	14	7	5,5600	3.9293
-6	15	7	13,4270	13.7798
-6	17	7	10,7260	12.0052
-6	19	7	6,4590	6.5537
-7	1	7	26,2650	27.4644
-7	2	7	8,7210	7.9785
-7	3	7	48,4450	47.8030
-7	4	7	16,9710	15.3775
-7	5	7	22,2430	23.5578
-7	6	7	25,5350	24.4394
-7	7	7	16,4630	17.3534
-7	8	7	8,9110	11.1039
-7	9	7	64,8650	67.5052
-7	10	7	19,0620	19.3223
-7	11	7	24,2120	22.1803
-7	12	7	19,5250	18.0352
-7	13	7	21,3410	21.0396
-7	14	7	32,2200	30.2506
-7	15	7	6,4260	4.7524
-7	16	7	8,6580	9.2064
-7	17	7	18,3210	19.0266
-8	1	7	24,0870	28.2987
-8	2	7	16,8320	16.8865
-8	3	7	41,0850	41.8143
-8	4	7	5,2320	5.4282
-8	5	7	23,5550	24.3677
-8	6	7	4,3070	3.5014
-8	8	7	24,0260	23.0179
-8	9	7	41,5770	43.9152
-8	10	7	12,7150	12.2398
-8	11	7	11,7590	12.9080
-8	12	7	20,4460	19.2772
-8	13	7	9,9130	8.5745
-8	14	7	40,2160	41.1336
-8	17	7	30,6600	32.3858
-9	1	7	45,2020	44.4402
-9	2	7	6,1600	5.6063
-9	3	7	32,0310	30.7692
-9	4	7	10,2280	10.9246
-9	5	7	32,0210	29.7750
-9	6	7	20,8490	23.1414
-9	7	7	20,4430	18.3308
-9	8	7	23,9780	24.1916
-9	9	7	29,6020	28.5044
-9	10	7	15,0010	15.9699
-9	11	7	15,3720	14.2717
-9	12	7	7,2060	5.4849
-9	13	7	14,6960	14.3527
-9	14	7	20,3470	20.1534
-9	15	7	17,7560	19.5909
-9	16	7	13,2210	16.8952
-10	1	7	40,0360	38.0263
-10	2	7	32,6110	31.7166
-10	3	7	19,1360	18.9149
-10	4	7	20,2490	20.2406
-10	5	7	25,1280	23.8708
-10	6	7	18,3620	17.9446
-10	7	7	24,3560	24.8687
-10	8	7	22,5660	24.6389
-10	9	7	10,9290	11.3589
-10	11	7	7,1220	6.6506
-10	12	7	24,5600	24.5785
-10	13	7	11,3630	11.7444
-10	14	7	13,2210	12.0492
-10	15	7	5,6530	4.0035
-11	1	7	22,7770	22.4284
-11	2	7	36,8890	37.4611
-11	3	7	15,3600	14.5739
-11	4	7	22,3920	22.3921
-11	5	7	6,0330	4.6168
-11	6	7	9,2970	11.4629
-11	8	7	31,7000	34.3694
-11	9	7	5,4450	4.1116
-11	10	7	14,2200	14.7672
-11	11	7	6,3200	6.1846
-11	12	7	9,0170	8.9451
-11	13	7	22,0900	21.0445
0	0	8	4,5650	5.3087
0	1	8	18,5630	21.2561
0	2	8	17,6930	17.1716
0	3	8	5,0030	2.8396
0	4	8	5,0240	3.4234
0	5	8	28,5860	30.4691
0	6	8	6,3880	5.3435
0	7	8	33,6410	33.2387
0	8	8	5,9410	6.4732
0	9	8	20,3500	21.2950
0	10	8	10,6770	9.9130
0	11	8	13,9030	15.4200
0	12	8	29,9120	29.7490
0	13	8	6,1560	5.7539
0	15	8	26,9090	26.7299
-1	0	8	21,0610	20.7053
1	1	8	8,9570	8.3890
-1	1	8	23,7830	23.5871
1	2	8	4,8140	4.0114
-1	2	8	11,4570	10.7172
1	3	8	7,7490	5.5098
-1	3	8	31,1340	34.9459
1	4	8	9,3570	9.6797
-1	4	8	5,4030	3.4557
1	5	8	5,5990	4.3325
-1	5	8	21,9030	21.9433
-1	6	8	23,7430	24.6630
1	7	8	46,3290	47.7599
-1	7	8	9,2760	7.7166
-1	8	8	19,1070	19.0063
1	9	8	9,6300	10.0342
-1	9	8	21,0190	21.0587
1	10	8	7,4020	5.8803
-1	10	8	15,7220	15.8441
1	11	8	11,6560	11.1922
-1	11	8	20,6140	21.3693
1	12	8	21,5500	21.8803
-1	12	8	16,6590	16.2289

H	K	L	Y(OBS)	Y(CALC)
-1	13	8	5.2130	7.3604
-1	15	8	21.9330	22.1540
2	0	8	10.7410	10.0159
-2	0	8	5.1000	4.4749
2	1	8	8.2230	9.0285
-2	1	8	27.5240	30.1307
2	2	8	9.3060	8.7175
-2	2	8	10.5400	10.5769
2	3	8	25.3130	26.9544
-2	3	8	49.1320	52.1389
-2	4	8	15.9540	17.2068
-2	5	8	13.2300	9.7492
2	6	8	10.6560	9.4822
-2	6	8	15.2460	17.0603
2	7	8	21.4590	22.4810
-2	7	8	21.6760	24.4119
2	8	8	5.4930	5.4963
-2	8	8	17.9740	18.1126
2	10	8	16.7290	18.1105
-2	10	8	25.0470	26.0319
2	11	8	20.2340	20.1082
-2	11	8	15.3330	17.3339
-2	12	8	23.8820	23.5981
-2	13	8	20.4370	20.8307
-2	13	8	21.3690	20.6307
-2	14	8	7.5030	7.1835
-2	16	8	17.3830	17.2967
-2	17	8	16.0730	15.5375
-3	0	8	11.1450	10.4148
3	1	8	10.5400	10.2883
-3	1	8	36.7760	39.2575
-3	2	8	34.9550	35.3249
3	3	8	15.4850	14.8627
-3	3	8	12.7210	10.9497
-3	4	8	59.4420	63.0285
3	5	8	14.0460	15.7950
-3	5	8	14.9140	11.9112
3	6	8	14.0750	13.9451
-3	6	8	17.9610	17.5702
3	7	8	13.1050	11.9915
-3	7	8	28.6760	28.5413
3	8	8	10.4180	10.7580
-3	8	8	34.3460	35.8131
-3	9	8	19.4200	18.4033
-3	10	8	22.7600	21.4365
-3	11	8	14.0730	13.7588
-3	12	8	14.4270	14.2771
-3	14	8	25.2410	25.4843
-3	15	8	36.9840	38.1220
-3	16	8	5.3470	3.5459
-3	17	8	16.3130	15.4856
4	0	8	10.0100	12.1536
-4	0	8	7.5590	7.6045
4	1	8	15.1590	16.5402
-4	1	8	36.6130	39.6824
-4	2	8	3.0610	3.1068
-4	3	8	4.9850	6.6034
-4	4	8	5.9830	5.1006
-4	5	8	19.0250	18.3075
-4	6	8	76.1890	74.7395
-4	7	8	29.2980	32.1444
-4	8	8	11.0610	10.6879
-4	9	8	16.0160	15.8281
-4	10	8	12.5930	12.8942
-4	11	8	35.6910	36.1459
-4	12	8	22.9170	22.0109
-4	13	8	12.7290	12.0586
-4	14	8	45.4170	45.1374
-4	15	8	26.3150	26.4285
-4	16	8	8.0900	5.8028
-4	17	8	5.1470	5.8514
-4	18	8	18.3670	17.5631
-5	0	8	75.5470	76.6855
-5	1	8	21.6450	22.9423
-5	2	8	5.0840	1.5510
-5	3	8	15.7170	15.3972
-5	4	8	65.2290	64.9501
-5	5	8	25.0210	26.1248
-5	6	8	18.9510	19.0461
-5	7	8	22.2900	21.2864
-5	8	8	11.2950	11.4892
-5	10	8	10.5080	10.2771
-5	11	8	26.7860	26.2434
-5	12	8	6.3390	6.4174
-5	13	8	5.1140	5.8547
-5	15	8	12.2080	11.4161
-5	16	8	11.8130	12.1311
-5	17	8	12.1370	12.6204
-5	18	8	18.6940	16.9093
-6	0	8	15.8340	15.1911
-6	1	8	8.6840	7.1300
-6	2	8	6.2550	2.5399
-6	3	8	8.6970	10.8100
-6	4	8	41.0130	39.3221
-6	5	8	16.8970	16.0291
-6	6	8	14.1500	13.1735
-6	7	8	15.2420	15.3955
-6	8	8	46.7730	44.5561
-6	10	8	20.5110	20.1946
-6	11	8	20.8890	21.2546
-6	12	8	16.3480	15.7864
-6	13	8	14.6270	12.4584
-6	14	8	16.1440	14.5983
-6	15	8	8.4410	7.8390
-6	16	8	10.8530	9.9963
-6	18	8	18.5690	17.1309
-7	0	8	51.9170	55.3706
-7	2	8	40.4210	42.1865

