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SOME CRYSTAL STRUCTURES OF
SULPHUR NITROGEN AND CARBON BORON COMPOUNDS

By

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A Thesis Submitted for the Degree of Doctor
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Memorandum

This thesis describes research in chemical crystallography carried out in the Chemistry Department of the University of Durham between October 1972 and July 1975. This is the original work of the author except where acknowledged by reference, and has not been submitted for any other degree.

Part of the work described in this thesis has been the subject of the following publication:

The structure of thiodithiazyl chlorodisulphate, $S_3N_2S_2O_6Cl$ and its preparation from thiodithiazl monochloride, S_3N_2Cl, Banister, A.J., Clarke, H.G., Rayment, I. and Shearer, H.M.M. (1974). Inorg. Nucl. Chem. Letters 10, 647.

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SUMMARY

The crystal structures of five compounds containing cyclic sulphur-nitrogen species and one carbon-boron compound have been studied using X-ray diffraction methods. The sulphur-nitrogen compounds all contain two-coordinate nitrogen atoms and short S-N bonds which are characteristic of multiple bonding.

$[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$

The cation consists of two, almost planar S_3N_2 rings related by a centre of symmetry and held together by a four-centre S-S interaction. Each ring is thought to contain an aromatic 6π system.

$P_3N_3F_5$-N-S_3N_2

The molecule consists of an S_3N_2 ring bonded at sulphur via a bridging nitrogen atom to a fluorophosphonitrilic ring. The S_3N_2 ring is thought to contain a pseudo-aromatic 6π system.

$S_5N_5^+S_3N_3O_4^-$

The cation is a roughly planar ten-membered ring of alternating sulphur and nitrogen atoms, and represents a 14π inorganic aromatic Hückel compound. Its shape is that of azulene except that the molecule does not have a transannular N-N bond. The anion is an S_3N_3 ring with two oxygen atoms on two of the sulphurs. The SO_2-N-SO_2 part of the ring which carries the negative charge is bonded by single bonds to a sulphur diimide fragment.

$S_5N_5^+[SnCl_5POCl_3]^-$

The $S_5N_5^+$ cation is essentially the same as in $S_5N_5^+S_3N_3O_4^-$. The anion consists of a tin atom bonded to five chlorine atoms and the oxygen of a $POCl_3$ ligand in a roughly octahedral arrangement.

$S_4N_4O_2$

This molecule consists of a non-planar S_4N_4 ring with both oxygen atoms attached to the same sulphur.

$(BCH_3)_6(CH)_4$

The molecule has a structure resembling that of adamantane. The framework of the molecule consists of a tetrahedron of carbon atoms held together by six boron atoms so that the molecular symmetry approximates to $\bar{4}3m$. Unlike normal carboranes the bonding can be described in terms of localised single B-C bonds.

CHAPTER 1

Structure Determination By X-Ray Diffraction Methods

1.1 Introduction.

The most important feature of the crystalline state is the three dimensional periodicity of the atomic or molecular arrangement within the crystals. Any position in a crystal is surrounded by a regular array of further positions which have exactly the same environment; this array defines the crystal lattice and gives a geometrical representation of the periodicity within a crystal. The lattice may be described in terms of any three non-coplanar vectors, $\underline{a}$, $\underline{b}$ and $\underline{c}$ which represent unit translations between lattice points. These vectors define a parallelopiped which is referred to as the unit cell. This is described as primitive if there is one lattice point associated with it. In general there are elements of symmetry associated with the unit cell, and the entire set will correspond to one of the thirty two possible crystallographic point groups. The symmetry elements of the unit cell together with the translational elements of symmetry provided by the lattice define the space group of the crystal.

The faces and planes within a crystal may be indexed according to their relationship with the vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$. A series of parallel planes which divide the vector $\underline{a}$ into h parts, $\underline{b}$ into k parts and $\underline{c}$ into l parts is given the indices hkl and these are known as Miller indices. Crystal faces normally contain a high concentration of lattice points and consequently have small values for h, k, and l.

1.2 Diffraction of X-rays and the Reciprocal Lattice.

In 1912 von Laue suggested that if X-rays were wave-like in nature and their wavelength was of the same magnitude as the distances between atoms, then it ought to be possible to observe X-ray diffraction effects. This suggestion was tested by Friedrich and Knipping who allowed a beam of white X-ray radiation to fall on a copper sulphate crystal and recorded the resulting diffraction pattern on photographic film. This established the wave properties of X-rays and started the science of X-ray crystallography.

Von Laue interpreted the results in terms of diffraction from a three-dimensional array of scattering centres according to the relationships

$$a\,(\cos\alpha - \cos\alpha_o) = h\lambda$$
$$b\,(\cos\beta - \cos\beta_o) = k\lambda$$
$$c\,(\cos\gamma - \cos\gamma_o) = 1\lambda$$

where each expression represents the conditions necessary for diffraction to occur from a line of scatterers parallel to the axial directions. α_o β_o and γ_o represent the angles of the incident radiation to the directions $\underline{a}$, $\underline{b}$ and $\underline{c}$, whereas α, β and γ represent the angles of diffraction. Whilst this approach is rigorous it is hard to visualise.

W.L. Bragg interpreted the diffraction patterns as being the result of the reflection of X-rays from planes within the crystal, and showed that for a set of planes with spacing d_{hkl} the necessary condition for diffraction is, $n\lambda = 2d_{hkl} \sin\theta$, where θ is the angle of the incident and diffracted radiation to the planes. This approach is much easier to understand but describes diffraction effects in terms of reflections.

A further concept of great value in interpreting diffraction patterns is that of the reciprocal lattice. This is defined by the three vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ such that

$$\begin{array}{lll} \underline{a}.^*\underline{a} = 1 & \underline{a}^*.\underline{b} = 0 & \underline{a}^*.\underline{c} = 0 \\ \underline{b}^*.\underline{a} = 0 & \underline{b}^*.\underline{b} = 1 & \underline{b}^*\underline{c} = 0 \\ \underline{c}^*.\underline{a} = 0 & \underline{c}^*.\underline{b} = 0 & \underline{c}^*.\underline{c} = 1 \end{array}$$

i.e. $\underline{a}^*$ is perpendicular to $\underline{b}$ and $\underline{c}$. If ϕ is the angle between $\underline{a}$ and $\underline{a}^*$ then

$$\underline{a}.\underline{a}^* = |\underline{a}|\ |\underline{a}^*| \cos\phi$$

Hence

$$|\underline{a}^*| = \frac{1}{|\underline{a}|.\cos\phi}$$

$$= \frac{1}{d_{100}}$$

Each point in the lattice is related to a series of parallel planes in the crystal. For the planes of index hkl, the vector $\underline{s}$ of magnitude $\frac{1}{d_{hkl}}$ and direction perpendicular to the planes corresponds exactly to the vector $h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$. The vector $\underline{s}$ is known as the scattering vector.

1.3 The Structure Factor.

A crystal which contains N atoms in its unit cell may be viewed as N interpenetrating lattices, each centred on the position of one atom. The intensity of diffraction from that crystal may then be explained in terms of the sum of the diffraction from the individual lattices. The scattering from these arrays will differ in phase according to their separation.

Consider one atom, A in the cell; its position may be defined by the vector

$$\underline{r_A} = x\underline{a} + y\underline{b} + z\underline{c}$$

where x y and z are the coordinates in the fractions of the cell edges. The scattering from the array based on this atom with respect to one electron at the origin of each unit cell is given by the expression, $f_A \exp(2\pi i\, \underline{r_A}.\underline{s})$, where f_A is the scattering factor for the atom A and $\underline{s}$ is the scattering vector such that $\underline{s} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$. Thus $\underline{r_A}.\underline{s}$ represents the perpendicular distance of the atom from the plane hkl. The exponential function, $\exp(2\pi i\, \underline{r_A}.\underline{s})$, may be viewed as a rotation function in the complex plane and represents the difference in phase between the position $\underline{r_A}$ and the origin i.e.

$$\frac{\phi_A}{2\pi} = \underline{r_A}.\underline{s}$$

The expression for the scattering by the entire contents of the unit cell is given by

$$F(hkl) = \sum_{n=1}^{N} f_n \exp(2\pi i \, \underline{r_n} . \underline{s})$$

Substituting for $\underline{r_n}$ and $\underline{s}$ gives

$$F(hkl) = \sum_{n=1}^{N} f_n \exp 2\pi i(x_n\underline{a} + y_n\underline{b} + z_n\underline{c}).(h\underline{a}^* + k\underline{b}^* + l\underline{c}^*)$$

which reduces to

$$= \sum_{n=1}^{N} f_n \exp[2\pi i(hx_n + ky_n + lz_n)]$$

this may be expressed in terms of its real and imaginary parts, i.e.

$$F(hkl) = A(hkl) + iB(hkl)$$

where

$$A(hkl) = \sum_{n=1}^{N} f_n \cos 2\pi(hx_n + ky_n + lz_n)$$

$$B(hkl) = \sum_{n=1}^{N} f_n \sin 2\pi(hx_n + ky_n + lz_n)$$

The scattering factors are calculated from the spatial distribution of electrons around the nucleus of the atom and are derived from the atom's atomic wave function.

Because the electrons associated with an atom occupy a finite volume, X-rays scattered from different parts of the atom differ increasingly in phase with increasing scattering angle. This results in destructive interference and consequently a decrease in the scattering factor with increasing scattering angle.

The quantity F(hkl) is known as the structure factor for the reflection hkl; its modulus $|F(hkl)|$ is known as the structure amplitude and is defined as the ratio of the amplitude of the radiation scattered by the contents of one unit cell, compared to that scattered by a single electron at the origin. The structure amplitude is given by

$$|F(hkl)|^2 = A(hkl)^2 + B(hkl)^2$$

and the phase angle for the scattered radiation is given by

$$\phi(hkl) = \tan^{-1} \frac{B}{A}$$

The presence of symmetry in the unit cell and lattice enables the structure factor calculation to be simplified. The most important element is the centre of symmetry, since this causes the B(hkl) terms to vanish. This occurs because $\sin(-\theta) = -\sin\theta$ and for every atom at x, y, z there is a corresponding one at $\bar{x},\bar{y},\bar{z}$. As a consequence the phase angle is either 0 or π and the structure factors are either positive or negative. If further elements of symmetry are present then the structure factor may be simplified by collecting together all the terms arising from the equivalent positions and combining them trignometrically. However when atoms are vibrating anisotropically the scattering factors may not be the same for atoms in different equivalent positions and may not contribute equally to the structure factor. In these cases the general expression has to be used.

The observed structure factor corresponds to diffraction from the electron density throughout the cell, and the form just given calculated on the basis of spherically symmetrical atoms is an approximation to the actual electron density. If the diffraction of an infinetessimally small volume of electron density is considered, then the diffraction from the whole cell is given by the expression

$$F(hkl) \int_0^1\int_0^1\int_0^1 \rho(xyz)\ \exp[2\pi i(hx + ky + lz)]\ V\ dxdydz$$

where V dxdydz is the small volume and $\rho(xyz)$ is the electron density at the point x, y, z.