H	K	L	Y(OBS)	Y(CALC)
-7	3	8	10.3310	9.4514
-7	4	8	21.0330	24.6594
-7	5	8	4.4490	5.6185
-7	6	8	16.1720	15.8330
-7	7	8	26.8850	26.7508
-7	8	8	42.7770	45.4382
-7	9	8	4.3050	3.5505
-7	10	8	26.0050	25.4384
-7	11	8	36.6820	35.3644
-7	12	8	22.4580	21.6878
-7	13	8	10.3690	9.5381
-7	15	8	16.4420	16.5195
-7	17	8	15.9040	17.8324
-7	18	8	15.5520	15.0649
-8	0	8	5.2830	1.6702
-8	1	8	20.9070	19.4184
-8	2	8	23.0100	23.1512
-8	3	8	3.9520	3.2072
-8	4	8	7.4250	8.0921
-8	5	8	9.9980	11.1437
-8	6	8	20.9010	23.1780
-8	7	8	28.7780	26.4559
-8	8	8	44.4400	45.1352
-8	10	8	41.7000	43.7508
-8	11	8	19.3200	19.9838
-8	12	8	29.5530	27.5271
-8	13	8	33.1950	33.6208
-8	15	8	8.9200	9.0620
-8	17	8	11.1100	10.9212
-9	0	8	29.5490	34.1166
-9	1	8	15.0620	17.0546
-9	2	8	12.5650	13.9138
-9	3	8	4.1190	6.5063
-9	4	8	41.3480	42.4560
-9	5	8	6.7770	5.8500
-9	6	8	40.0670	40.9024
-9	7	8	13.9370	11.8668
-9	8	8	37.7340	38.9534
-9	10	8	28.0780	28.7269
-9	11	8	6.1110	5.3645
-9	12	8	14.7830	13.5052
-9	13	8	29.0640	28.3219
-9	14	8	14.4560	13.5468
-9	16	8	20.5770	19.4772
-10	0	8	11.4820	12.3456
-10	2	8	12.4920	12.4977
-10	3	8	17.5170	17.0219
-10	4	8	39.5880	40.0763
-10	6	8	23.1910	21.0691
-10	7	8	9.2700	9.3215
-10	8	8	40.4360	41.8811
-10	9	8	8.6910	8.7238
-10	12	8	10.4850	8.3166
-10	14	8	8.6330	8.4828
-10	15	8	8.4120	7.9845
-11	0	8	14.0770	15.4672
-11	1	8	7.5100	7.8483
-11	3	8	16.6800	17.1058
-11	4	8	18.7230	20.5300
-11	5	8	27.6450	28.3611
-11	6	8	5.7910	4.7161
-11	8	8	9.0120	8.9168
-11	9	8	19.4300	17.6475
-11	10	8	13.0050	13.4327
-11	11	8	9.7880	8.9307
-11	12	8	30.0530	29.0642
-11	13	8	11.0030	10.5057
0	1	9	13.0860	11.1418
0	2	9	12.7510	12.8334
0	4	9	16.7990	17.5519
0	5	9	7.9080	9.2780
0	6	9	22.7390	22.5709
0	8	9	27.2890	28.1554
0	9	9	14.1920	16.3282
0	10	9	10.6910	10.1558
0	11	9	11.4980	12.5671
0	12	9	6.5660	6.4323
0	13	9	22.0170	21.9570
0	14	9	22.2130	22.1859
1	2	9	21.3700	24.9899
-1	2	9	20.2560	22.2064
1	3	9	9.9570	9.1100
-1	3	9	29.6880	30.3250
1	4	9	14.8410	15.7425
-1	4	9	4.5430	1.6999
1	5	9	9.9940	9.3575
-1	5	9	6.9770	7.7538
1	6	9	16.7190	17.6920
-1	6	9	37.4740	40.6273
1	7	9	6.9130	6.1867
-1	7	9	11.7930	13.6676
1	8	9	14.0710	13.6680
-1	8	9	24.7500	24.5900
1	9	9	14.6930	14.8626
-1	10	9	19.7350	21.4446
1	11	9	12.9920	13.8812
-1	11	9	14.6540	15.4862
-1	12	9	10.2050	9.6128
-1	13	9	26.0440	27.5219
-1	14	9	24.5200	24.2466
2	1	9	6.5160	5.0293
-2	1	9	14.9720	13.7579
2	2	9	29.0560	30.6798
-2	2	9	22.3650	21.4950
-2	3	9	25.3540	24.1353
-2	4	9	42.4090	42.6840
2	6	9	11.3710	10.1435
-2	6	9	17.3280	15.8978

H	K	L	Y(OBS)	Y(CALC)
2	7	9	7.9300	9.3583
-2	7	9	15.2150	15.3689
2	8	9	6.6700	6.7937
-2	8	9	21.3600	22.6573
-2	9	9	27.1030	25.6744
-2	10	9	15.9890	16.0552
-2	11	9	14.7440	14.7398
-2	12	9	5.0040	3.5248
-2	13	9	10.8710	10.4966
-2	14	9	15.7560	15.3348
-2	15	9	23.6340	24.0591
-2	16	9	5.2810	4.5779
3	1	9	9.6530	8.8130
-3	1	9	8.2740	8.7423
3	2	9	19.4110	19.2636
-3	2	9	17.7770	18.4500
-3	3	9	30.1210	31.2418
-3	4	9	22.6870	22.8232
-3	5	9	34.0680	32.6989
-3	6	9	20.5790	22.9713
-3	7	9	29.9760	30.0739
-3	8	9	14.6630	14.7360
-3	9	9	27.5280	23.2472
-3	10	9	37.7150	37.4648
-3	12	9	5.8350	3.4002
-3	14	9	26.7780	25.3014
-3	15	9	14.5140	13.8438
-3	16	9	19.4320	18.4892
-3	17	9	20.6820	19.3938
-4	1	9	6.9290	5.9921
-4	2	9	12.7250	11.7210
-4	3	9	31.8990	28.2019
-4	4	9	7.6580	7.8397
-4	5	9	5.4460	4.1430
-4	6	9	25.5440	25.4013
-4	7	9	11.1380	11.6717
-4	8	9	5.0360	2.7698
-4	10	9	41.3450	38.9936
-4	11	9	7.1140	4.4226
-4	12	9	21.9450	21.2970
-4	13	9	29.3130	28.5280
-4	14	9	31.5580	31.9092
-4	15	9	8.3380	7.4697
-4	16	9	32.0980	29.3789
-4	18	9	6.3400	4.1793
-5	1	9	15.7160	14.3532
-5	2	9	51.0240	51.4624
-5	3	9	14.8880	14.1405
-5	4	9	6.1680	7.3993
-5	5	9	9.0890	5.5632
-5	6	9	13.2130	14.3644
-5	7	9	5.0080	3.5506
-5	8	9	5.1440	4.4583
-5	9	9	5.8430	3.9779
-5	10	9	11.4640	11.1467
-5	11	9	6.0410	5.1122
-5	12	9	32.2190	31.2383
-5	13	9	6.5530	7.3103
-5	14	9	6.4550	5.0380
-5	15	9	10.3610	11.3164
-5	16	9	23.6400	22.7586
-5	17	9	7.7680	6.9530
-6	1	9	47.4460	51.4794
-6	2	9	27.1320	31.0482
-6	3	9	44.3980	44.6799
-6	4	9	34.7820	32.6616
-6	5	9	11.6520	11.7182
-6	6	9	40.3240	40.6890
-6	7	9	9.0700	7.3903
-6	9	9	17.0550	17.1555
-6	10	9	26.0850	27.2374
-6	11	9	9.1960	10.4501
-6	12	9	14.9400	13.8208
-6	16	9	20.6930	18.9062
-6	17	9	15.1720	13.2782
-7	1	9	56.9540	55.0324
-7	2	9	19.0610	17.4312
-7	3	9	8.0090	7.0028
-7	4	9	8.6450	7.8918
-7	6	9	13.0100	12.8364
-7	7	9	26.6640	25.1658
-7	8	9	12.8060	11.4914
-7	9	9	11.6990	12.5576
-7	10	9	12.5330	13.4598
-7	11	9	14.1290	14.3990
-7	12	9	21.4980	21.3465
-7	14	9	31.3940	30.5264
-7	15	9	7.4740	6.0112
-7	16	9	8.2050	8.5087
-7	17	9	14.4890	13.3903
-7	18	9	7.4930	5.6206
-8	1	9	44.0790	43.7252
-8	2	9	11.7120	12.7731
-8	3	9	4.3380	1.0222
-8	5	9	15.2450	13.9111
-8	6	9	9.0630	8.5068
-8	7	9	6.1150	6.0366
-8	9	9	29.2170	28.8533
-8	10	9	34.3760	33.4343
-8	11	9	8.0120	9.4183
-8	12	9	24.8480	22.4174
-8	13	9	5.6290	5.3864
-8	14	9	20.8600	20.5940
-8	15	9	18.1490	18.7461
-8	17	9	19.9130	20.1770
-9	1	9	13.5080	12.4803
-9	2	9	15.1910	15.8417
-9	3	9	21.1450	19.8266

H	K	L	Y(OBS)	Y(CALC)
-9	4	9	6.6280	6.6234
-9	5	9	19.7820	19.2205
-9	6	9	4.7930	1.6137
-9	7	9	7.3310	7.6389
-9	8	9	6.0660	3.5517
-9	9	9	43.3420	43.0741
-9	10	9	26.6910	27.0019
-9	12	9	11.8170	12.0160
-9	13	9	6.4250	5.5570
-9	14	9	11.3630	9.6348
-9	16	9	6.1420	5.7513
-10	1	9	23.4610	26.1654
-10	2	9	10.6950	10.2991
-10	4	9	19.4640	16.8352
-10	5	9	80.7300	81.4389
-10	6	9	10.5970	8.8356
-10	7	9	4.6330	3.8048
-10	8	9	23.1320	21.8517
-10	9	9	29.0000	27.9449
-10	10	9	20.2650	20.2450
-10	11	9	15.3410	16.4656
-10	12	9	14.8980	15.1806
-10	13	9	12.6720	10.2850
-10	14	9	15.7250	14.3260
-10	15	9	11.3330	12.1398
-11	1	9	5.9950	6.4324
-11	2	9	11.4850	11.8392
-11	4	9	27.1160	30.2543
-11	5	9	29.9710	29.0687
-11	6	9	20.6730	23.6373
-11	7	9	7.3100	8.2391
-11	8	9	12.7980	10.8696
-11	9	9	21.2250	19.0573
-11	10	9	9.1610	8.3991
-11	11	9	9.8300	11.0785
-11	12	9	7.9340	8.7810
-11	13	9	35.0140	34.4055
-11	14	9	22.3890	22.3036
0	0	10	11.1330	12.7007
0	1	10	18.8610	21.8217
0	2	10	14.1740	14.7967
0	4	10	13.2600	11.8496
0	6	10	10.0710	10.7045
0	7	10	5.7570	5.8903
0	8	10	21.9170	21.3432
0	11	10	6.0790	7.5184
1	0	10	4.9050	1.2000
-1	0	10	4.6910	4.1253
1	1	10	15.1980	15.3478
-1	1	10	22.7060	22.7149
1	2	10	9.6000	9.7053
1	3	10	7.5040	6.7972
-1	3	10	8.7450	8.7569
1	4	10	14.6650	13.5728
-1	4	10	21.6620	18.6470
1	5	10	11.5930	10.9188
-1	5	10	10.3090	10.6819
-1	6	10	21.5160	22.3711
1	7	10	10.4350	10.2791
-1	7	10	26.4280	25.6363
1	8	10	17.7920	18.4453
-1	8	10	22.6390	21.1174
-1	9	10	16.9850	17.7922
-1	12	10	29.4740	30.8212
-1	13	10	7.0720	5.7411
2	0	10	25.4180	24.7347
-2	0	10	8.7840	6.4411
2	1	10	8.9010	8.8093
-2	1	10	4.9450	4.2928
-2	2	10	8.2050	8.9151
-2	3	10	9.4950	11.0676
-2	4	10	23.3610	24.2758
-2	5	10	13.3960	15.2367
-2	6	10	34.0600	35.9691
-2	7	10	37.2510	38.2978
-2	8	10	5.1160	3.0395
-2	9	10	22.5550	22.2658
-2	10	10	8.3250	8.7210
-2	11	10	14.9000	15.6958
-2	12	10	22.6270	22.2076
-2	15	10	9.1580	8.8363
-3	0	10	21.4380	20.5447
-3	1	10	5.1300	2.6406
-3	2	10	6.4950	2.9647
-3	3	10	21.4860	20.9523
-3	4	10	10.7900	9.0798
-3	5	10	23.4330	24.3763
-3	6	10	28.0490	28.7556
-3	7	10	49.2930	49.6755
-3	8	10	5.6180	4.3481
-3	9	10	14.4360	15.9486
-3	10	10	13.2540	14.8598
-3	11	10	30.6450	30.6986
-3	14	10	16.9160	17.6228
-3	15	10	5.1220	4.7411
-4	0	10	60.9420	62.1807
-4	1	10	20.5300	21.1168
-4	2	10	18.0360	18.4295
-4	3	10	12.3300	11.6452
-4	4	10	15.1260	14.2803
-4	5	10	23.2190	22.9127
-4	6	10	5.6550	5.0484
-4	7	10	36.9440	36.6215
-4	8	10	11.9970	12.1576
-4	9	10	25.1880	26.0802
-4	10	10	22.4050	22.2260
-4	11	10	32.4870	32.1222
-4	12	10	7.6390	6.9343

H	K	L	Y(OBS)	Y(CALC)
-4	13	10	5.1090	6.2914
-4	14	10	15.1100	14.6534
-4	15	10	33.5210	35.6630
-5	0	10	58.9490	61.7298
-5	1	10	40.9030	42.0163
-5	2	10	8.6340	8.5555
-5	3	10	7.1680	4.8552
-5	4	10	24.4000	22.0866
-5	5	10	24.7110	24.3463
-5	6	10	8.3920	7.4898
-5	7	10	10.5570	8.4792
-5	8	10	10.3270	8.8052
-5	10	10	22.2310	22.1565
-5	11	10	20.6150	19.3525
-5	12	10	10.7590	7.2864
-5	13	10	27.5240	26.4527
-5	14	10	16.5570	15.3460
-5	15	10	20.1590	18.4547
-5	16	10	5.9980	7.0227
-6	0	10	8.4970	8.0977
-6	1	10	52.2720	51.0929
-6	2	10	10.9510	10.9598
-6	3	10	36.0830	35.6517
-6	4	10	9.3820	10.4062
-6	5	10	47.6850	47.0046
-6	6	10	22.5100	22.4873
-6	7	10	20.5970	16.9230
-6	8	10	22.7070	23.3351
-6	10	10	15.5780	17.0614
-6	11	10	12.2970	12.2762
-6	12	10	12.3920	11.0078
-6	13	10	33.4470	31.3345
-6	14	10	6.5170	6.1344
-6	15	10	7.1520	4.9050
-6	16	10	9.6390	9.5714
-6	17	10	9.9200	11.3959
-7	0	10	13.9320	15.6045
-7	1	10	47.6020	48.2118
-7	2	10	11.6000	11.9142
-7	3	10	37.6910	37.4713
-7	4	10	5.7220	3.8393
-7	5	10	34.1760	36.3636
-7	7	10	6.7980	6.7430
-7	8	10	12.4450	11.2588
-7	9	10	7.6070	6.2466
-7	11	10	9.0570	8.1070
-7	12	10	7.4960	9.2930
-7	13	10	16.2200	16.1011
-7	14	10	19.7040	20.7172
-7	15	10	25.2580	25.8035
-7	17	10	16.5510	14.9789
-8	0	10	40.1790	40.2830
-8	1	10	50.3270	54.5558
-8	2	10	8.2560	8.6830
-8	3	10	25.1830	26.9329
-8	4	10	9.6970	7.5680
-8	5	10	25.6520	24.3895
-8	6	10	30.1560	29.8991
-8	7	10	16.0920	15.9101
-8	8	10	16.0960	17.0084
-8	9	10	8.0670	6.8760
-8	11	10	8.6690	7.5350
-8	12	10	6.6160	5.1350
-8	13	10	10.2590	9.8227
-8	14	10	15.2690	16.1983
-8	15	10	33.1480	32.0694
-8	16	10	10.3550	9.9375
-9	0	10	37.1490	36.4037
-9	1	10	28.1720	29.9795
-9	2	10	28.5780	29.6329
-9	3	10	5.6130	2.4134
-9	4	10	5.5610	3.6124
-9	5	10	15.1220	17.0880
-9	6	10	22.5590	23.6441
-9	7	10	28.2750	29.3675
-9	8	10	18.4300	18.0679
-9	9	10	17.6760	19.2572
-9	10	10	16.1990	16.7625
-9	11	10	7.9840	6.7308
-9	13	10	7.7440	7.2957
-9	14	10	14.9270	14.5759
-9	15	10	22.2000	21.6661
-9	16	10	8.6200	7.7184
-10	0	10	13.5780	15.6879
-10	1	10	23.5830	24.9947
-10	2	10	6.8870	5.0626
-10	3	10	37.4360	35.7376
-10	4	10	31.7500	31.5558
-10	5	10	5.8370	4.9903
-10	6	10	14.5010	14.5159
-10	7	10	45.6940	44.2898
-10	8	10	12.9650	11.7182
-10	10	10	6.6730	3.8094
-10	11	10	17.7890	16.8841
-10	12	10	4.9430	3.3314
-10	13	10	15.7470	14.7799
-10	15	10	13.1510	12.2946
-11	0	10	6.6140	6.6824
-11	1	10	9.3610	9.0262
-11	2	10	7.9360	9.1429
-11	3	10	13.2290	12.5708
-11	4	10	15.2480	14.9865
-11	6	10	10.2210	9.5553
-11	7	10	14.6020	11.3649
-11	8	10	11.7410	10.1183
-11	9	10	24.3450	24.8804
-11	10	10	27.0420	28.4376
-11	11	10	33.1560	34.2911

H	K	L	Y(OBS)	Y(CALC)
-11	12	10	8.6260	9.7752
-11	13	10	22.4560	23.6450
0	1	11	10.6390	11.3555
0	2	11	11.9250	9.6729
0	3	11	13.9170	14.5931
0	5	11	15.0510	14.5343
0	6	11	7.3710	7.7637
0	7	11	16.5830	17.1258
0	8	11	20.3540	19.1297
-1	1	11	15.7920	15.8837
-1	2	11	28.6800	28.0438
-1	3	11	10.2710	9.4708
-1	4	11	8.6210	9.9000
-1	5	11	16.0680	13.5794
-1	6	11	7.3480	8.1966
-1	7	11	13.9020	14.0262
-1	8	11	14.4850	14.8788
-1	9	11	9.4330	7.4974
-1	10	11	11.2680	11.7438
-1	11	11	6.2410	6.9922
-2	1	11	7.0240	5.5971
-2	3	11	9.4740	7.7193
-2	4	11	25.0520	25.8677
-2	5	11	22.6450	23.9145
-2	6	11	27.0690	28.1301
-2	7	11	11.8100	11.5603
-2	9	11	18.2240	17.0618
-2	10	11	5.9750	5.9440
-2	11	11	12.9470	13.2726
-2	13	11	22.1580	21.5719
-3	1	11	10.0120	9.3854
-3	2	11	11.5190	12.4193
-3	3	11	5.9420	2.8593
-3	4	11	18.6430	19.3026
-3	5	11	33.2340	32.0247
-3	6	11	21.8230	21.9306
-3	7	11	5.1770	4.1576
-3	8	11	30.6840	31.9391
-3	9	11	27.4160	26.2345
-3	10	11	15.3310	15.6457
-3	12	11	8.6900	9.3437
-3	13	11	17.6930	17.5092
-4	1	11	12.7460	11.6863
-4	2	11	10.6850	10.3393
-4	3	11	7.4730	4.6875
-4	4	11	24.3470	24.8022
-4	5	11	4.9380	1.9020
-4	6	11	25.9050	25.9863
-4	7	11	8.9620	8.3422
-4	8	11	24.6220	24.7470
-4	9	11	30.6200	29.7010
-4	10	11	54.8160	54.7095
-4	11	11	31.9630	31.6357
-4	12	11	13.7420	13.8606
-4	13	11	26.6750	27.6830
-4	14	11	19.5640	18.6169
-5	1	11	26.0660	29.2959
-5	3	11	24.6790	26.4577
-5	4	11	17.9110	18.7079
-5	5	11	23.9630	24.3350
-5	6	11	7.6680	8.5566
-5	7	11	8.0050	7.5531
-5	8	11	30.8940	31.8245
-5	9	11	35.2530	34.7406
-5	10	11	27.8850	26.1762
-5	11	11	6.1690	6.3737
-5	12	11	26.1020	27.3254
-5	13	11	15.8360	15.8839
-5	14	11	30.7500	30.7531
-5	15	11	14.5790	13.0017
-6	1	11	11.9330	12.5627
-6	2	11	37.9960	37.7656
-6	3	11	29.6240	31.6415
-6	4	11	13.7160	13.8677
-6	5	11	9.6550	9.2115
-6	6	11	32.3350	32.8546
-6	7	11	24.5200	24.2833
-6	8	11	19.4140	19.5885
-6	9	11	5.6840	5.4313
-6	10	11	24.1600	22.5745
-6	11	11	8.8330	9.0442
-6	12	11	12.3260	10.0284
-6	13	11	8.8790	7.9000
-6	14	11	13.3570	11.1969
-6	15	11	16.6720	16.9970
-6	16	11	5.2090	6.6175
-7	1	11	36.8670	37.7042
-7	2	11	47.8820	48.5700
-7	3	11	38.1100	40.8674
-7	4	11	7.8500	8.6677
-7	5	11	7.7110	7.8381
-7	6	11	34.2270	33.4521
-7	7	11	19.0600	19.9312
-7	8	11	8.2620	7.5580
-7	10	11	24.7190	24.2300
-7	11	11	25.3430	23.9768
-7	12	11	15.1410	15.0894
-7	14	11	10.3410	9.7182
-7	15	11	19.4350	17.7976
-7	16	11	12.0210	12.1505
-8	1	11	11.5560	10.3465
-8	2	11	48.3880	49.9174
-8	3	11	21.3260	21.1151
-8	4	11	6.3940	6.3501
-8	5	11	11.6490	12.7135
-8	6	11	31.9350	33.3501
-8	7	11	25.1090	25.3684
-8	8	11	5.3630	2.7556