1.4 Temperature Factor.

The description of the structure factor just given is based on diffraction from a periodic array of stationary atoms; in reality the atoms in a crystal are subject to vibration about their mean position. The frequencies of vibration are very small compared to that of the X-rays i.e. $\approx 10^{13}$Hz for thermal vibration as compared to $\approx 10^{18}$Hz for X-rays, so that the X-rays effectively encounter a stationary model, in which the atoms are displaced slightly from their mean positions. As a consequence of destructive interference the scattering factor falls off more rapidly with increasing sin θ/λ than for the atom at rest.

The scattering factor for an atom in thermal vibration is given by the product of f_o for the atom at rest multiplied by the transform q of the smearing function t

i.e. $$f_t(hkl) = f_o(hkl)\, q(hkl)$$

For isotropic thermal motion q becomes

$$q = \exp[-B(\sin\theta/\lambda)^2]$$

where $$B = 8\pi^2\overline{u^2}$$

B is known as the Debye factor and $\overline{u^2}$ is the mean square amplitude of vibration.

In most cases the vibrations are not isotropic and the electron density time averages to ellipsoids. These may be described by a symmetrical tensor U with six independent components, such that the mean square amplitude of vibration in the direction of the unit vector $\underline{l} = (l_1, l_2, l_3)$ is

$$\overline{U} = \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} l_i l_j$$

or $$\overline{U} = U_{11}l_1^2 + U_{22}l_2^{\,2} + U_{33}l_3^{\,2} + 2U_{23}l_2l_3 + 2U_{31}l_3l_1 + 2U_{12}l_1l_2$$

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

For ease of computation these terms may be expressed as

$$q(hkl) = \exp[-(\beta_{11}h^2 + \ldots. + \beta_{23}kl + \ldots.)]$$

where $\beta_{11} = 2\pi^2 a^{*2} U_{11}$

$$\beta_{23} = 4\pi^2 b^* c^* U_{23}$$

It is often of value to have an estimate of the overall temperature factor and scale factor before the structure is known, and these can be estimated by a method due to Wilson (1942). He showed that the average of the square of the structure amplitude over a range of $(\sin\theta/\lambda)^2$ tends to be given by

$$\overline{|F|}^2 = \sum_j \overline{f_j}^2$$

Where $\sum \overline{f_j}^2$ represents the sum of the squares of the atomic scattering factors for the atoms in the cell, and are calculated for the centre of the $(\sin\theta/\lambda)^2$ range. $\overline{|F_o|}^2$ is usually known on an arbitrary scale, so that

$$\overline{|F_o|}^2 = K\overline{|F|}^2$$

and therefore

$$\overline{|F_o|}^2 = K\sum_j \overline{f_j}^2$$

Assuming the Debye-Waller correction

$$f_j^2 = f_{oj}^2 \exp(-2\,B\,\sin^2\theta/\lambda^2)$$

Substituting and taking logarithms gives

$$\ln\left(\frac{\overline{|F_o|^2}}{\sum_j \overline{f_{oj}^2}}\right) = \ln K - \frac{2B}{\lambda^2}\sin^2\theta$$

A plot of $\sin^2\theta$ against $\ln \overline{|F_o|^2} / \sum_j \overline{f_{oj}^2}$ gives from the intercept an estimate of the scale factor and from the slope an estimate of the temperature factor.

1.5 Anomolous Dispersion.

For both centrosymmetric and noncentrosymmetric crystals the intensities of the rays diffracted from the planes hkl and $\overline{hkl}$ are identical (Friedel's law) unless one of the atoms has an absorption edge which lies close to but on the long-wavelength side of the radiation used for diffraction. In this case the wave scattered by that atom shows an anomolous phase shift. The scattering factor f can now be expressed in terms of the normal scattering factor f_o and two additional correction factors i.e.

$$f = f_o + f' + if''$$

For noncentric crystals this produces a breakdown of Friedal's law and may be used to determine absolute configurations. In the case of centric crystals Friedal's law still holds, but the intensities are modified and unless a correction is made for this effect there may be systematic errors in the atomic parameters (Templeton, 1955).

1.6 Fourier Series

In X-ray diffraction a crystal may be described in terms of a periodic distribution of electron density which can be represented by a three-dimensional Fourier series

$$\rho(xyz) = \sum_{h'k'l'}\sum\sum C(h'k'l')\ \exp[2\pi i(h'x + k'y + l'z)]$$

where h', k' and l' are integers from $-\infty \rightarrow +\infty$. This expression for $\rho(xyz)$ may be substituted into the expression for F(hkl)

$$F(hkl) = \int_V \rho(xyz)\exp[2\pi i(hx + ky + lz)]dV$$

and becomes

$$F(hkl) = \int_V \sum_{h'k'l'}\sum\sum C(h'k'l')\exp 2\pi i[(h+h')x + (k+k')y + (l+l')z]dV$$

The individual terms in this integration are all zero except when $h' = -h$, $k' = -k$ and $l' = -l$, so that

$$F(hkl) = V\ C(\overline{hkl})$$

and therefore

$$\rho(xyz) = \frac{1}{V}\sum_{h\,k\,l}\sum\sum F(hkl)\exp[-2\pi i(hx + ky + lz)]$$

These relationships show that the structure factors are the Fourier transform of the electron density. It is significant that the expression for the electron density, which is a real quantity, involves not only the magnitude of the structure factor but also its phase. This constitutes the phase problem, since only the magnitudes can be measured experimentally. So that before the electron density can be calculated from the observed structure factors, their phases must be found.

This form of the expression for $\rho(xyz)$ is not the most convenient for computation. Remembering that $F(hkl) = A(hkl) + iB(hkl)$ and since

$$A(hkl) = |F(hkl)| \cos \phi(hkl)$$
$$B(hkl) = |F(hkl)| \sin \phi(hkl)$$

$F(hkl)$ may be written as

$$F(hkl) = |F(hkl)| \exp[i\,\phi(hkl)]$$

so that $\rho(xyz)$ may be written as

$$\rho(xyz) = \sum_{hkl} |F(hkl)| \exp-[2\pi i(hx + ky + lz) - \phi(hkl)]$$

but since $|F(hkl)| = |F(\overline{hkl})|$ the contributions due to these terms may be collected together, and then the expression reduces to

$$\rho(xyz) = \frac{F_{000}}{V} + \frac{2}{V} \sum_{h=0}^{\infty} \sum^{\infty} \sum_{k,l=-\infty}^{\infty} |F(hkl)| \cos[2\pi(hx + ky + lz) - \phi(hkl)]$$

This may be simplified considerably if there are additional elements of symmetry present in the unit cell. These simplified forms are given in International Tables Vol I for all space groups.

1.7 Patterson Function.

In an attempt to overcome the phase problem Patterson (1934) suggested calculating a Fourier synthesis using the squares of the structure amplitudes as Fourier coefficients. He defined a function

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

Substitution of the expression for $\rho(xyz)$ gives

$$P(uvw) = \frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|^2 \exp[2\pi i(hu + kv + lw)]$$

where $P(uvw)$ is known as the Patterson function and is real for all values of u, v and w. This may be expanded to give

$$P(uvw) = \frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|^2 \cos[2\pi(hw + kv + lw)]$$

The magnitude of the Patterson function, $P(uvw)$ for a point u, v, w in the Patterson vector map represents the summation of the product of the electron density at a point x, y, z and at a point x + u, y + v, z + w over the entire cell. Hence large peaks will be found in the vector map corresponding to the vectors between atoms, and their magnitude will be related to the product of their atomic numbers. There is always a large peak at the origin corresponding to the vector between each atom and itself.

Interpretation of these vector maps is greatly simplified by the presence of symmetry in the unit cell. In certain cases peaks between atoms in equivalent positions are observed whose positions in the vector map are restricted to certain sections or lines. These were first discovered by Harker (1936) and bear his name. For example, if a cell contains a two-fold axis parallel to b, then for an atom at x, y, z there will be a symmetry related atom at $\bar{x}$, y, $\bar{z}$ and a maximum will occur in the vector map at u = 2x, v = 0, w = 2z. With this knowledge it is often possible to locate directly the position of an atom in the unit cell.

1.8 Heavy atom method.

The most important practical case where the Patterson function can be used to solve a structure fairly directly is when the crystal contains a relatively small number of heavy atoms. The Patterson peaks due to these atoms then stand out against a background of overlapping smaller peaks and give immediately the coordinates of the heavy atoms. The coordinates of the lighter atoms may then be determined by computing a Fourier synthesis based on the phases obtained from the heavy atom positions. The expression for the structure factor may be written in the form

$$F(hkl) = f_H \exp 2\pi i(hx + ky + lz) + \sum_j f_j \exp 2\pi i(hx_j+ky_j+lz_j)$$

where f_H is the scattering factor for the heavy atom. The heavy atom will tend to dominate the phases whenever its contribution to the structure factor is greater than that of the remaining atoms. This technique has been found to be most effective if

$$\sum f^2_{\text{heavy atoms}} \approx \sum f^2_{\text{light atoms}}$$

This is applicable since the contribution to the intensity by each atom depends approximately on the square of its scattering factor. If the atom is too heavy then the errors in the intensity measurement become comparable with the contribution from the lighter atoms.

1.9 Direct methods.

The second major approach to the phase problem uses the statistical relationships which exist between the magnitude and phases of the structure factors. Sayre (1952) showed that for a centrosymmetric space group the sign S_H of a reflection H could be derived from a simple product of the signs of algebraically related reflections,

$$\text{i.e.} \qquad S_H \approx S_K . S_{H-K}$$

This expression has a high probability of being correct if the magnitude of the three structure factors F_H, F_K and F_{H-K} are all large.

Hauptman and Karle (1953) devised a statistical approach in which they used a normalised structure factor given by

$$|E_H|^2 = \frac{|F_H|^2}{\epsilon \sum\limits_{j=1}^{N} f_j^2(H)}$$

where ϵ is a factor which takes into account space group extinctions.

They also introduced the Σ_2 relationship expressed as

$$S_H \approx S[\sum_K E_K.E_{H-K}]$$

This is similar to that introduced by Sayre except that the relationship involves more than one interaction. The probability that a sign will be positive is given by (Cochran and Woolfson, 1955)

$$P(E_H)_+ = \frac{1}{2} + \frac{1}{2}\tanh(\sigma_3\sigma_2^{-\frac{3}{2}}|E_H|\sum E_K.E_{H-K})$$

where $\sigma_n = \sum_{j=1}^{N} Z_j^n$

This shows that if the three reflections involved in a triple relationship have large E-values then the probability that the sign relationship will be correct will be large. So that by using probability relationships it is possible to start the assignment of phases from a few strong planes whose phases are either known or represented by symbols, and this is known as the symbolic addition procedure.

A strategy for using this method outlined by Karle and Karle (1966) first involves estimating a set of normalised structure factors and finding the triple relationships which exist amongst the stronger reflections. Next it is necessary to define the origin. This is required since in general there are a number of non-equivalent centres of symmetry and movement from one to another produces systematic changes in the signs of the reflections. The origin is specified by choosing n linearly independent reflections and arbitrarily fixing their signs where n has a maximum value of three and depends upon the space group. These reflections are used to define the signs of further reflections using the Σ_2 relationship. Subsequently several strong planes are given symbolic phases as necessary in order to phase all of the reflections. Signs are only accepted when the total probability for a predicted sign exceeds a specified value. The acceptance limit decreases as the symbolic addition procedure continues but high values initially reduce the number of incorrect sign allocations. At the end of this procedure each reflection may have its sign correctly determined or represented by more than one symbol or combination of symbols, and using these it is possible to predict the most likely signs for the symbols used.

An alternative strategy for using the Σ_2 relationship involves the choice of a few strong reflections whose signs are systematically varied. Each of the possible sign combinations for these reflections, together with the origin determining reflections as before is used as a starting set for reiterative application of Sayre's relationship. This gives a series of solutions and is known as the multisolution method. In the program described by Long (1968) the signs determined from the starting set, are used to predict more signs and redetermine those predicted before. The signs of the starting set are calculated at the end of each cycle but are not allowed to change.

A measure of the self consistency of the predicted signs is given by

$$C = \frac{< |E_A \sum\limits_{A=B+C} E_B E_C| >}{< |E_A| \sum\limits_{A=B+C} |E_B||E_C| >}$$

where $< >$ means averaged over all values of A. The expression compares the observed Σ_2 sum to that which would be observed if all the interactions were consistent. Usually the set with the largest consistency index represents the correct solution.

Sayre's equation applies equally well to noncentrosymmetric structures and in its general form refers to the addition of phases so that

$$< \phi_H > \approx < \phi_H + \phi_{H-K} >_K$$

where K ranges over reflections with large $|E|$ values. In centrosymmetric structures the phases are 0 or π so that this expression simplifies to the product of the signs of the structure factors. This expression is suitable for direct use if the phases of only a few reflections are known. Where there is more than one term contributing to $< \phi_H >$ these may be combined by regarding each term as a vector of length $|E_K . E_{H-K}|$ and direction $|\phi_K + \phi_{H-K}|$. The most probable phase is then given by

$$\tan \phi_H = \frac{\sum_K |E_K E_{H+K}| \sin(\phi_K + \phi_{H-K})}{\sum_K |E_K E_{H-K}| \cos(\phi_K + \phi_{H-K})}$$

which is known as the tangent formula and represents the combination of the vectors by summation of their components parallel to the real and imaginary axes.

1.10 Structure Refinement.

The object of structure refinement is to find the model which gives the best fit to the experimental data. There are far more experimental measurements than parameters to be determined so that the problem is well suited to the method of least squares.

Consider an observable quantity q_i which is a linear function of a set of variables x, y, z ..... then

$$q_i = a_i x + b_i y + c_i z + \ldots\ldots$$

If there are errors involved in the measurement of q_i this may be expressed as

$$q_i + E_i = a_i x + b_i y + c_i z + \ldots\ldots$$

or

$$E_i = a_i x + b_i y + c_i z + \ldots\ldots - q_i$$

then for a series of measurements in which $i = 1 \rightarrow n$ the optimum solution of these n equations for the parameters x, y, z .... requires that $\sum E_i^2$ is a minimum.

In the refinement of a structure it is desirable to make the calculated structure factors agree as closely as possible with those observed, so that using the method of least squares it is usual to minimise the square of the difference between the observed and calculated structure factors. The function most commonly used is

$$R = \sum_{hkl} w'(|F_o| - |F_c|)^2$$

where w(hkl) reflects the reliability of that observation. For R to be a minimum

$$\frac{\partial R}{\partial p_j} = 0 \ (j = 1 \rightarrow n)$$

where p_j is the jth parameter, and hence

$$\sum_{hkl} w\Delta \frac{\partial |F_c|}{\partial p_j} = 0 \quad \text{where } \Delta = |F_o| - |F_c|$$

This process applies to linear functions, however the structure factor is calculated from an exponential function of the form

$$F_c = \sum_r f_r \exp i2\pi(hx_r + ky_r + lz_r)$$

A linear expression relating F_c to its parameters may be obtained by taking the first two terms in Taylor's series. This is a reasonable approximation if the differences between F_o and F_c are small. Taylor's series takes the form

$$f(x+\epsilon) = f(x) + \epsilon \frac{d(fx)}{dx} + \frac{\epsilon^2}{2!} \frac{d^2(fx)}{dx^2} \; \ldots\ldots.$$

In the process of refinement $|F_c| \rightarrow |F_c'|$ where $|F_c'|$ is the structure factor based on the improved parameters $(p_1 + \epsilon_1)$, $(p_2 + \epsilon_2) \ldots\ldots (p_n + \epsilon_n)$

so that

$$\sum_{hkl} w(|F_o| - |F_c'|) \frac{\partial |F_c|}{\partial p_j} = 0 \quad (j = 1 \rightarrow n)$$

But Taylor's theorem gives

$$F_c' = F_c + \sum_{i=1}^{n} \epsilon_i \frac{\partial |F_c|}{\partial p_i}$$

so that

$$|F_o| - |F_c'| = |F_o| - |F_c| - \sum_{i=1}^{n} \epsilon_i \frac{\partial |F_c|}{\partial p_i}$$

Substituting this into $\frac{\partial R}{\partial p_j} = 0$ and letting $|F_o| - |F_c| = \Delta$ gives

$$\sum_{hkl} w\Delta \frac{\partial |F_c|}{\partial p_j} - \sum_{i=1}^{n} \left[\sum_{hkl} w \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j} \right] \epsilon_i = 0$$

$$j = (1 \rightarrow n)$$

This may be rearranged and expanded to give the so called normal equations,

$$\sum_{hkl} w \left(\frac{\partial|F_c|}{\partial p_1}\right)^2 \epsilon_1 + \sum_{hkl} w\left(\frac{\partial|F_c|}{\partial p_2}\right)\left(\frac{\partial|F_c|}{\partial p_1}\right)\epsilon_2 \ldots\ldots = \sum_{hkl} w\Delta \frac{\partial|F_c|}{\partial p_1}$$

$$\sum_{hkl} w\left(\frac{\partial|F_c|}{\partial p_1}\right)\left(\frac{\partial|F_c|}{\partial p_2}\right)\epsilon_1 + \sum_{hkl} w\left(\frac{\partial|F_c|}{\partial p_2}\right)^2 \epsilon_2 \ldots\ldots = \sum_{hkl} w\Delta \frac{\partial|F_c|}{\partial p_2}$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

Alternatively these n equations may be expressed in matrix notation

$$\sum_i a_{ij}\, \epsilon_i = b_j$$

where

$$a_{ij} = \sum_{hkl} w \frac{\partial|F_c|}{\partial p_i} \cdot \frac{\partial|F_c|}{\partial p_j}$$

$$b_j = \sum_{hkl} w\Delta \frac{\partial|F_c|}{\partial p_j}$$

In a structure containing many atomic parameters it is frequently impractical to calculate all the terms a_{ij} of the normal equations. The simplest approximation is to ignore all off-diagonal terms, $(i \neq j)$ but this approach converges slowly and does not yield the best solution. The block-diagonal approximation neglects all off-diagonal elements between different atoms. So that a 9 x 9 matrix is used for the positional and anisotropic thermal parameters for each atom, or a 4 x 4 if the atom is refined with an isotropic temperature factor. A 2 x 2 matrix is used for the scale and overall isotropic temperature parameter. This method requires a larger number of iterations than the full matrix method. In the work described here the block-diagonal approximation was used initially but the refinement was completed using full matrix least squares methods.

1.11 The Accuracy of Parameters derived from Least Squares Methods

In order to obtain a reliable estimate of the accuracy of the atomic parameters the weighting scheme used in the refinement should correspond to $w = \frac{1}{\sigma^2(F_o)}$ where $\sigma^2(F_o)$ is the variance for the observation. In this case the variance of the parameter p_i is given by

$$\sigma^2(p_i) = (a^{-1})_{ii}$$

where $(a^{-1})_{ii}$ is diagonal element of the inverse matrix to the normal equation matrix. Generally $\sigma(F_o)$ is not known exactly so that relative weights of the form $w = \frac{k}{\sigma^2(F_o)}$ are used, in which case the estimated standard deviation is given by

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

where m-n is the number of degrees of freedom. The variances estimated from the block-diagonal approximation underestimate the true variances because of the neglect of the interatomic correlations (Hodgson and Rollett, 1963).

The accuracy of interatomic distances and angles depends upon the estimated standard deviation (e.s.d.) of the atomic coordinates involved (Cruickshank and Robertson, 1953) thus if a molecular parameter $m = \Sigma\, l_i x_i$ is a linear function of a number of atomic parameters then

$$\sigma^2(m) = \sum_i \sum_j l_i l_j \operatorname{cov}(x_i x_j)$$

If the atomic parameters are assumed to be independent the covariances between different atoms are taken as zero. So that for a bond ℓ between two independent atoms having variances of $\sigma^2(a)$ and $\sigma^2(b)$ in the direction of the bond, $\sigma^2(\ell) = \sigma^2(a) + \sigma^2(b)$.

For an angle at B between two bonds AB and BC

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

It is often desirable to compare bond lengths or angles so that a criterion of significance is required. If it is assumed that the errors in the observed structure factors are random and if the number of degrees of freedom ν in estimating a parameter ℓ is large ($\nu > 30$) then the observed parameter will have a normal distribution about its unknown real position λ. For $\nu > 30$ the estimated standard deviation s is a good estimate of the unknown standard deviation. Then $t = (\ell - \lambda)/s$ where t is a random variable which has a Student distribution for ν degrees of freedom.

It is often necessary to test the hypothesis that a theoretical value λ_o is compatible with an observed value ℓ_o. In this case $t_o = (\ell_o - \lambda_o)/s$ and from tables of the Student distribution it is possible to give an estimate of the probability that the hypothesis is correct. If the value of the probability P is small then the hypothesis may be neglected. A larger value of P means that the experimental measurement ℓ_o is not inconsistent with λ_o but does not prove that λ_o is the correct value. For $\nu > 30$ the values of t_o for the usual significance points are

$P = 0.05 \quad t_o = 1.960$

$P = 0.01 \quad t_o = 2.576$

$P = 0.001 \quad t_o = 3.291$

so that if $t_o = 2.576$ then the difference between ℓ_o and λ_o is said to be significant at the 1% level. A difference is often taken as significant if $t > 3.0$.