H	K	L	Y(OBS)	Y(CALC)
-8	9	11	17.4250	17.4434
-8	10	11	5.9600	5.1433
-8	11	11	20.0560	20.3598
-8	12	11	13.6200	11.4871
-8	13	11	5.7630	4.0542
-8	14	11	24.0830	22.6651
-8	16	11	27.9700	24.6183
-9	1	11	5.6440	3.0306
-9	2	11	40.2360	41.7875
-9	5	11	26.0930	22.9301
-9	6	11	39.7400	41.2645
-9	7	11	22.8270	23.7532
-9	8	11	7.8480	7.8532
-9	9	11	15.0290	16.1088
-9	10	11	5.1130	2.3230
-9	11	11	20.6090	20.3085
-9	12	11	8.9550	9.0873
-9	14	11	17.2600	17.0986
-9	15	11	14.3250	13.5417
-10	1	11	6.9570	6.5187
-10	2	11	46.1620	47.8960
-10	3	11	16.6060	19.2147
-10	4	11	12.4850	12.9799
-10	5	11	6.9730	6.2976
-10	6	11	48.1550	47.4019
-10	7	11	16.0720	14.9904
-10	8	11	30.5330	30.7500
-10	9	11	5.3370	5.5814
-10	10	11	9.0390	7.1893
-10	11	11	18.1600	18.6366
-10	13	11	9.0780	9.6619
-11	1	11	6.5940	5.6492
-11	2	11	7.6160	4.5941
-11	3	11	13.4300	13.8875
-11	4	11	8.7190	8.7932
-11	5	11	9.5540	11.3036
-11	6	11	54.6840	57.7221
-11	7	11	13.3960	15.8918
-11	8	11	9.0220	10.5609
-11	9	11	15.5840	16.2990
-11	10	11	42.1760	42.7638
-11	11	11	5.8510	1.7746
-11	13	11	16.6970	17.1202
-1	0	12	29.9030	32.0222
-1	1	12	6.1540	4.6687
-1	2	12	8.8150	9.0966
-1	4	12	22.0260	20.9726
-1	5	12	15.6540	15.1167
-1	6	12	5.0120	4.3329
-1	7	12	6.2920	7.8233
-2	0	12	33.6300	36.5514
-2	3	12	9.9810	9.8613
-2	4	12	20.9330	20.4560
-2	5	12	8.8830	8.8005
-2	6	12	6.2090	5.1198
-2	7	12	11.9860	12.2546
-2	8	12	18.1730	19.0478
-2	9	12	7.9220	6.8630
-2	10	12	13.3140	12.8787
-3	0	12	32.9750	32.8506
-3	2	12	18.8550	18.7672
-3	3	12	10.3290	10.3124
-3	4	12	17.6240	15.8000
-3	5	12	22.1400	21.6360
-3	6	12	24.5000	27.3630
-3	7	12	24.6040	7.6566
-3	8	12	8.0160	7.5862
-3	9	12	8.9350	8.5695
-3	10	12	14.4520	16.0219
-3	11	12	10.0940	8.7387
-3	12	12	5.2130	1.5701
-4	0	12	4.7840	1.7203
-4	1	12	5.2450	6.8496
-4	2	12	5.7860	6.2831
-4	3	12	5.3820	3.9753
-4	4	12	6.1970	4.6734
-4	5	12	5.8440	4.3536
-4	6	12	6.2370	6.8778
-4	7	12	19.8950	19.2407
-4	8	12	38.1810	38.0334
-4	9	12	24.6450	25.2926
-4	10	12	9.5250	10.2235
-4	12	12	41.4920	41.2223
-5	0	12	20.1940	20.1818
-5	1	12	4.6160	3.7727
-5	2	12	10.1530	9.0230
-5	3	12	12.6850	13.9979
-5	4	12	7.7120	4.3927
-5	5	12	21.1560	21.3009
-5	6	12	28.6270	27.4357
-5	7	12	18.7940	19.6530
-5	8	12	48.4640	49.1230
-5	9	12	9.7360	9.3892
-5	10	12	9.3110	8.9368
-5	11	12	6.0090	4.9430
-5	12	12	48.1820	49.0605
-5	13	12	5.7780	5.3726
-6	0	12	6.4620	7.8465
-6	3	12	18.6940	19.2391
-6	4	12	15.2690	15.9001
-6	5	12	20.0310	20.4566
-6	6	12	21.2830	21.9590
-6	7	12	31.1340	32.8136
-6	8	12	32.1470	32.7185
-6	9	12	5.3800	3.9087
-6	12	12	26.1090	23.0496
-6	13	12	5.5770	4.7548
-6	14	12	6.8300	7.1176

H	K	L	Y(OBS)	Y(CALC)
-7	0	12	34.6900	36.7380
-7	1	12	7.2590	7.1588
-7	2	12	7.6210	6.9582
-7	3	12	23.3620	23.2307
-7	4	12	24.2700	23.4725
-7	6	12	5.5290	6.0203
-7	7	12	14.2280	13.3714
-7	8	12	27.7250	26.7211
-7	9	12	6.0600	7.9112
-7	10	12	9.6100	7.4764
-7	11	12	14.7170	13.0092
-7	12	12	9.7700	8.0380
-7	13	12	14.3010	13.9003
-7	14	12	17.1200	16.8744
-8	0	12	49.6850	53.4208
-8	1	12	11.4720	11.2264
-8	2	12	15.6900	15.3594
-8	3	12	22.9180	22.6261
-8	4	12	8.3690	5.5227
-8	6	12	12.8880	11.4665
-8	7	12	12.7300	12.6096
-8	8	12	20.4470	19.2819
-8	10	12	19.2860	20.2147
-8	11	12	10.0270	10.1756
-8	12	12	6.1860	4.0411
-8	13	12	13.7590	13.1540
-8	14	12	26.3160	26.7073
-8	15	12	11.3730	10.9081
-9	0	12	21.7680	23.7531
-9	1	12	27.2960	29.2450
-9	2	12	5.2850	4.0550
-9	3	12	6.7640	5.5920
-9	4	12	21.4690	20.3630
-9	5	12	8.0100	7.5369
-9	6	12	25.8010	26.1473
-9	7	12	8.5350	8.1210
-9	8	12	27.1240	26.3694
-9	11	12	13.4450	13.2497
-9	12	12	3.5580	1.8002
-9	14	12	11.4490	9.2666
-10	0	12	10.8370	12.2307
-10	1	12	42.2890	45.4177
-10	3	12	6.9320	5.4482
-10	4	12	28.1720	27.8475
-10	5	12	23.8080	22.8346
-10	7	12	19.0190	18.4284
-10	8	12	7.1280	7.3875
-10	10	12	8.8680	7.8674
-10	11	12	12.3960	13.4900
-10	12	12	10.5420	10.1215
-10	13	12	11.1580	11.0723
-10	14	12	5.8120	5.8973
-11	1	12	28.8200	29.8051
-11	3	12	43.1760	43.4615
-11	5	12	18.6830	18.1034
-11	6	12	10.3290	8.7409
-11	7	12	34.2310	33.4808
-11	8	12	5.6100	2.6590
-11	10	12	5.1860	3.6154
-11	11	12	10.2380	10.0157
-11	12	12	29.2010	27.1671

2. Observed and Calculated Structure Amplitudes of Porphine

H	K	L	Y(OBS)	Y(CALC)
0	4	C	17,0000	19,5205
0	10	0	4,3000	4,1234
0	12	0	15,8000	15,8975
-1	0	0	60,2000	76,5570
-1	1	0	6,0000	6,6411
-1	2	0	1,6000	,3358
-1	3	0	3,3000	2,5648
-1	4	0	2,2000	2,5112
-1	5	0	2,2000	2,2711
-1	6	0	3,1000	2,6149
1	7	0	2,6000	1,7152
-1	8	0	4,0000	5,7505
-1	9	0	7,3000	6,9466
-1	11	0	9,6000	10,9583
-2	0	0	117,7000	153,4956
-2	1	0	17,6000	17,7449
-2	2	0	2,5000	1,8813
-2	3	0	3,7000	3,5864
-2	4	0	10,2000	9,7667
-2	6	0	10,4000	10,3250
-2	7	0	12,1000	11,3982
-2	9	0	3,3000	3,4469
-3	0	0	33,2000	34,7342
-3	1	0	1,8000	2,1129
-3	2	0	2,4000	2,9992
-3	3	0	6,7000	6,4387
-3	4	0	49,4000	47,7231
-3	5	0	24,8000	23,9978
-3	6	0	7,6000	7,5129
-3	7	0	3,7000	4,2739
-3	9	0	8,1000	6,8275
-3	10	0	4,0000	4,3423
-3	11	0	6,6000	6,4662
-4	0	0	30,2000	28,9670
-4	1	0	29,0000	27,3571
-4	2	0	10,8000	10,7340
-4	3	0	18,2000	17,6103
-4	4	0	43,5000	43,0494
-4	5	0	16,3000	15,3917
-4	6	0	8,3000	8,3268
-4	7	0	9,0000	8,1811
-4	8	0	18,1000	17,9373
-4	11	0	12,4000	12,5639
-5	0	0	36,8000	36,4112
-5	1	0	26,5000	25,9214
-5	2	0	6,4000	5,7216
-5	3	0	8,1000	7,4551
-5	4	0	9,8000	9,7051
-5	5	0	8,0000	8,0067
-5	6	0	10,6000	9,2263
-5	7	0	14,3000	13,7518
-5	8	0	13,2000	12,0871
-5	9	0	4,7000	6,1961
-5.	10	0	6,2000	4,6332
-6	0	0	14,5000	14,7802
-6	1	0	17,1000	17,2978
-6	2	0	8,1000	6,9388
-6	3	0	5,2000	4,7931
-6	4	0	4,9000	4,6821
-6	5	0	9,3000	10,2259
-6	6	0	7,9000	7,5380
-6	7	0	3,4000	1,1640
-7	0	0	13,2000	13,2098
-7	1	0	18,6000	17,4663
-7	2	0	5,1000	3,9736
-7	3	0	9,5000	9,5827
-7	4	0	6,1000	7,1080
-7	5	0	20,0000	20,4387
-7	6	0	6,3000	7,5133
-7	7	0	18,5000	18,3339
-8	0	0	3,5000	4,8452
-8	1	0	7,3000	8,9836
-8	2	0	5,9000	5,0805
-8	3	0	13,3000	13,2362
-8	5	0	3,9000	2,6628
-8	6	0	14,3000	13,1789
-9	2	0	3,2000	1,7578
-9	5	0	19,0000	18,4074
0	1	1	40,6000	44,1647
0	2	1	21,6000	21,4250
0	3	1	71,8000	77,3726
0	4	1	38,7000	40,9050
0	5	1	11,8000	11,7416
0	6	1	21,5000	22,0914
0	7	1	29,1000	29,4680
0	8	1	21,0000	21,2425
0	9	1	18,5000	19,2183
0	10	1	12,9000	13,3616
-1	1	1	18,8000	19,9633
1	1	1	25,8000	26,3808
-1	2	1	13,0000	13,3306
1	2	1	32,7000	33,6226
-1	3	1	46,9000	48,2150
1	3	1	12,6000	12,9625
-1	4	1	7,2000	7,2137
1	4	1	7,7000	7,1545
-1	5	1	21,2000	20,9264
1	5	1	27,3000	27,0393
-1	6	1	14,0000	13,9950
1	6	1	25,5000	24,8058
-1	7	1	27,6000	27,0886
1	7	1	9,2000	9,2086
-1	8	1	28,3000	19,5314
1	8	1	10,7000	10,3277
-1	9	1	9,7000	9,2776
1	9	1	11,7000	11,7747
-1	10	1	6,2000	3,4239
1	10	1	4,6000	5,5917

H	K	L	Y(OBS)	Y(CALC
-1	11	1	7,2000	8,0680
1	11	1	3,3000	4,6162
-2	1	1	57,6000	62,3724
2	1	1	3,3000	3,3589
-2	2	1	6,0000	6,2323
2	2	1	7,7000	7,4494
-2	3	1	5,9000	5,9947
2	3	1	3,7000	4,0957
2	4	1	8,5000	8,9317
-2	4	1	6,9000	6,9098
-2	5	1	17,5000	17,1157
2	5	1	19,4000	19,8227
-2	6	1	2,5000	2,0086
2	6	1	33,5000	32,5882
2	7	1	23,7000	23,1871
-2	8	1	3,8000	4,2421
2	8	1	5,6000	3,4431
-2	9	1	4,5000	3,6157
2	9	1	3,2000	1,6986
2	10	1	11,7000	11,3640
-2	11	1	7,3000	7,7631
2	11	1	6,9000	7,1720
-3	1	1	3,4000	3,9975
3	1	1	14,8000	15,1974
-3	2	1	1,7000	1,1588
3	2	1	4,6000	5,8743
-3	3	1	15,6000	15,3280
3	3	1	13,6000	12,9517
-3	4	1	18,9000	18,0294
3	4	1	4,7000	4,4304
-3	5	1	29,5000	29,6968
3	5	1	8,6000	8,4475
3	6	1	9,7000	10,3466
-3	7	1	17,9000	17,1674
3	7	1	10,1000	9,7812
-3	8	1	5,5000	5,6626
-3	9	1	9,0000	8,5267
3	9	1	10,4000	9,0048
3	10	1	7,8000	7,2275
-3	11	1	3,2000	1,2204
3	11	1	11,2000	11,6850
-4	1	1	25,1000	24,1311
4	1	1	5,3000	5,0263
-4	2	1	2,6000	1,8188
4	2	1	11,4000	10,9134
-4	3	1	37,3000	36,1929
4	3	1	23,7000	23,2822
4	4	1	9,6000	8,9441
-4	4	1	19,5000	19,7197
-4	5	1	6,9000	5,1627
4	5	1	39,2000	37,0523
-4	6	1	7,1000	6,6451
4	6	1	28,9000	28,0062
-4	7	1	3,9000	2,8285
4	7	1	23,2000	22,3711
-4	8	1	9,4000	8,3560
4	9	1	19,4000	19,9569
-4	10	1	5,5000	5,8045
4	10	1	15,0000	15,7494
-4	11	1	10,5000	10,4335
-5	1	1	39,9000	39,4500
5	1	1	7,9000	7,3423
-5	2	1	6,3000	5,8225
5	2	1	4,9000	3,5880
-5	3	1	18,6000	17,8252
5	3	1	6,1000	6,1319
-5	4	1	13,9000	14,8515
5	5	1	2,8000	1,5657
-5	6	1	3,6000	3,2273
5	6	1	15,6000	16,2139
-5	7	1	10,0000	11,0560
-5	8	1	5,4000	7,7164
-5	9	1	3,9000	2,9911
5	9	1	13,4000	13,9278
-5	10	1	6,3000	8,2919
5	10	1	13,2000	14,2359
-6	1	1	9,9000	10,6280
6	1	1	11,0000	10,5507
-6	2	1	3,8000	3,4317
6	2	1	11,9000	12,1995
-6	3	1	7,8000	6,6268
6	3	1	9,6000	8,3007
-6	5	1	4,5000	5,5411
6	5	1	15,1000	14,3556
-6	6	1	11,3000	10,9952
6	6	1	5,0000	3,3946
-6	7	1	6,9000	5,0742
-6	8	1	8,1000	8,7481
6	9	1	4,6000	4,7730
-7	1	1	21,3000	19,8633
7	1	1	19,3000	18,6920
-7	2	1	3,3000	2,3228
7	2	1	4,4000	3,8921
-7	3	1	8,2000	10,3210
7	3	1	6,2000	5,1618
-7	5	1	8,2000	7,3096
7	5	1	4,9000	2,7277
-7	6	1	18,6000	19,3121
7	6	1	27,6000	28,2397
-7	7	1	13,9000	14,3190
7	7	1	5,2000	5,3433
-7	8	1	6,9000	7,6494
7	8	1	6,2000	6,4198
-8	1	1	11,8000	12,6913
8	1	1	20,0000	21,6110
-8	2	1	15,7000	15,4863
8	2	1	3,2000	1,5613
-8	3	1	7,0000	8,0095

H	K	L	Y(OBS)	Y(CALC)
8	3	1	4,7000	7,1279
-8	4	1	3,4000	2,7831
8	4	1	4,4000	3,9662
-8	5	1	6,4000	5,5849
8	5	1	6,2000	6,4231
-8	6	1	16,0000	15,1605
8	6	1	3,7000	3,2990
-9	1	1	4,1000	3,9762
-9	2	1	15,2000	15,1787
9	3	1	9,4000	9,6298
9	4	1	7,1000	5,0315
-9	5	1	5,2000	5,5465
-10	1	1	4,3000	4,3579
0	0	2	43,1000	44,9447
0	1	2	4,9000	4,4808
2	2	3	11,2000	11,1109
0	2	2	160,6000	166,9679
0	3	2	14,2000	14,3868
0	4	2	21,4000	21,5668
0	5	2	37,0000	35,7919
0	6	2	23,9000	23,6233
0	7	2	13,6000	13,2412
0	8	2	4,3000	2,8787
0	9	2	15,5000	16,7665
0	10	2	5,8000	8,5696
0	11	2	8,5000	8,3254
-1	0	2	40,1000	39,9002
1	0	2	14,2000	14,0941
1	1	2	38,7000	40,4877
-1	1	2	30,5000	32,6175
-1	2	2	111,1000	111,1350
1	2	2	49,9000	52,2959
-1	3	2	23,2000	23,9578
1	3	2	19,5000	19,0387
-1	4	2	36,0000	37,1641
1	4	2	6,9000	6,2183
-1	5	2	36,8000	38,1144
1	5	2	22,4000	22,8374
-1	6	2	17,7000	17,7141
1	6	2	8,2000	7,0460
-1	7	2	13,4000	13,9262
1	7	2	3,4000	3,5451
1	8	2	4,5000	4,2845
-1	9	2	5,1000	4,7660
1	9	2	4,0000	3,8712
-1	10	2	9,8000	10,0113
-1	11	2	9,1000	9,7393
-2	0	2	58,7000	63,5695
2	0	2	2,2000	1,3442
-2	1	2	2,0000	1,6229
2	1	2	13,2000	13,0631
-2	2	2	44,6000	45,7021
2	2	2	23,1000	24,5597
-2	3	2	13,4000	13,2309
2	3	2	10,9000	11,1040
-2	4	2	6,5000	7,0464
2	4	2	4,8000	4,8808
-2	5	2	10,5000	10,2411
2	5	2	29,5000	29,9691
-2	6	2	8,3000	8,3639
2	6	2	13,0000	13,1584
-2	7	2	9,0000	9,2455
2	7	2	12,4000	13,1505
-2	8	2	8,0000	6,9356
2	8	2	3,2000	2,1706
-2	9	2	6,7000	6,7788
2	9	2	3,6000	3,3173
-2	10	2	9,6000	11,8507
2	10	2	5,6000	4,3302
-2	11	2	4,4000	5,1364
2	11	2	7,9000	7,6030
-3	0	2	5,0000	5,3753
3	0	2	2,3000	,6398
-3	1	2	2,4000	1,1350
3	1	2	7,1000	7,7832
-3	2	2	7,9000	7,4306
3	2	2	25,8000	26,1542
-3	3	2	6,6000	6,2835
3	3	2	12,7000	12,5678
-3	4	2	33,1000	31,5409
3	4	2	2,8000	2,1715
-3	5	2	23,7000	23,0710
3	5	2	22,9000	22,8737
-3	6	2	9,1000	9,6018
3	6	2	7,8000	8,3684
-3	7	2	23,4000	23,2288
3	7	2	8,8000	7,2282
3	8	2	3,6000	2,4214
-3	9	2	9,8000	9,6380
3	9	2	4,8000	3,5813
3	10	2	5,8000	3,4525
-3	11	2	7,5000	7,1763
-4	0	2	26,7000	26,5508
4	0	2	16,5000	16,6192
-4	1	2	12,4000	12,3115
4	1	2	26,8000	26,7932
-4	2	2	14,5000	13,9994
4	2	2	63,8000	65,6309
-4	3	2	22,6000	22,2430
4	3	2	4,6000	3,2046
4	4	2	6,1000	5,5758
-4	5	2	36,5000	35,8911
4	5	2	6,9000	6,7393
-4	6	2	5,5000	5,8165
4	6	2	6,7000	8,1949
-4	7	2	11,6000	11,3889
4	7	2	5,0000	4,7158
4	8	2	5,2000	4,9491

H	K	L	Y(OBS)	Y(CALC)
-4	9	2	18,7000	19,5921
4	9	2	3,3000	1,6748
-4	10	2	4,2000	3,9983
4	10	2	10,2000	10,3394
-4	11	2	10,2000	9,8867
5	0	2	4,4000	3,8125
-5	0	2	60,4000	62,7206
-5	1	2	7,3000	7,4722
5	1	2	8,5000	7,0006
-5	2	2	12,0000	11,7960
5	2	2	10,9000	10,2150
-5	3	2	19,5000	18,7638
5	3	2	4,6000	5,6658
-5	4	2	8,9000	7,7496
5	4	2	3,2000	2,7896
-5	5	2	17,0000	16,4984
5	5	2	3,7000	3,8170
-5	6	2	4,9000	4,0636
5	6	2	12,6000	12,2731
-5	7	2	25,6000	24,9471
5	7	2	5,8000	4,8969
-5	8	2	5,5000	5,4788
5	8	2	4,5000	3,6831
-5	9	2	16,6000	16,9482
-6	0	2	5,8000	8,0110
6	0	2	15,4000	15,4211
-6	1	2	4,1000	2,5689
6	1	2	20,9000	19,8302
6	2	2	24,6000	23,0967
-6	3	2	4,7000	3,2766
6	3	2	3,5000	2,4771
-6	4	2	7,2000	8,6034
6	4	2	3,0000	2,2458
-6	5	2	10,5000	10,6939
6	5	2	7,4000	8,0712
6	6	2	4,3000	4,2342
-6	7	2	8,9000	9,1101
-6	8	2	9,8000	9,3900
6	8	2	4,5000	4,6197
6	9	2	4,8000	5,3394
-7	0	2	35,8000	32,8368
-7	1	2	14,7000	13,9062
7	1	2	15,7000	16,6508
-7	2	2	2,8000	1,6919
7	2	2	17,4000	17,3672
-7	3	2	12,9000	13,0515
7	3	2	12,7000	12,2789
-7	4	2	18,8000	19,2713
7	4	2	22,6000	22,3810
-7	5	2	3,3000	4,8745
7	5	2	7,6000	8,6906
-7	6	2	3,7000	3,4517
7	6	2	3,3000	1,7494
7	7	2	9,5000	9,2404
-7	8	2	6,5000	6,8877
-8	0	2	17,3000	18,5843
8	0	2	12,3000	12,7540
-8	1	2	19,5000	20,5971
8	1	2	11,7000	13,6802
-8	2	2	4,9000	5,2466
8	2	2	6,5000	6,3727
8	3	2	7,2000	8,6115
-8	4	2	13,1000	12,5539
8	4	2	8,9000	9,0031
8	6	2	3,2000	3,4725
-8	7	2	11,4000	10,8567
-9	0	2	9,6000	9,4526
9	0	2	7,9000	10,2470
-9	1	2	13,1000	14,1174
9	1	2	3,5000	3,5359
-9	2	2	4,3000	3,1416
9	2	2	4,1000	3,8081
-9	3	2	9,1000	10,0867
9	3	2	12,6000	11,8333
-9	4	2	8,7000	9,5283
-9	5	2	3,7000	3,5827
-10	0	2	9,4000	10,1424
-10	1	2	6,5000	6,7620
-10	2	2	4,1000	4,9632
0	1	3	99,8000	100,6487
0	2	3	129,7000	133,5235
0	3	3	16,8000	16,4647
0	5	3	8,0000	6,5958
0	6	3	2,6000	,7969
0	7	3	18,0000	17,0106
0	8	3	4,2000	4,8734
0	9	3	21,5000	22,7995
0	10	3	15,7000	18,5539
-1	1	3	122,3000	123,5261
1	1	3	43,9000	45,0364
-1	2	3	172,8000	181,7694
1	2	3	62,6000	63,0066
1	4	3	2,9000	2,9153
-1	3	3	41,2000	42,2739
1	3	3	4,8000	5,3400
-1	5	3	6,1000	5,2903
1	5	3	8,6000	9,4155
-1	6	3	3,4000	3,9576
1	6	3	3,5000	4,8871
-1	7	3	10,3000	9,7411
1	7	3	6,5000	6,0971
-1	8	3	3,1000	2,6427
-1	9	3	14,8000	15,5243
1	9	3	7,4000	8,4306
-1	10	3	3,4000	2,6522
1	10	3	7,4000	8,3520
-1	11	3	8,7000	8,3979
1	11	3	4,6000	4,3748