If it is required to compare the difference between two bond lengths ℓ_1 and ℓ_2 with estimated standard deviations of s_1 and s_2 then for independent bond lengths $t_o = (\ell_1 - \ell_2)/(s_1^2 + s_2^2)^{\frac{1}{2}}$. So that the difference may be taken as significant if $t_o > 3.0$. If the two bonds are not independent i.e. they depend upon the common position of one atom then estimated standard deviation for the difference, $(s_1^2 + s_2^2)^{\frac{1}{2}}$ will be an underestimate of the true value. This may be corrected by including the covariance of the two bonds in the calculation of the e.s.d. of their difference. Cruickshank and Robertson (1953) suggest that the covariance takes the form

$$\mathrm{cov}(\ell_1, \ell_2) = \sigma^2(B) \cos\beta$$

where B is the common atom, $\sigma^2(B)$ is the variance of B in the direction of the tangent to the circle through A, B and C and β is the angle between ℓ_1 and ℓ_2.

1.12 Diffractometer Geometry.

The introduction of diffractometers has considerably improved the ease and speed of data collection whilst also improving the reliability of the data. The geometry of the Hilger and Watts Y290 four-circle diffractometer as shown in figure 1.1 is similar to that used by W.H. Bragg in his spectrometer. The counter, crystal and incident beam lie in the equatorial plane of the instrument so that the first requirement for diffraction from a plane hkl is that its scattering vector $\underline{s} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$ should lie in the equatorial plane. This may be attained by rotating the crystal about the ϕ axis until $\underline{s}$ lies in the plane of the χ circle; rotation using this circle brings $\underline{s}$ into the equatorial plane. The plane may then be brought into the diffracting position by rotating the crystal using the ω circle until the scattering vector touches the sphere of reflection, so that the diffracted beam may be collected by placing

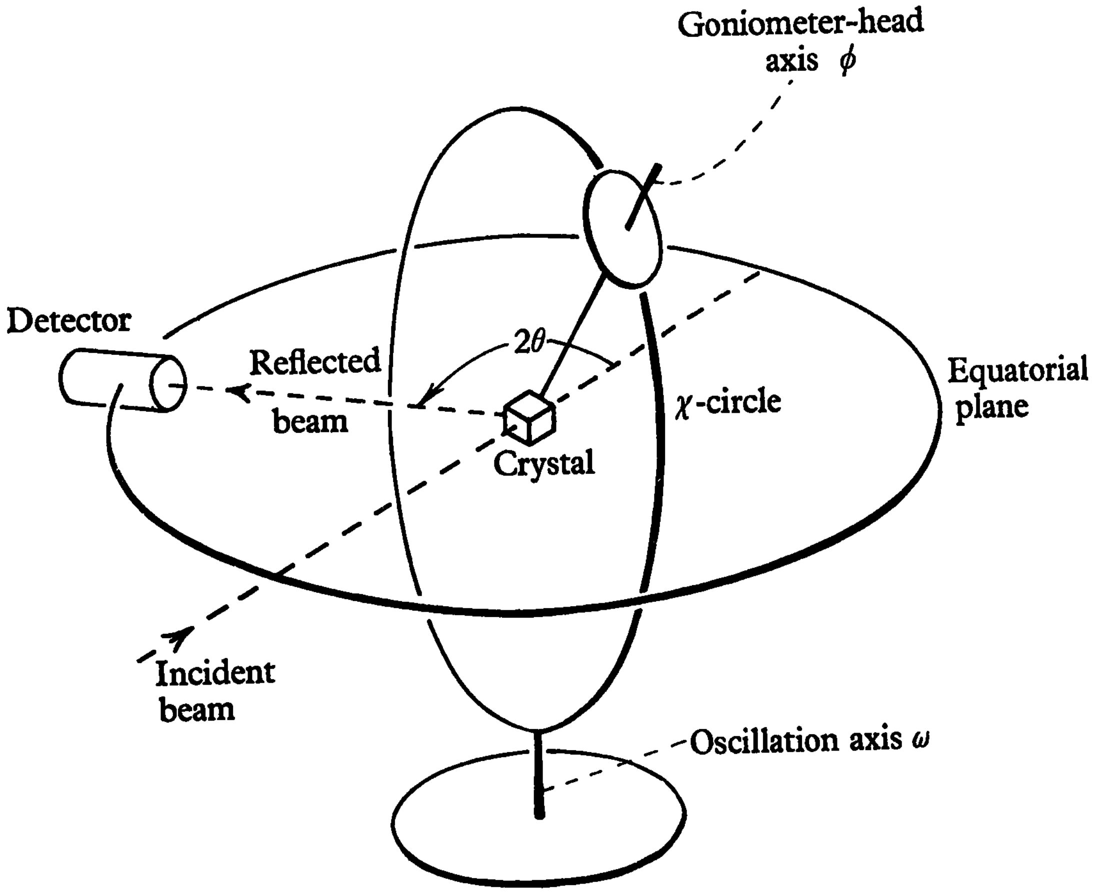

Goniometer-head axis ϕ
Detector
Reflected beam
2θ
χ-circle
Equatorial plane
Crystal
Incident beam
Oscillation axis ω

Figure 1.1

the counter mounted on the θ circle at twice the angle on the ω circle. This is known as the bisecting geometry since the hkl plane is orthogonal to the plane of the χ circle which bisects the angle between the incident and diffracted beams. At large angles of θ the χ circle obstructs the diffracted beam so that it is necessary to change to perpendicular geometry in which the scattering vector is perpendicular to the χ circle and $\theta = 90 - \omega$.

1.13 Lorentz and Polarisation corrections.

The Lorentz factor is introduced to account for the different times that different planes in the crystal spend in the reflecting position, or alternatively how long the reciprocal lattice points remain in contact with the sphere of reflection. For real crystals reflection occurs over a finite angular range, which means that the reciprocal lattice point has a finite size. The time that a reciprocal lattice point takes to cut the sphere of reflection will depend upon the distance of the point from the origin and the way in which it moves through the sphere of reflection.

The Lorentz factor for data collected on a four-circle diffractometer is given by

$$L = \frac{1}{\sin 2\theta}$$

The incident X-ray beam is unpolarised, which means that the azimuth of the electric vector assumes all directions with time. The beam reflected from a crystal is partially polarised and this leads to a reduction in intensity by a factor p which is given by

$$p = \frac{1}{2}(1 + \cos^2 2\theta)$$

this depends only on the angle of diffraction and is independent of the mode of data collection.

CHAPTER 2

Unsaturated Cyclic Sulphur-Nitrogen Compounds

2.1 Introduction.

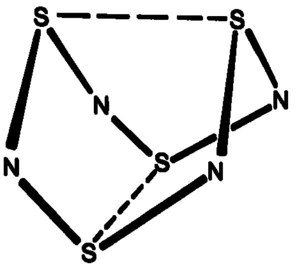
Research into sulphur-nitrogen chemistry was started early in the 19th century. Indeed many of the simpler compounds were discovered before 1900, although the exact nature of the majority of these has not been elucidated until more recently. Early structural work using the techniques of chemical degradation was mostly inconclusive because of problems of analysis and instability of the reaction products. The most successful analyses have been completed using diffraction methods. The more usual techniques of spectroscopy are of great value in this field, but the structural information that they yield is often inconclusive. Sulphur-nitrogen compounds usually lack the structural probes necessary for the satisfactory application of n.m.r. spectroscopy and their infrared spectra are difficult to interpret because of the wide variety of bonding found in these compounds.

Cyclic sulphur-nitrogen compounds may be broadly classified into two groups according to whether they contain a saturated or unsaturated ring system. The chemistry of these compounds has been reviewed recently (Banister, 1974) so that the major emphasis in this review will be placed on the unsaturated species since they are more relevant to the work described later. These are characterised by containing nitrogen atoms which are two-coordinate.

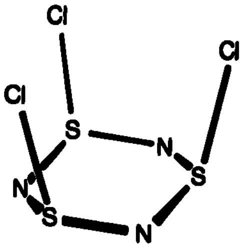
2.2 Tetrasulphur tetranitride.

The most well known unsaturated sulphur-nitrogen compound is tetrasulphur tetranitride, S_4N_4 which was first prepared by Gregory in 1835 by the reaction of disulphur dichloride with ammonia. Early work established its molecular formula, but attempts to deduce its structure from infrared and early X-ray diffraction studies were unsuccessful. Its correct molecular structure was first deduced by electron diffraction (Lu and Donohue, 1944) and has been subsequently confirmed by X-ray diffraction studies (Clarke, 1952 and Sharma and Donohue, 1963). As shown in figure 2.1 the molecule consists of a ring of alternating sulphur and nitrogen atoms which is buckled such that the sulphur atoms lie at the corners of a slightly distorted tetrahedron. There are two main features of interest in this structure. Firstly all the S-N bond distances are the same within experimental error and their mean distance of 1.62Å is considerably shorter than the normal single bond distance of 1.73Å found in S_7NH (Weiss and Neubert, 1965). Secondly the S---S distance of 2.58Å across the ring is much shorter than the S---S van der Waals distance of 3.60Å (Bondi, 1964).

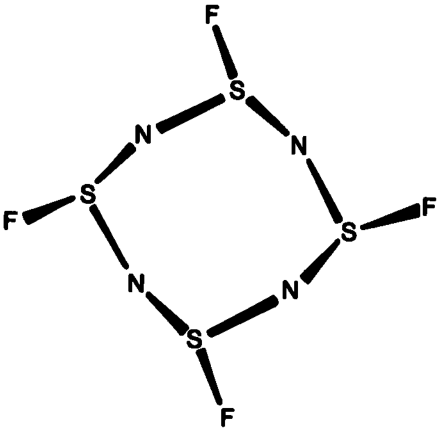
Several models have been proposed in order to describe the bonding in S_4N_4. The short S---S cross-ring contacts have been attributed to the presence of a σ-bond composed primarily of p orbitals (Lindqvist, 1958), which would be consistent with the observation that the S---S contact is approximately perpendicular to the S-N bonds. Sulphur-sulphur single bond lengths vary considerably with the hybridisation of the sulphur atoms. The sp^3-sp^3 single bond distance is normally taken as about 2.048Å as is found in S_8 (Cooper, Bond and Abrahams, 1961), however longer



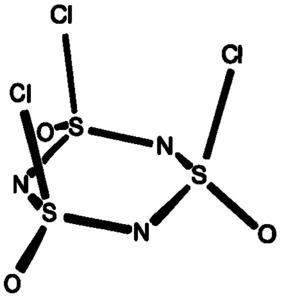
S_4N_4



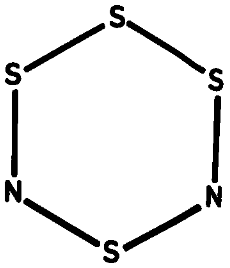
$(NSCl)_3$



$(NSF)_4$



$(NSOCl)_3$



S_4N_2

Figure 2.1

single bond distances of 2.15Å and 2.39Å are seen in $S_2O_6^{2-}$ and $S_2O_4^{2-}$ (Lindqvist and Mortsell, 1958). The length of these bonds is attributed to an increase in p character; from which it was deduced that an S-S bond composed entirely of p orbitals would be of the same magnitude as the S---S separation in S_4N_4.