H	K	L	Y(OBS)	Y(CALC)
-2	1	3	26,6000	27,1254
2	1	3	6,3000	6,8512
-2	2	3	46,0000	44,3275
-2	3	3	16,4000	17,1549
2	3	3	35,6000	36,3043
2	4	3	16,0000	16,0391
2	5	3	2,4000	1,8899
2	6	3	9,8000	9,1525
-2	7	3	5,6000	6,4831
2	7	3	12,1000	10,9470
2	8	3	10,9000	10,2555
-2	9	3	5,9000	7,5153
2	9	3	8,5000	8,2214
-2	10	3	9,3000	9,5893
2	10	3	4,8000	5,5078
-2	11	3	6,5000	6,3354
-3	1	3	9,8000	9,9192
3	1	3	14,1000	13,6202
-3	2	3	9,2000	9,6432
3	2	3	28,6000	29,1355
-4	2	3	37,5000	36,4607
-3	3	3	20,9000	20,3544
3	3	3	4,2000	5,1374
-3	4	3	15,5000	15,0640
-3	5	3	18,7000	17,4146
3	5	3	16,8000	16,3954
-3	6	3	9,0000	8,1547
3	6	3	21,5000	21,9726
-3	7	3	15,9000	15,4335
3	7	3	4,3000	3,7501
-3	8	3	8,5000	8,1991
3	8	3	5,4000	5,6204
-3	9	3	9,7000	10,2652
3	9	3	4,6000	4,6269
-3	10	3	3,2000	2,5808
3	10	3	13,5000	14,2711
-3	11	3	5,2000	3,9274
-4	1	3	10,3000	10,6577
4	1	3	28,5000	28,5377
4	2	3	6,3000	5,8519
-4	3	3	7,2000	7,2933
4	3	3	21,6000	21,6106
-4	4	3	11,7000	11,3489
4	4	3	10,9000	10,2321
-4	5	3	18,4000	18,0825
4	5	3	11,3000	11,8013
-4	6	3	22,4000	21,8781
4	6	3	19,4000	20,3408
-4	7	3	5,0000	5,3353
-4	8	3	10,0000	10,1449
4	8	3	10,7000	10,2173
-4	9	3	17,4000	17,1753
4	9	3	6,2000	7,4328
-4	10	3	3,2000	2,1925
4	10	3	6,2000	8,2018
-5	1	3	13,0000	13,1324
-5	2	3	3,2000	4,3509
-5	3	3	25,4000	24,7741
5	3	3	10,1000	10,5501
-5	4	3	17,4000	17,3540
5	4	3	9,6000	9,6360
-5	5	3	6,1000	5,1749
-5	6	3	16,7000	16,3058
-5	7	3	15,8000	15,2503
5	7	3	3,7000	4,4492
5	8	3	15,9000	16,5891
-5	9	3	15,0000	15,8104
5	9	3	5,7000	5,4005
-5	10	3	5,8000	5,9373
6	1	3	9,8000	9,7747
-6	2	3	6,1000	6,0013
6	2	3	3,2000	2,7659
-6	3	3	3,8000	3,3220
6	3	3	4,4000	3,1324
-6	4	3	12,2000	12,7460
6	4	3	7,6000	7,5828
-6	5	3	17,5000	16,2594
6	5	3	5,8000	6,2180
-6	6	3	5,0000	4,1486
6	6	3	3,5000	4,4976
-6	8	3	4,6000	5,5607
6	8	3	19,5000	19,7718
-6	9	3	6,8000	6,4404
-7	1	3	3,8000	3,5814
-7	2	3	4,4000	3,7339
-7	3	3	7,9000	7,6312
7	3	3	7,8000	6,7600
-7	4	3	7,9000	9,7627
7	4	3	16,4000	15,7781
-7	5	3	12,6000	13,5324
7	5	3	13,3000	14,3875
-7	6	3	4,9000	4,7618
-7	7	3	4,6000	5,4392
7	7	3	6,0000	4,2670
-7	8	3	8,2000	10,0897
8	1	3	3,7000	2,4877
-8	2	3	3,1000	2,3781
8	3	3	10,2000	11,1938
-8	4	3	11,1000	11,5728
8	4	3	10,1000	9,9482
-8	5	3	15,4000	14,9627
8	5	3	3,9000	4,4061
-8	6	3	4,2000	4,0574
-8	7	3	7,7000	7,0472
-9	3	3	4,9000	5,9992
-9	4	3	22,6000	21,5110
-9	5	3	5,2000	4,6338
-10	1	3	3,4000	3,6969

H	K	L	Y(OBS)	Y(CALC)
0	0	4	53,5000	52,8010
0	1	4	6,2000	5,7924
0	2	4	39,0000	38,0532
0	3	4	18,4000	18,1706
0	4	4	25,2000	25,0080
0	5	4	21,6000	21,3036
0	6	4	15,0000	14,7391
0	7	4	23,2000	22,0631
0	8	4	3,2000	2,9907
0	9	4	6,1000	8,2372
0	10	4	7,8000	7,3262
0	11	4	5,0000	5,4276
-1	0	4	60,4000	62,4463
1	0	4	7,6000	7,5524
-1	1	4	9,4000	9,2095
1	1	4	13,8000	14,1706
-1	2	4	106,8000	114,7615
1	2	4	28,6000	28,7148
-1	3	4	17,5000	17,7754
1	3	4	5,3000	5,8843
-1	4	4	7,4000	5,9799
1	4	4	16,4000	16,3974
-1	5	4	44,0000	43,6374
1	5	4	3,3000	2,8935
-1	6	4	22,3000	21,9937
-1	7	4	23,5000	21,9527
1	8	4	3,5000	3,4451
-1	9	4	10,2000	9,1791
1	9	4	7,9000	7,1219
-1	10	4	9,1000	8,8756
1	10	4	9,0000	9,3096
1	11	4	3,5000	3,5660
-2	0	4	5,0000	5,1083
2	0	4	4,5000	6,2732
-2	1	4	17,3000	17,1152
2	1	4	6,6000	6,3819
-2	2	4	5,4000	5,4404
2	2	4	15,4000	15,4719
-2	3	4	15,2000	14,8402
2	3	4	33,8000	34,4531
-2	4	4	10,2000	10,4281
2	4	4	21,8000	21,8942
-2	5	4	11,5000	11,6249
-2	6	4	6,2000	7,0274
2	6	4	9,3000	7,7575
-2	7	4	3,2000	2,8608
2	7	4	13,6000	13,1936
-2	8	4	5,5000	7,3159
-2	9	4	17,2000	18,1796
2	9	4	4,2000	2,9827
-2	10	4	6,7000	8,8558
-3	0	4	1,9000	1,7940
3	0	4	23,0000	23,1889
3	3	4	15,4000	14,8458
-3	1	4	5,6000	6,5100
3	1	4	27,9000	28,1889
-3	2	4	54,9000	53,1207
3	2	4	5,9000	5,7186
-3	3	4	12,3000	11,9216
3	4	4	27,2000	26,7652
-3	5	4	6,8000	5,6600
3	5	4	4,9000	4,9622
-3	6	4	11,1000	10,2422
3	6	4	3,7000	3,3824
-3	7	4	5,4000	5,8395
3	7	4	15,9000	16,2480
3	8	4	24,8000	24,5086
-3	9	4	4,3000	4,0555
3	9	4	14,3000	15,2189
-3	10	4	3,7000	3,7356
3	10	4	5,2000	4,9113
-3	11	4	5,0000	4,8281
-4	0	4	2,1000	2,9863
4	0	4	19,2000	19,9247
-4	1	4	15,8000	15,9375
4	1	4	23,1000	22,8465
-4	2	4	13,3000	13,1949
4	2	4	3,2000	2,1852
-4	3	4	4,5000	5,9719
4	4	4	21,0000	19,3553
-4	5	4	4,6000	3,1478
4	5	4	9,0000	9,2155
-4	6	4	5,3000	5,7419
-4	7	4	4,0000	3,7439
4	7	4	16,6000	17,2161
-4	8	4	3,1000	2,3056
4	8	4	21,2000	22,4340
4	9	4	3,3000	2,2199
-4	10	4	11,4000	12,1262
5	0	4	4,7000	3,1440
-5	1	4	10,5000	10,1412
5	1	4	4,7000	4,3236
-5	2	4	33,2000	32,7405
-5	3	4	27,9000	27,9368
5	3	4	5,6000	5,3461
-5	4	4	6,6000	8,0208
5	4	4	23,9000	23,7038
-5	5	4	12,1000	12,1555
5	5	4	3,1000	2,8725
-5	7	4	4,0000	4,2677
-5	8	4	6,7000	9,8050
5	8	4	4,0000	4,0185
-5	9	4	13,6000	14,7498
6	0	4	9,5000	8,2574
6	1	4	10,2000	10,3766
-6	2	4	16,6000	16,4595
6	2	4	6,1000	5,9376
-6	3	4	9,3000	8,9498

H	K	L	Y(OBS)	Y(CALC)
6	3	4	20,2000	20,8488
-6	4	4	4,2000	4,3392
-6	5	4	14,4000	13,9141
-6	6	4	3,1000	4,9949
6	7	4	12,7000	13,7087
-6	9	4	6,2000	6,6085
-7	0	4	3,3000	2,6357
7	0	4	14,4000	14,8810
-7	1	4	4,7000	4,4125
-7	2	4	20,4000	20,4016
7	2	4	6,6000	6,1973
-7	3	4	11,8000	11,6048
7	3	4	22,0000	23,4829
7	4	4	8,5000	8,9801
-7	5	4	6,1000	6,9340
7	5	4	3,8000	4,0150
7	6	4	5,3000	5,6330
-7	7	4	3,3000	3,0989
-7	8	4	10,9000	11,2942
-8	0	4	6,9000	7,7953
8	0	4	8,6000	8,7134
-8	1	4	7,0000	8,7665
8	1	4	8,4000	9,5738
-8	2	4	18,2000	19,0494
8	2	4	5,8000	5,6400
-8	3	4	11,7000	11,5229
8	3	4	4,2000	4,9850
-8	4	4	15,6000	16,0125
8	4	4	3,9000	1,0248
-8	5	4	11,7000	12,0924
-8	6	4	7,8000	7,9117
-8	7	4	8,4000	8,2818
-9	0	4	18,8000	18,7680
-9	1	4	6,3000	7,2713
-9	2	4	5,4000	5,6680
-9	3	4	4,5000	4,3478
-9	5	4	4,1000	3,2983
-10	0	4	7,3000	7,3133
0	1	5	20,9000	21,5532
0	2	5	3,2000	2,8091
0	3	5	24,5000	24,8894
0	4	5	21,7000	21,3415
0	5	5	8,7000	7,5645
0	6	5	5,0000	4,3649
0	7	5	13,2000	12,5064
0	8	5	11,6000	12,8477
-1	1	5	44,6000	45,4710
1	1	5	5,6000	5,8627
-1	2	5	24,8000	24,9925
1	2	5	2,5000	1,5978
-1	3	5	13,9000	14,4528
1	3	5	17,1000	16,7770
-1	4	5	89,1000	92,4125
1	4	5	28,0000	28,0476
-1	5	5	14,6000	14,3849
-1	6	5	2,9000	2,0032
-1	7	5	19,9000	19,0334
1	7	5	3,4000	1,5714
-1	8	5	11,2000	11,8339
1	8	5	20,0000	20,1592
-1	9	5	7,5000	7,6383
-1	10	5	4,9000	5,3606
-2	1	5	18,3000	19,0383
2	1	5	16,6000	16,5037
-2	2	5	9,4000	9,0659
2	2	5	3,0000	3,6750
-2	3	5	23,5000	23,0610
2	3	5	22,7000	22,9176
-2	4	5	14,9000	14,8518
2	4	5	3,3000	2,8663
-2	5	5	12,6000	12,6276
2	5	5	6,1000	5,6222
2	7	5	3,3000	4,1696
-2	8	5	6,1000	6,9552
2	8	5	11,4000	10,5286
-2	9	5	10,1000	9,8617
-2	10	5	9,0000	9,8803
-3	1	5	2,1000	,0635
3	1	5	12,5000	13,5707
3	2	5	8,5000	7,2669
-3	3	5	27,0000	27,8998
3	3	5	26,0000	25,4000
-3	4	5	25,6000	26,3044
3	4	5	16,7000	17,3785
3	5	5	4,4000	3,7136
-3	6	5	4,9000	5,1720
-3	7	5	8,9000	9,8981
-3	8	5	6,9000	6,9292
3	8	5	4,9000	4,2353
-3	9	5	4,3000	3,4651
3	9	5	5,2000	3,6594
-4	1	5	8,3000	8,6900
4	1	5	5,9000	7,5155
-4	2	5	15,7000	15,8190
4	2	5	8,3000	7,6792
-4	3	5	3,4000	1,8676
4	3	5	18,6000	17,6367
4	4	5	25,6000	25,7503
4	5	5	10,0000	9,9140
-4	7	5	15,0000	16,0703
4	7	5	5,5000	5,6727
-4	8	5	11,9000	11,4709
4	8	5	8,5000	8,5975
-4	9	5	5,1000	3,6116
4	9	5	6,2000	5,6706
-4	10	5	16,4000	16,5370
-5	1	5	19,0000	19,2783
-5	2	5	27,5000	26,4363

H	K	L	Y(OBS)	Y(CALC)
5	2	5	11,5000	12,1810
-5	3	5	25,7000	24,4594
5	3	5	13,4000	13,8901
-5	4	5	3,2000	3,1154
-5	5	5	13,3000	12,9013
-5	6	5	15,8000	14,3300
-5	7	5	22,6000	23,2911
5	7	5	3,8000	3,5522
-5	8	5	3,2000	2,4605
5	8	5	5,2000	4,9422
-5	9	5	12,0000	12,1929
-6	1	5	8,8000	8,9592
6	1	5	10,9000	11,6484
-6	2	5	11,9000	11,5202
6	2	5	6,6000	6,5361
-6	3	5	14,6000	14,5315
6	3	5	13,7000	14,1715
-6	4	5	5,5000	5,6884
6	4	5	14,7000	16,5817
-6	5	5	8,0000	7,9051
6	5	5	3,6000	3,4010
-6	6	5	4,5000	2,2934
6	6	5	4,7000	3,3361
-6	7	5	8,8000	7,6395
6	7	5	4,2000	4,9641
-6	9	5	5,0000	4,5406
-7	1	5	9,3000	8,5386
-7	2	5	10,4000	10,6227
7	2	5	10,3000	9,2625
7	3	5	12,6000	14,2572
7	4	5	6,3000	9,8536
-7	5	5	5,5000	5,0177
7	5	5	7,0000	6,1479
-7	7	5	8,7000	8,7420
-8	1	5	7,7000	8,0705
8	1	5	12,8000	14,0062
8	2	5	7,2000	5,7407
-8	3	5	23,2000	23,1437
-8	4	5	5,1000	3,9870
-8	6	5	5,4000	6,5332
-9	2	5	11,6000	12,2741
-9	3	5	10,5000	11,2441
0	0	6	3,9000	2,4327
0	1	6	4,4000	3,3453
0	2	6	2,8000	2,4723
0	3	6	4,5000	5,1043
0	4	6	9,8000	8,8023
0	5	6	16,9000	16,5335
0	6	6	4,3000	3,6596
0	7	6	2,7000	2,2354
1	0	6	9,3000	9,6818
-1	0	6	8,7000	8,6748
-1	1	6	37,1000	38,6804
1	1	6	12,0000	12,2172
-1	2	6	3,7000	4,4550
1	2	6	10,4000	10,2797
1	3	6	20,6000	20,6678
-1	3	6	79,2000	79,4779
-1	4	6	79,7000	80,1550
1	4	6	18,4000	18,1705
1	6	6	2,9000	1,7386
-1	7	6	24,6000	24,7679
1	7	6	6,4000	7,4774
-1	8	6	21,1000	22,1586
1	8	6	8,3000	8,4567
-1	9	6	4,5000	3,8312
1	9	6	8,1000	8,7271
1	10	6	5,2000	5,7505
-2	0	6	6,5000	6,3903
2	0	6	31,7000	31,8953
-2	1	6	11,3000	11,7024
2	1	6	17,3000	17,9603
2	2	6	9,5000	9,3545
-2	3	6	36,1000	36,2550
-2	4	6	36,5000	36,8081
2	4	6	6,5000	6,2968
2	5	6	7,0000	5,5070
-2	6	6	3,9000	4,1563
2	6	6	5,6000	4,3455
2	7	6	9,5000	8,7522
-2	8	6	6,9000	8,6545
2	8	6	13,1000	14,0455
-2	9	6	3,2000	2,7393
2	9	6	8,9000	8,2413
-3	0	6	6,8000	7,2651
3	0	6	30,1000	29,8666
3	1	6	11,9000	11,1888
-3	2	6	6,2000	6,1424
3	2	6	14,7000	14,1816
-3	3	6	26,2000	27,3541
3	3	6	16,8000	16,5632
-3	4	6	27,5000	28,1984
-3	5	6	8,3000	7,9512
-3	6	6	3,5000	3,0578
3	5	6	3,0000	,9654
-3	7	6	8,2000	9,4579
3	7	6	10,4000	12,3743
3	6	6	8,9000	9,4184
-3	8	6	6,6000	8,7350
3	8	6	9,4000	10,6682
3	9	6	12,4000	11,2189
-4	0	6	22,9000	23,3072
4	0	6	7,7000	8,3371
-4	1	6	5,3000	5,8488
-4	2	6	8,7000	9,1392
4	2	6	4,3000	3,7164
-4	3	6	6,4000	5,5644
4	3	6	7,3000	6,2488

H	K	L	Y(OBS)	Y(CALC)
-4	4	6	4,2000	4,3873
4	4	6	3,3000	3,4674
4	5	6	4,1000	5,5875
-4	6	6	6,2000	5,6285
4	6	6	13,0000	13,0209
-4	7	6	11,8000	11,4769
-4	8	6	10,8000	11,3605
-4	9	6	5,4000	5,9511
-5	0	6	33,4000	34,4606
5	0	6	5,1000	4,4606
-5	1	6	5,4000	5,3518
5	1	6	3,1000	2,6919
-5	2	6	10,3000	9,8742
5	2	6	5,7000	5,2933
-5	3	6	17,9000	17,4274
5	3	6	10,8000	10,4322
-5	4	6	3,5000	2,0917
5	4	6	3,2000	2,4956
-5	5	6	7,7000	7,1583
5	5	6	4,6000	4,1406
-5	6	6	9,1000	10,2754
-5	7	6	24,1000	25,0742
-5	9	6	4,3000	4,1429
-6	0	6	13,1000	13,2251
-6	1	6	2,9000	2,4249
6	1	6	15,8000	16,2005
-6	2	6	5,3000	4,6273
6	2	6	16,4000	17,1993
-6	3	6	6,2000	6,9365
-6	4	6	4,3000	5,4430
6	4	6	3,8000	2,6641
-6	5	6	10,3000	10,4097
6	5	6	12,6000	12,9728
-6	6	6	8,9000	11,2048
6	6	6	10,7000	9,3395
-6	7	6	8,3000	9,2058
-7	0	6	6,0000	5,2455
7	1	6	4,0000	2,5147
-7	2	6	4,6000	4,4020
7	2	6	3,3000	2,8981
-7	3	6	9,7000	9,1781
-7	4	6	4,5000	2,7752
-7	5	6	3,5000	2,3247
-7	6	6	5,7000	5,5681
-7	7	6	9,5000	10,0604
-8	0	6	5,2000	6,6696
-8	1	6	4,7000	6,5903
-8	2	6	20,5000	21,0434
-8	3	6	11,3000	12,9404
-8	5	6	7,2000	8,9763
-8	6	6	10,9000	12,9286
-9	1	6	6,3000	7,3450
-9	2	6	3,2000	2,2134
0	1	7	12,0000	11,6127
0	2	7	15,7000	15,7825
0	3	7	10,2000	9,8140
0	4	7	14,9000	15,1598
0	5	7	14,4000	14,0405
0	6	7	6,3000	6,1320
0	8	7	4,6000	5,5022
0	9	7	4,9000	5,0875
-1	1	7	6,2000	5,3298
1	1	7	21,1000	20,9053
-1	2	7	32,5000	32,8193
1	2	7	17,1000	17,9116
-1	3	7	9,5000	8,9304
1	3	7	5,6000	5,4981
-1	4	7	39,3000	37,2932
-1	5	7	22,3000	24,0961
1	5	7	5,7000	2,8295
-1	6	7	14,4000	14,7202
1	6	7	7,5000	6,1585
-1	7	7	10,5000	9,8469
-1	8	7	13,6000	13,4286
1	8	7	5,9000	5,1886
-1	9	7	3,5000	3,3090
-2	1	7	13,9000	13,9276
2	1	7	4,2000	2,1170
-2	2	7	19,4000	19,2278
2	2	7	4,1000	3,9398
-2	3	7	5,0000	4,5944
2	3	7	5,1000	5,3903
-2	4	7	33,8000	32,3337
-2	5	7	23,8000	23,3728
2	5	7	10,6000	10,2156
2	6	7	11,0000	9,7860
-2	7	7	14,4000	14,2116
-2	9	7	3,5000	1,9882
2	9	7	6,0000	4,1127
-3	1	7	5,1000	3,9199
3	1	7	30,1000	28,9794
-3	2	7	2,8000	1,5667
3	2	7	9,4000	8,9540
-3	3	7	11,3000	10,6345
3	3	7	14,2000	13,7880
-3	4	7	21,7000	20,7770
3	4	7	5,5000	5,4407
-3	5	7	8,5000	9,1034
-3	6	7	5,4000	7,4843
3	6	7	31,7000	32,4915
-3	7	7	8,2000	9,0897
-3	8	7	8,8000	10,1569
-4	1	7	18,5000	19,6754
-4	2	7	2,9000	3,1114
4	2	7	11,6000	11,4987
4	3	7	9,6000	9,1597
4	5	7	6,5000	6,2065
4	6	7	10,1000	10,8025