The length of the S-N bonds and the two-fold coordination at the nitrogen atoms suggest that there is considerable delocalisation in these bonds. Gleiter (1970) using symmetry arguments and extended Hückel calculations concluded that the structure consists of eight single S-N bonds and two cross-ring S-S bonds. This necessitates a positive charge on each sulphur atom and a negative charge on each nitrogen atom. However there is considerable evidence for delocalisation in S_4N_4. The e.s.r. spectrum of the $S_4N_4^-$ radical anion, produced in liquid ammonia by reduction with sodium or potassium, indicates that the unpaired electron is delocalised over the whole molecule and provides direct evidence for delocalisation in the bonding (Braterman, 1965). Further experimental evidence is provided by its high diamagnetic susceptibility which probably arises from a ring current analogous to those in aromatic compounds. On the basis of CNDO/2 calculations it was concluded that the S-N bond order is about 1.5 and also that there is a strong S-S transannular interaction (Cassoux et al. 1972). The authors interpreted their results in terms of islands of delocalisation over the S-N-S fragments so that this bonding description is analogous to that proposed by Dewar, et al, 1960 for cyclophosphazenes.

2.3 Cyclothiazenes.

S_4N_4 is exothermic with respect to decomposition to its elements. (Enthalpy of formation = 500 kJ mol^{-1}); consequently it is a very reactive compound and the starting material for many syntheses. Some of the first compounds prepared from S_4N_4 were the cyclothiazenes which are six- or eight-membered heterocycles of the type $(NSX)_n$. The structures of two trimeric cyclothiazenes and one tetrameric cyclothiazene have been determined, ie $(NSCl)_3$, $(NSF)_3$ and $(NSF)_4$.

The trichlorocyclotrithiazene, $(NSCl)_3$ may be prepared in high yield by the action of chlorine on a solution of S_4N_4 in chloroform (Demarcay, 1880). The mechanism for this reaction is unknown, but since it results in contraction of the S_4N_4 ring it is thought to involve monomeric SN and ClSN units. Its structure has been determined by X-ray diffraction methods (Wiegers and Vos, 1966). The molecule as shown in figure 2.1 consists of a puckered S_3N_3 ring with the chlorine atoms attached to the sulphur atoms in an equotorial conformation. The nitrogen atoms are situated no more than 0.18Å away from the plane of the sulphur atoms such that the molecule shows 3m symmetry within experimental error. All of the S-N distances are equivalent and their mean of 1.605Å is considerably shorter than the normal single bond distance of 1.73Å. These points may be explained by Npπ-Sdπ delocalised bonding within the ring which is in agreement with the angle of 124.3° found at nitrogen. Also the ring is roughly planar although this is not a necessity for pπ-dπ bonding. This description is similar to that used for phosphonitrilic compounds such as $P_3N_3F_6$ in which the P_3N_3 ring is exactly planar. An alternative explanation of the bonding is to consider the shortness of the S-N bond to be a consequence of the bond polarity, ie. $\overset{+}{S}-\overset{-}{N}$; however this would require an angle of 109°28' at the nitrogen atoms.

The d orbitals on sulphur atoms are normally too diffuse to participate in the bonding and need to be contracted in order to interact effectively with say the p orbital on a sp^2 hybridised nitrogen. This contraction may be provided by the attachment of an electronegative element to the sulphur atom as in $(NSCl)_3$ or by a formal positive charge as in $S_4N_3^+$ (section 2.5).

It is significant that all the chlorines in $(NSCl)_3$ are axial in orientation, whereas they might have been expected to be equatorial in order to minimise the repulsions between the lone pairs on the chlorine atoms. The probable explanation for this, is that the interactions between the lone pairs on the nitrogen atoms and those on the chlorine atoms are greater than the chlorine-chlorine lone pair interactions.

The second trimeric cyclothiazene, $(NSF)_3$ can be prepared by fluorinating $(NSCl)_3$ using AgF_2 (Glemser, 1964). Its structure has been determined by X-ray diffraction (Krebs, Pohl and Glemser, 1972) which showed it to be the fluorine analogue of $(NSCl)_3$. The molecular symmetry is close to 3m with the nitrogen atoms lying 0.23Å away from the plane of the sulphur atoms. The mean S-N bond length of 1.593Å is shorter, though not significantly than that observed in $(NSCl)_3$. Some shortening of the S-N bonds is expected on account of the higher electronegativity of fluorine. The angles within the ring are similar to those seen in $(NSCl)_3$. However the average N-S-F angle of 101.5° is less than the corresponding N-S-Cl angle of 113.7° in $(NSCl)_3$ and this is probably a result of smaller lone pair interactions between the axial fluorine atoms. A bond order of 1.4 has been estimated for the S-N bonds in this compound from studies of the correlation between force constants and bond lengths in sulphur-nitrogen compounds (Glemser et.al. 1968).

These are the only halide derivatives of the trimeric cyclothiazenes. A preparation of $(NSBr)_x$ reported in 1896 has not been confirmed (Zborilova et al, 1972), however esters of the general composition $(NSOR)_3$ have been prepared where for example $R = CH(CH_2Cl)_2$ but their structures have not been studied (Banister and Bell, 1972).

There is only one known tetrameric cyclothiazene, namely $(NSF)_4$ which may be prepared by fluorination of S_4N_4 using AgF_2 in carbon tetrachloride (Glemser, 1964). The molecule, as shown in figure 2.1 consists of a puckered eight-membered S_4N_4 ring, however in contrast to the trimeric thiazenes there are two types of S-N bonds of length 1.540Å and 1.660Å (Wiegers and Vos, 1963). This is usually interpreted as a system of alternating single and double bonds. The bond angles at sulphur and at nitrogen are similar to those seen in $(NSF)_3$.

The lack of bond equalisation in $(NSF)_4$ cannot be attributed to an effect of the fluorine atoms attached to the sulphur atoms, as was first thought, before the structure of $(NSF)_3$ was known;

since in the latter compound bond equalisation is seen to occur. The puckering of the S_4N_4 ring has been ascribed to the steric effects of the equitorial sulphur and nitrogen lone pairs (Krebs, Pohl and Glemser, 1972). Alternatively the puckering may be a consequence of the σ-bonding in the ring. In $(NSF)_3$ the bonding involves sp^3 hybridised sulphur and sp^2 hybridised nitrogen atoms and by comparison $(NSF)_4$ would seem to have a similar σ framework, which is attained by puckering of the ring. A planar eight-membered ring would require angles at sulphur and nitrogen of 135° and it would appear that the additional delocalisation possible does not outweigh the changes in the σ-bonding. The adoption of $\bar{4}$ symmetry in preference to 4m symmetry may be a consequence of lone pair interactions.

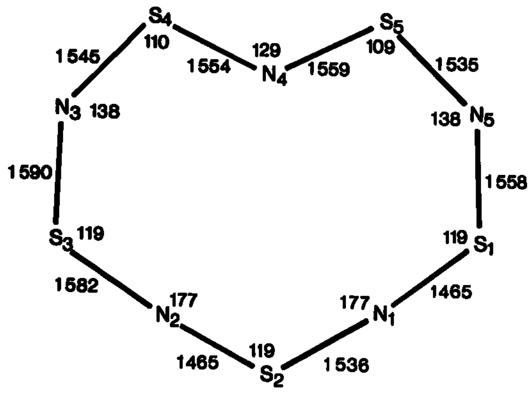
2.4 Sulphanuric chloride.

In the cyclothiazenes just mentioned the sulphur is formally in oxidation state IV, however there is another group of sulphur-nitrogen heterocycles in which the sulphur is formally in oxidation state VI. The best known of these is sulphanuric chloride, $(NSOCl)_3$ and as shown in figure 2.1 it consists of a puckered six-membered S_3N_3 ring with a chlorine and oxygen atom bonded to each sulphur atom. The S-N bond distances are all the same within experimental error and their mean of 1.564Å indicates that there is considerable multiple bonding within the ring (Hazell, Wiegers and Vos, 1966). Many other sulphanuric derivatives are known in which chlorine atoms have been replaced by fluorine atoms, secondary amines, R_2N-, esters RO- or phenyl groups, (Banister, 1974).

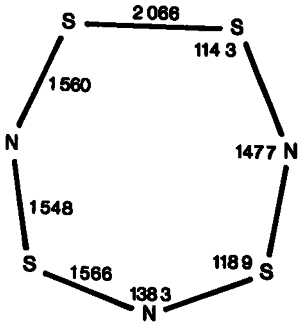
2.5 Aromatic Sulphur-Nitrogen Compounds

One of the first sulphur-nitrogen compounds prepared was S_4N_3Cl which was made in 1880 by heating S_4N_4 with S_2Cl_2 (Demarcay and Hebel, 1880). It occurs as bright yellow crystals which are remarkably stable in dry air. S_4N_3Cl itself is insoluble in most solvents however many derivatives of the form S_4N_3X have been prepared and several of these have been studied by X-ray diffraction, for example $S_4N_3NO_3$ (Cordes, Kruh and Gordon, 1965), $S_4N_3BiCl_4$ (Kruss and Ziegler 1972a) and $(S_4N_3)_2SbCl_5$ (Kruss and Ziegler 1972b). All of these determinations have shown that the sulphur-nitrogen species consists of a cationic planar seven-membered ring as illustrated in figure 2.2. The dimensions given are taken from the determination of the structure of $(S_4N_3{}^+)_2SbCl_5$.

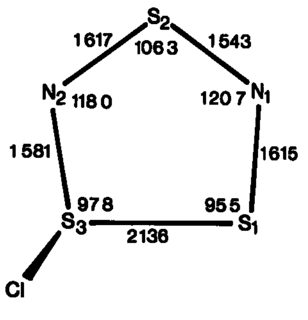
The features of significance in this ion are firstly that the ring is planar and shows 2m symmetry within experimental error, and secondly that the S-N bonds which range from 1.548-1.566Å are much shorter than the normal single bond distance of 1.73Å. The latter suggests that there is a high degree of multiple bonding within this ion. It was found that the u.v. spectrum for this cation could only be interpreted in terms of a delocalised 10π system, to which each sulphur contributes two electrons and each nitrogen one electron



$S_5N_5^+$



$S_4N_3^+$



$S_3N_2Cl^+$

Figure 2.2

(Friedman, 1969). This ion is the first known member of a series of cyclic sulphur-nitrogen compounds which are approximately planar and show short S-N bond distances. They are characterised by containing (4n + 2)π electrons and represent inorganic analogues of the organic aromatic Hückel series.

The second example of this type of compound was found in $S_3N_2Cl_2$ which has been known since 1881 (Demarcay, 1881). The crystal structures of $S_3N_2Cl_2$ (Zalkin, Hopkins and Templeton, 1966) and also a derivative, $S_3N_2ClFeCl_4$ (Shearer, 1972) have been studied; both of which have been found to contain the cation $S_3N_2Cl^+$. As shown in figure 2.2 it consists of a five membered S_3N_2 ring with an exocyclic chlorine atom attached to one sulphur atom. This sulphur lies 0.2Å above the plane of the remaining S_2N_2 fragment which is almost exactly planar. The S-N bond distances which range from 1.543 - 1.617Å indicate a considerable degree of multiple bonding in this ion. Because of the lack of planarity $S_3N_2Cl^+$ is considered to be a pseudo-aromatic species. The number of π electrons available in these cations can be estimated by presuming that each sulphur atom is in an oxidation state IV so that it can contribute two electrons to the π system and that each nitrogen atom can contribute one electron. When a sulphur atom is bonded to an exocyclic group as in $S_3N_2Cl^+$ then that sulphur atom can only contribute one electron to the π system. Hence formally the addition of an $Cl\text{-}S^+$ unit to the S_2N_2 fragment contributes no electrons to the π system, so that in $S_3N_2Cl^+$ there are 6π electrons available.

The third example found was the cation $S_5N_5^+$ in the salt $S_5N_5^+AlCl_4^-$ (Hazell and Hazell, 1972) and as shown in figure 2.2 it consists of a roughly planar heart-shaped ten-membered ring. This molecule shows remarkably short S-N bond distances which vary from 1.465 - 1.590Å and formally possesses a 14π system. This electron counting formalism has been supported by theoretical calculations which confirmed, using an all valence SCF MO treatment, the existence of a 6π system in $S_3N_2Cl^+$, a 10π system in $S_4N_3^+$ and a 14π system in $S_5N_5^+$. (Adams et al. 1971) A measure of the π bonding between two atoms is given by the total π bond overlap populations and for $S_3N_2Cl^+$, $S_4N_3^+$ and $S_5N_5^+$ the average values were calculated to be 0.86 (0.50), 1.08 (0.60) and 1.05 (0.58) respectively. The figures in parentheses refer to the contribution from the d orbitals on sulphur, although this theoretical treatment over-emphasizes the d orbital participation. These figures indicate extensive π bonding between the sulphur and nitrogen atoms. These calculations also showed that there is appreciable π bonding in the S-S bond in $S_4N_3^+$, whereas comparison of its bond length of 2.066Å with the normal single bond distance of 2.048Å found in S_8 would have suggested that this was essentially a single bond. This again illustrates the hazards in correlations of bond length with bond order. The positive charge in these ions makes an important contribution to their stability, since it contracts the orbitals on the sulphur atoms and enables them to bond more effectively to the nitrogen atoms.

The electron counting formalism mentioned above may be used to predict the number of π electrons available in any S_xN_y species (Banister, 1972) a summary of which is shown in table 2.1. Compounds with an excess of nitrogen are likely to be explosive since they will contain a N-N bond, whereas neutral species containing a high sulphur content are likely to be unstable or will exist as S(II) compounds because of insufficient contraction of the orbitals on the sulphur atoms. The number of possible unsaturated cyclic sulphur-nitrogen compounds may be extended by including an atom or group which formally does not contribute any electrons to the π system. An example of this is the $Cl-S^+$ group in $S_3N_2Cl^+$ which has the effects of relieving the strain present in an S_3N_2 ring and stabilising the π system by its positive charge.

The only two neutral cyclic sulphur-nitrogen compounds known are S_2N_2 and S_4N_2. The first of these which formally contains a 6π system has been shown to be a planar four-membered ring with alternating sulphur and nitrogen atoms from its infrared spectrum. Its crystal structure has not been examined for reasons of its thermal instability however an adduct $S_2N_2(SbCl_5)_2$ has been studied (Patton and Raymond, 1969). The S_2N_2 ring in this adduct shows mmm symmetry within experimental error and has S-N distances of 1.619Å which are short taking into account the angles of 95.1° at nitrogen and 84.9 at sulphur. These features are consistent with delocalised multiple bonding. The structure of the S_2N_2 ring in the adduct is thought to be close to that of the free S_2N_2 molecule because of the similarities of their infrared spectra and also because of the ease with which the $SbCl_5$ may be removed from the adduct.

Table 2.1

π-electron counts for neutral S_xN_y species.

x y	2	3	4	5	6
2	6^*	8	10^*		
3	7	9	$11^†$	13	
4	8	10	12	14	16
5		11	13	$15^†$	17
6			14	16	18
7				17	19

* Existing neutral S_xN_y species.

† Existing cationic S_xN_y species.

The second neutral compound S_4N_2 exists as a thermally unstable deep red liquid freezing at 24° and has been shown to be a cyclic compound with the basic configuration shown in figure 2.1. This was deduced from its dipole moment, mass spectrum, u.v. spectrum and vibrational spectra, using both Raman and infrared methods. These measurements were unable to determine whether the ring is planar or whether it has a boat or chair conformation. This compound formally contains a ten π system and if the orbitals on the sulphur atoms are sufficiently contracted the molecule would be expected to be planar (Nelson and Heal, 1971).

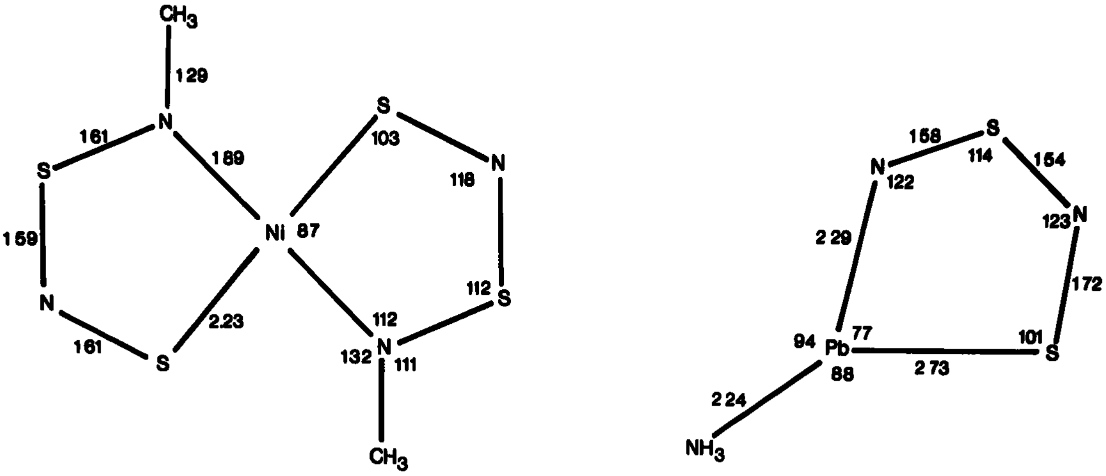
Other unsaturated cyclic sulphur-nitrogen compounds.

A compound of formula S_3N_3Cl has been prepared (Zborilova et al., 1972) and is thought to contain an S-Cl bond although its crystal structure has not been studied. A derivative $S_3N_3NP(Ph)_3$ has been studied and, as shown in figure 2.3 it consists of an S_3N_3 ring bonded at sulphur to a triphenyl phosphine group via an exocyclic nitrogen atom (Holt and Holt, 1970). Except for the three-coordinate sulphur atom the S_3N_3 ring is roughly planar. Likewise the S-N bond lengths in the ring except for those involving the substituted sulphur atom are quite short which suggest that there is considerable multiple bonding in this part of the ring.

A compound containing an N-substituted S_3N_3 ring has also been reported, namely $S_3N_3POF_2$ (Roesky and Grimm, 1972). The structure was proposed on the basis of the compound's infrared and ^{31}P and ^{19}F n.m.r. spectra but has yet to be confirmed by crystallographic studies.

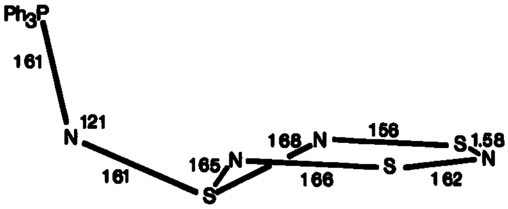
Sulphur-nitrogen compounds may also act as chelating ligands thus forming a ring system. Earlier work on these complexes has been the subject of a review by Weiss, 1966. The most well known chelating ligands contain an S-N-S-N fragment, in which the terminal sulphur and nitrogen atoms bond to the metal atom to form a five-membered ring. These compounds fall into two groups; those in which the ligand is the S_2N_2 fragment itself and those in which there is a group attached to the terminal nitrogen atom.

An example of the first type is $PbS_2N_2NH_3$ whose structure has been studied by X-ray diffraction (Neubauer, 1958). The bond lengths as



$Ni(S_2N_2CH_3)$

$Pb(S_2N_2)NH_3$



S_3N_3-N-Ph_3P

Figure 2.3

shown on figure 2.3 would suggest that the five-membered ring consists of a sulphur diimide fragment, N=S=N connected by single bonds to a lead and sulphur atom.

The substituted S_2N_2 chelating groups are of interest because of the effects of substitution on the bond lengths in the sulphur-nitrogen ligand. In the compound $Ni(CH_3N_2S_2)_2$ all the S-N bonds are shorter than the normal single bond length of 1.73Å as shown in figure 2.3 (Ziegler, 1963). Since the coordination at the substituted nitrogen atom is roughly planar there would appear to be delocalised bonding encompassing the entire sulphur nitrogen fragment.

CHAPTER 3

The Crystal Structure of $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$

3.1 Introduction.

The compound of empirical formula S_3N_2Cl has been known since 1880 (Demarcay, 1880). It may be conveniently prepared by heating $S_3N_2Cl_2$ in vacuo at 80-90^o (Banister et al., 1974). This gives a dark green powder which is virtually insoluble in all common solvents, so that little was known of its chemistry and no crystals suitable for structure analysis had been prepared.

This compound was of interest because it could contain another pseudo-aromatic sulphur-nitrogen system. S_3N_2Cl itself would be an odd electron species, but magnetic susceptibility measurements carried out on a solid sample showed the material to be diamagnetic. This indicated that in the solid the S_3N_2Cl units are associated with formulation $[S_3N_2Cl]_{2n}$ where n is probably 1. Hereafter this compound will be referred to as $[S_3N_2Cl]_2$.

N.q.r. measurements on this material failed to show a chlorine resonance (Lynch and Waddington, 1973), which would have been expected if the chlorine was covalently bound to the sulphur-nitrogen fragment. This suggested that the material is ionic and contains a sulphur-nitrogen cation. At this stage the most likely description for the cation was in terms of a large ring with formula $S_6N_4^{2+}$, which would contain a 14π system as in $S_5N_5^+$.