H	K	L	Y(OBS)	Y(CALC)
-4	8	7	6,8000	8,7497
-4	9	7	10,6000	10,8331
-5	1	7	3,9000	6,3149
5	1	7	7,5000	7,1857
-5	2	7	3,2000	2,9628
-5	3	7	3,1000	2,4248
5	3	7	4,2000	3,8612
-5	4	7	10,9000	10,4080
5	5	7	6,0000	4,9435
-5	6	7	4,3000	4,0521
5	6	7	14,9000	14,4285
-5	7	7	4,7000	4,6028
-6	1	7	7,0000	6,9438
6	2	7	19,2000	19,9900
-6	4	7	24,2000	24,8292
-6	5	7	12,4000	13,6680
-6	6	7	5,9000	7,4112
-6	7	7	3,2000	4,1498
-6	8	7	3,2000	3,8896
-7	2	7	6,7000	5,5930
-7	3	7	7,9000	6,8590
-7	6	7	3,7000	2,4670
-7	7	7	7,4000	8,0332
-8	1	7	7,0000	7,0218
-8	2	7	6,6000	7,2149
-8	3	7	8,9000	9,7805
-8	4	7	10,4000	9,8538
-8	5	7	9,0000	8,6144
-9	1	7	6,4000	6,9705
-9	2	7	12,2000	11,7411
-9	3	7	6,0000	6,5448
0	1	8	7,7000	7,4340
0	2	8	6,5000	6,1648
0	5	8	12,6000	12,5185
0	6	8	5,9000	6,6841
0	7	8	7,1000	5,8690
-1	1	8	19,7000	19,6365
1	1	8	22,5000	21,9173
-1	2	8	3,5000	1,4455
1	2	8	5,9000	5,6758
-1	3	8	14,1000	13,9386
1	3	8	3,2000	2,5651
-1	4	8	13,0000	11,5821
-1	5	8	34,2000	32,5893
1	5	8	5,7000	5,5375
-1	6	8	3,4000	3,4338
1	6	8	7,0000	5,4729
1	7	8	4,2000	2,7509
-1	8	8	3,2000	3,6168
-1	9	8	10,6000	10,7152
-2	1	8	20,1000	19,4000
2	1	8	5,7000	6,0658
2	2	8	10,8000	9,8000
-2	3	8	16,5000	15,6413
2	3	8	3,3000	2,7627
-2	4	8	21,0000	20,0657
-2	5	8	27,7000	26,4174
2	5	6	8,2000	7,6187
-2	6	8	17,0000	16,9711
-2	7	8	9,1000	9,3084
2	7	8	6,9000	6,1042
-2	8	8	6,9000	8,3555
-2	9	8	6,2000	5,3145
-3	0	8	3,2000	2,4182
3	0	8	7,9000	7,0858
-3	1	8	2,8000	2,4495
3	2	8	7,9000	7,0210
-3	3	8	5,5000	5,0998
3	3	8	12,0000	11,9937
-3	4	8	6,4000	4,1746
3	4	8	6,5000	5,9342
-3	5	8	8,7000	7,7188
3	5	8	23,2000	23,2987
-3	7	8	4,5000	4,3838
3	7	8	5,9000	4,7575
-3	8	8	5,1000	4,2859
-4	0	8	24,6000	24,9288
4	0	8	9,9000	10,3301
-4	1	8	18,3000	18,7924
4	1	8	5,7000	5,7569
-4	2	8	5,3000	5,0373
4	2	8	8,7000	9,0085
4	3	8	3,5000	2,6535
-4	4	8	11,4000	11,7224
-4	5	8	6,9000	8,5379
-4	8	8	8,6000	9,3572
-5	0	8	3,6000	4,8889
5	0	8	5,5000	5,9277
-5	1	8	15,3000	15,7835
5	1	8	6,1000	6,0002
-5	2	8	5,9000	6,0701
-5	3	8	5,4000	5,0057
-5	4	8	3,1000	3,3486
5	4	8	9,1000	8,8285
-5	5	8	13,4000	14,3946
-5	6	8	6,4000	6,4611
-5	7	8	3,2000	3,5811
-5	8	8	15,6000	16,7227
-6	0	8	7,6000	7,9814
6	0	8	17,9000	19,6261
-6	1	8	17,5000	17,1630
-6	3	8	12,5000	12,7351
-6	4	8	7,3000	8,6227
-6	5	8	8,3000	9,2813
-7	0	8	8,6000	10,4723
-7	1	8	8,5000	8,8561
-7	3	8	3,2000	2,1943
-7	4	8	4,8000	5,7285

H	K	L	Y(OBS)	Y(CALC)
-7	5	8	3,2000	2,7733
-8	0	6	10,1000	12,2595
-8	3	8	6,5000	5,9046
-8	4	8	13,0000	13,1384
0	4	9	4,0000	2,6479
0	5	9	10,1000	10,3446
0	6	9	24,7000	24,4193
0	7	9	6,2000	7,0056
-1	1	9	11,0000	11,4594
1	1	9	11,7000	11,7856
-1	2	9	9,2000	8,7244
1	2	9	5,5000	5,4724
-1	3	9	17,3000	16,5241
1	3	9	6,7000	6,1029
1	4	9	4,3000	2,7803
-1	5	9	5,0000	4,3956
-1	6	9	26,1000	25,8225
-1	7	9	5,4000	4,7774
-2	1	9	16,4000	16,8421
-2	2	9	12,9000	12,9942
2	2	9	15,6000	14,8917
-2	3	9	23,6000	22,4840
-2	4	9	4,0000	3,5038
2	4	9	5,1000	5,1727
-2	5	9	21,3000	20,5341
-2	6	9	49,9000	48,5959
2	6	9	4,0000	3,4584
-2	7	9	3,2000	2,5746
-3	1	9	3,0000	3,0257
3	1	9	3,2000	2,9216
3	2	9	14,1000	14,0499
-3	3	9	5,0000	4,2014
3	3	9	4,0000	2,8737
3	4	9	8,7000	9,2915
-3	5	9	3,9000	4,3309
3	5	9	10,6000	10,0675
-3	6	9	15,2000	15,5762
3	6	9	4,1000	3,6945
-3	7	9	3,2000	3,2584
-4	1	9	8,2000	6,8418
4	1	9	8,0000	8,2640
-4	3	9	4,7000	3,0572
4	4	9	4,4000	3,9203
-4	6	9	12,7000	12,1818
-4	7	9	5,7000	5,4831
-5	1	9	7,4000	7,1083
5	1	9	8,9000	9,9601
-5	2	9	9,3000	8,8886
-5	4	9	3,7000	3,1114
-5	5	9	14,3000	14,9566
-6	1	9	11,8000	11,5550
-6	2	9	11,2000	11,4707
-6	5	9	15,8000	16,2547
-6	6	9	10,6000	11,7462
-7	1	9	8,7000	9,8451
-7	2	9	5,7000	6,3757
-8	2	9	4,2000	3,8898
0	0	10	8,4000	8,1409
0	1	10	4,5000	4,3385
0	4	10	4,6000	3,9043
0	5	10	4,6000	4,9958
-1	0	10	18,9000	19,2179
1	0	10	17,8000	17,7927
-1	1	10	6,7000	5,9804
1	1	10	8,6000	8,4444
-1	2	10	3,7000	2,5769
1	2	10	4,9000	4,4995
-1	3	10	13,6000	12,6641
1	3	10	8,7000	7,5648
1	4	10	3,8000	3,1625
-2	0	10	13,6000	14,8968
2	0	10	23,5000	22,7945
-2	1	10	3,4000	2,3806
2	1	10	11,6000	11,0717
-2	3	10	13,1000	12,9280
2	3	10	11,7000	10,5518
2	4	10	11,7000	11,3772
-2	5	10	16,7000	15,5763
2	5	10	3,9000	3,0209
-2	6	10	19,6000	20,1700
-3	0	10	7,3000	7,7739
-3	1	10	6,1000	5,8194
3	1	10	8,8000	8,1188
-3	2	10	3,9000	3,7298
-3	3	10	3,9000	4,1899
3	3	10	11,0000	11,0383
-3	5	10	4,0000	4,2516
-3	6	10	16,5000	16,7282
-4	0	10	6,2000	5,5310
4	0	10	15,8000	15,3062
-4	1	10	10,5000	9,6868
-4	2	10	6,5000	5,4717
-4	3	10	4,9000	4,2840
-4	5	10	10,1000	9,5671
-4	6	10	9,8000	9,7053
-5	1	10	5,7000	5,8347
-5	2	10	5,2000	5,7595
-6	1	10	4,2000	4,6373
-6	3	10	5,4000	6,2935
-7	1	10	6,2000	8,1826
0	1	11	6,0000	5,3982
0	4	11	10,0000	8,9483
-1	1	11	7,0000	7,1844
1	1	11	3,2000	2,6683
-1	3	11	4,0000	3,9393
-1	4	11	5,5000	5,5193
1	4	11	4,5000	3,1678
-2	2	11	6,1000	6,9582

H	K	L	Y(OBS)	Y(CALC)
-2	3	11	11,3000	10,7157
-2	4	11	25,0000	25,6864
-3	1	11	8,8000	8,6413
-3	2	11	4,6000	5,2934
-3	5	11	6,1000	5,5795
-4	1	11	7,1000	5,7030
-4	3	11	3,2000	4,4227
-4	4	11	5,7000	6,6870
-5	1	11	4,6000	6,2458
-5	3	11	4,5000	7,4508
-6	1	11	10,2000	14,2823
-6	2	11	3,2000	3,4523
-1	0	12	3,7000	3,4988
-1	1	12	6,3000	6,2063
-2	0	12	10,8000	12,1918
-2	1	12	11,6000	11,8255
-3	0	12	8,0000	8,0502
-3	1	12	8,9000	9,3558