The u.v. spectra of the sulphur-nitrogen species present in $[S_3N_2Cl]_2$ was recorded in 100% sulphuric acid, which is a technique generally applicable to sulphur-nitrogen cations (Clarke, 1974). This showed firstly that the material could be dissolved giving the possibility of preparing crystalline derivatives, and secondly that the species present in solution is different from any previously examined sulphur-nitrogen cation. The wavelengths and intensities of the absorptions indicated π-delocalisation similar to that seen in $S_4N_3^+$ or $S_3N_2Cl^+$.

The material was slowly hydrolised by this solvent and it was impossible to isolate a derivative. Chlorosulphuric acid was tried as an alternative, since this is self-dehydrating.

$$ClSO_3H + H_2O \rightarrow HCl \uparrow + H_2SO_4$$

The $[S_3N_2Cl]_2$ dissolved rapidly with the evolution of HCl gas, to give a dark brown solution. Excess solvent was pumped off at room temperature over a period of several days, whereupon small plate-like crystals formed at the bottom of the flask. These were separated and sealed in thin walled quartz capillary tubes to prevent decomposition. At this stage it was believed that the chlorosulphate derivative had been prepared.

3.2 Crystal Data.

The crystals were obtained directly from the reaction of $(S_3N_2Cl)_2$ and chlorosulphuric acid as dark green irregular plates showing prominent $\{10\bar{1}\}$ faces. The crystal used for intensity measurements had dimensions 0.6 x 0.4 x 0.25mm. Initial measurements using precession methods showed the unit cell to be triclinic, with possible space groups of P1 or $P\bar{1}$. The normalised structure factors showed a centrosymmetric distribution corresponding to $P\bar{1}$ as shown in table 3.1, and this was confirmed by solution of the structure.

Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections (Busing and Levy, 1967) measured on a diffractometer.

$[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$ M = 639.56

a = 7.689(1) Å α = 101.00°

b = 10.726(1) Å β = 114.42°

c = 6.614(1) Å γ = 90.35°

Z = 1

U = 485.38 $Å^3$

Dc = 2.19gm cm^{-3}

Absorption coefficient for MoKα radiation (λ = 0.7107Å) = 14.27cm^{-1} The density of the crystals was not measured due to the small number available from the preparation.

3.3 Data Collection.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer (section 1.12) using Zr-filtered MoKα radiation. A $2\theta - \omega$ scan was employed using 80 steps of 0.01°. A counting time of 3 seconds per step, together with a background count of 40 seconds at the beginning and end of each scan were chosen. Three standard reflections were measured every fifty reflections. These showed no systematic change throughout data measurement, indicating that the crystal neither decomposed nor moved significantly during the experiment. These standard reflections were used to compute a scale factor which was applied to the data to place the measurements on a common scale.

The whole sphere of reflection was recorded to a limit of $\theta = 25^{o}$, yielding two equivalent sets of reflections. These gave, after averaging, a total of 1707 independent reflections of which 1337 reflections were considered to be observed having net counts $>$ 3 esd's.

The intensities were corrected for Lorentz and polarisation effects (section 1.13) but no corrections were made for absorption.

3.4 Solution and Refinement.

An attempt was made to solve the structure using the symbolic addition procedure. This lead to the correct solution which was not recognised at that time, because the cation was different in shape from the ten-membered ring expected and the anion was $ClS_2O_6^-$ and not $ClSO_3^-$. In addition the peak due to the chlorine atom in the E-map was small so there was no evidence of chlorine bonded to sulphur. Also the analytical data for this compound were unreliable because of the small sample prepared, and for the same reason the density was not measured.

Prior to attempting the symbolic addition procedure, an overall temperature factor and scale were estimated using the Wilson plot method described earlier, these are given in table 3.1.

The structure was solved from its Patterson function which, for the space group $P\bar{1}$, takes the form

$$P(u,v,w) = \frac{2}{v} \sum_h \sum_k \sum_l \{ |F(hkl)|^2 \cos 2\pi(hu + kv + lw) + |F(\bar{h}kl)|^2 \cos 2\pi(-hu + kv + lw) + |F(h\bar{k}l|^2 \cos 2\pi(hu - kv + lw) + |F(hk\bar{l})|^2 \cos 2\pi(hu + kv - lw) \}$$

this function was computed for half the unit cell from

$u = 0 \rightarrow 1$ at intervals of 0.27558Å

$v = 0 \rightarrow 1$ " 0.25630Å

$w = 0 \rightarrow \frac{1}{2}$ " 0.26815Å

the coefficients used were $|F_{obs}|^2$ weighted by $(Lp)^{-1}$ for each reflection. This increased the importance of the higher order reflections and thus enhanced the magnitude of the sulphur-sulphur vectors in the map.

A single weight sulphur-sulphur peak was found by observing that the vector 0.467, -0.05, 0.083 occurred between six pairs of the twenty larger peaks in the map. There was a small peak corresponding to this vector. This was tried as a possible single weight peak, corresponding to there being a sulphur atom at 0.233, -0.025, 0.042. One application of the superposition method yielded possible positions for six further atoms. All possible vectors between these seven positions were calculated, but only five of these positions gave vectors corresponding to those seen in the vector map. These positions were,

u	v	w
0.233	-0.025	0.042
0.200	0.100	0.250
0.300	0.225	0.042
-0.167	0.219	0.573
0.633	0.533	0.792

these coordinates were refined by two cycles of least squares refinement using the block-diagonal approximation when R became 0.45. The sulphur atoms were given isotropic temperature factors of 2.65Å^2, as calculated from the Wilson plot. An electron density map was calculated in which the additional peaks were all of about the same height, so that once again the S-Cl fragment could not be picked out. The peak corresponding to the chlorine atom was small due to its high temperature factor. Five further atoms were included in the refinement and the R value fell to 0.28. During this process the temperature factor of one of the additional atoms, which were taken as oxygens, became negative indicating that this was the chlorine atom. At this stage the structure became clear and the inclusion of the remaining atoms caused R to fall to 0.16. With anisotropic thermal parameters for all the atoms R became 0.0338. Further refinement using the full matrix least squares method saw R converge on its final value of 0.0307. The parameter shifts in the last cycle were all $< 0.3\ \sigma$. A difference synthesis was calculated at the end of refinement and showed no peaks greater than 0.3e.Å^{-3} in general areas of the map; however there were negative regions of about -1.1e.Å^{-3} associated with the sulphur positions.

The weighting scheme used throughout the block-diagonal refinement was of the form

$$\sqrt{w} = 1/[P_1 + |F_o| + P_2|F_o|^2]^{\frac{1}{2}}$$

where

$$P_1 = 10.0 \quad \text{and} \quad P_2 = 0.01$$

this scheme was replaced in the final stages of refinement by one based on counting statistics. This was of the form

$$\sqrt{w} = \frac{1}{\sigma Fo}$$

where σFo represents the standard deviation of Fo. σFo may be derived thus

$$Fo = \frac{k.\sqrt{N}}{\sqrt{Lp}}$$

where k is the scale and Lp is the Lorentz-polarisation factor. Then using the approximation $dFo \simeq \sigma Fo$ and $dN \simeq \sigma N$ and differentiating gives

$$\sigma Fo = \tfrac{1}{2} . \frac{k. \ \sigma N}{\sqrt{Lp}. \ \sqrt{N}}$$

$$= \tfrac{1}{2} . Fo . \frac{\sigma N}{N}$$

the expression used for σN was

$$\sigma N = [T + B.G. + (P.N)^2]^{\frac{1}{2}}$$

where B is the ratio between the total background count (G) and the total peak count (T). The term $(T + B.G)^{\frac{1}{2}}$ represents the standard deviation based on counting statistics. This underestimates the error in the very intense reflections, so the term $(P.N)^2$ is introduced

Table 3.1 $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$

Final Least Squares Totals †

$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	R
22421.95	22415.61	688.79	0.0307

Weighting Analysis

$\|F_o\|$ Ranges	N	$\Sigma w\Delta^2/N$	R
0 - 5	76	0.03	0.142
5 - 7	222	0.03	0.085
7 - 10	172	0.03	0.050
10 - 15	293	0.02	0.029
15 - 20	216	0.03	0.023
20 - 45	299	0.02	0.021
45 - 70	50	0.02	0.022
70 - upwards	8	0.03	0.030

† Excluding reflection(2 $\bar{1}$ 1)

The Statistical Distribution of Normalised Structure Factors and the Estimated Scale and Temperature Factor.

	Observed	Centrosymmetric	Noncentrosymmetric
$<\|E\|>$	0.799	0.798	0.886
$<\|E\|^2>$	1.000	1.000	1.000
$<\|E^2-1\|>$	0.968	0.968	0.736
$\|E\|>3$	0.41%	0.3%	0.01%
$\|E\|>2$	4.69%	5.0%	1.8 %
$\|E\|>1$	31.75%	32.0%	37.0.%

Overall Temperature Factor	B = 2.65
Overall Scale	k = 0.1396

Table 3.2 $[S_3N_2]_2^{2+} (ClS_2O_6^-)_2$

Final Atomic Coordinates with their Estimated Standard Deviations ($\times 10^5$) and Isotropic Temperature Factors (Å^2).†

Atom	$^x/a$	$^y/b$	$^3/c$	B
Cl	0.16310 (18)	-0.40500 (13)	-0.11392 (18)	4.10
S(1)	0.30556 (13)	0.23302 (9)	0.03092 (16)	2.42
S(2)	0.18355 (13)	0.09889 (9)	0.26863 (15)	2.40
S(3)	0.24138 (12)	-0.02176 (8)	0.00940 (15)	2.31
S(4)	0.16996 (13)	-0.21259 (9)	0.42716 (15)	2.45
S(5)	0.36104 (13)	-0.38092 (8)	0.20389 (16)	2.48
O(1)	0.11388 (35)	-0.15639 (23)	0.23129 (42)	2.64
O(2)	0.01382 (42)	-0.25515 (30)	0.46755 (51)	4.24
O(3)	0.33641 (42)	-0.15420 (28)	0.61780 (45)	3.75
O(4)	0.23706 (36)	-0.35827 (22)	0.34008 (42)	3.32
O(5)	0.48091 (39)	-0.27070 (25)	0.24602 (49)	3.86
O(6)	0.43640 (49)	-0.49782 (26)	0.23149 (54)	4.95
N(1)	0.24028 (41)	0.23254 (27)	0.22712 (48)	2.85
N(2)	0.30665 (39)	0.09103 (27)	-0.08086 (48)	2.66

† The temperature factors given by the last cycle of isotropic refinement.

Table 3.3 $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$

Anisotropic Thermal Parameters with their Estimated Standard Deviations (Both $Å^2 \times 10^5$) †

Atom	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Cl	2592 (21)	1794 (9)	1886 (30)	- 90 (38)	1443 (51)	684(37)
S(1)	1477 (21)	614 (9)	2197 (30)	402 (25)	1927 (41)	92(21)
S(2)	1395 (20)	692(10)	1585 (27)	204 (24)	1549 (37)	92(21)
S(3)	1234 (20)	577 (9)	2062 (29)	320 (24)	1858 (39)	253(20)
S(4)	1476 (21)	724(10)	1566 (27)	384 (24)	1491 (39)	600(22)
S(5)	1724 (23)	583 (9)	2113 (29)	314 (25)	2289 (42)	295(22)
O(1)	1648 (61)	809(28)	2270 (85)	1194 (76)	1815 (117)	633(64)
O(2)	2110 (71)	1488(39)	3546(112)	2030(107)	4052 (152)	1201(84)
O(3)	2092 (74)	1109(34)	2376(100)	-700 (91)	327 (138)	662(80)
O(4)	2163 (67)	583(25)	2587 (88)	691 (74)	3189 (131)	401(64)
O(5)	2061 (71)	858(30)	3648(111)	265 (90)	3334 (151)	- 272(72)
O(6)	3345 (89)	802(31)	3792(118)	987 (94)	4211 (173)	1521(85)
N(1)	1399 (69)	650(31)	1815 (94)	- 10 (83)	1528 (131)	- 41(71)
N(2)	1198 (64)	681(31)	2070 (97)	526 (85)	1817 (132)	215(68)

† Where β_{ij} refers to the expression

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$$

to down weight these reflections. P was varied to make $w\Delta^2$ as uniform as possible over the whole range of $|Fo|$. The optimum value was 0.06. One reflection $(2\ \bar{1}\ 1)$ was excluded from the refinement because of its unusually large Δ. The unobserved reflections were not included in the refinement. The final least squares totals and weighting analysis are given in table 3.1. The final atomic parameters and thermal parameters are given in tables 3.2 and 3.3 respectively.

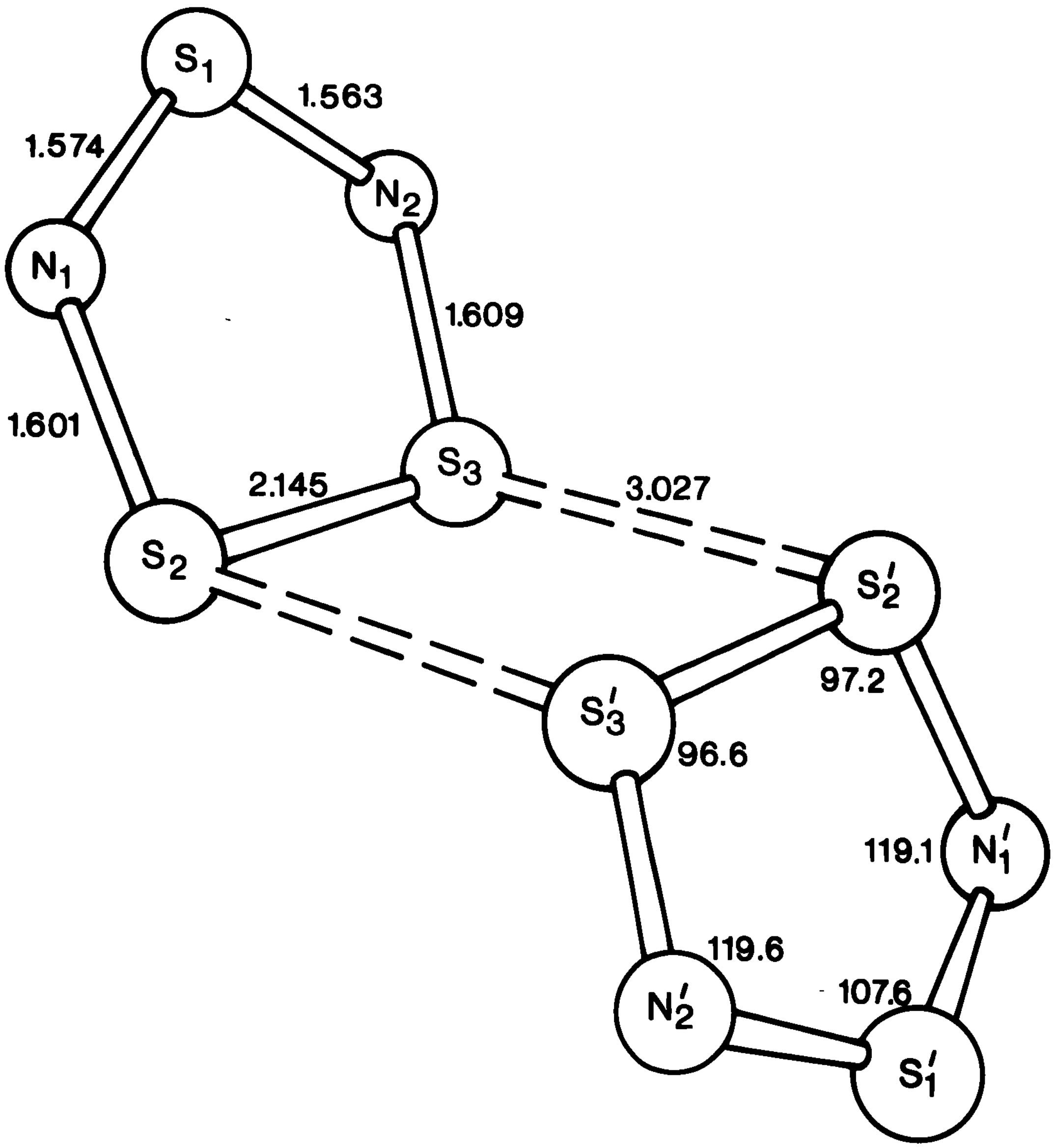
The scattering factors used in this refinement were taken from International Tables Vol. III. The chlorine and sulphur atoms were corrected for anomolous dispersion, the correction factors also being taken from International Tables Vol. III. The final structure factors are shown in table 3.8.

3.5 Results and Discussion.

The compound is ionic and contains $[S_3N_2]_2^{2+}$ cations and chlorodisulphate anions, $ClS_2O_6^-$. The bond distances and angles are given in tables 3.4 and 3.5 respectively.

3.5.a The Structure of $[S_3N_2]_2^{2+}$

The $[S_3N_2]_2^{2+}$ cation consists of two S_3N_2 rings held together by a four-centre S-S interaction, as shown in figure 3.1. The two rings which are separated by S-S distances of 3.027Å are related to one another by a centre of symmetry and are inclined at an angle of 108° to the plane of the four sulphur atoms involved in the interaction. The individual S_3N_2 rings are nearly planar (table 3.6), the maximum



$[S_3N_2]_2^{2+}$

Figure 3.1

Table 3.4 $[S_3N_2]_2^{2+}\ (ClS_2O_6^-)_2$

Bond Distances (Å) and their Estimated Standard Deviations (Å x 10^3)

S(1) - N(1)	1.574(3)
S(1) - N(2)	1.563(3)
S(2) - S(3)	2.145(1)
S(2) - S(3')	3.027(1)
S(2) - N(1)	1.601(3)
S(3) - N(2)	1.609(3)
S(4) - O(1)	1.438(3)
S(4) - O(2)	1.423(4)
S(4) - O(3)	1.405(3)
S(4) - O(4)	1.718(3)
S(5) - Cl	1.986(2)
S(5) - O(4)	1.552(3)
S(5) - O(5)	1.405(3)
S(5) - O(6)	1.396(3)

Some Non-Bonding Intramolecular Distances and their Estimated Standard Deviations (Å x 10^3).

S(1) - S(2)	2.736(1)
S(1) - S(3)	2.740(1)
S(2) - N(2)	2.825(3)
S(3) - N(1)	2.833(3)
N(1) - N(2)	2.530(4)
Cl - O(1)	3.297(3)
O(1) - O(5)	3.056(4)
O(3) - O(5)	3.154(4)

' represents the equivalent position $\bar{x}\ \bar{y}\ \bar{z}$

Table 3.5 $[S_3N_2]_2^{2+} (ClS_2O_6^-)_2$

Final Bond Angles and their Estimated Standard Deviations

(Deg. x 10^2)

N(1) - S(1) - N(2)	107.56(17)
S(3) - S(2) - N(1)	97.19(12)
S(2) - S(3) - N(2)	96.58(12)
O(1) - S(4) - O(2)	114.21(18)
O(1) - S(4) - O(3)	116.17(18)
O(1) - S(4) - O(4)	103.36(15)
O(2) - S(4) - O(3)	117.22(20)
O(2) - S(4) - O(4)	99.02(17)
O(3) - S(4) - O(4)	103.26(16)
Cl - S(5) - O(4)	101.69(12)
Cl - S(5) - O(5)	107.03(14)
Cl - S(5) - O(6)	107.39(16)
O(4) - S(5) - O(5)	111.09(17)
O(4) - S(5) - O(6)	107.11(18)
O(5) - S(5) - O(6)	120.83(20)
S(1) - N(1) - S(2)	119.08(20)
S(1) - N(2) - S(3)	119.55(20)
S(4) - O(4) - S(5)	124.86(17)

deviation from the mean plane being 0.02Å.

The sulphur-nitrogen bond lengths, S(2) - N(1) of 1.601(3)Å and S(3) - N(2) of 1.609(3)Å are the same within experimental error using the criterion described in section 1.11. For these bonds

$$t = \frac{1.609 - 1.601}{(0.003^2 + 0.003^2)^{\frac{1}{2}}} = 1.9$$

so that $P \approx 0.05$ and the difference is not significant. Similarly the bonds S(1) - N(1) of 1.574(3)Å and S(1) - N(2) of 1.563(3)Å do not differ from one another significantly. The angles S(1) - N(1) - S(2) of 119.08(20)° and S(1) - N(2) - S(3) of 119.55(20)° are also the same within experimental error. The angles S(3) - S(2) - N(1) of 97.19(12)° and S(2) - S(3) - N(2) of 96.58(12)° both depend upon the common positions of S(1) and S(2) so that, allowing for this, the difference between these angles does not appear to be significant, and consequently the ring approaches mm symmetry.

The mean S-N distances of 1.569Å and 1.605Å are characteristic of a π-delocalised sulphur-nitrogen cation. They may be compared with the distances of 1.548 - 1.566Å in $S_4N_3^+$ (Kruss and Ziegler, 1972b) which formally contains a 10π system or 1.543 - 1.617Å in $S_3N_2Cl^+$ (Zalkin, Hopkins and Templeton, 1966) which formally contains a 6π system. The S-S distance of 2.145Å within the ring is similar to that of 2.066Å in $S_4N_3^+$ or 2.136Å in $S_3N_2Cl^+$.

3.5.b The Bonding in $[S_3N_2]_2^{2+}$

The lengths of the S-N bonds and the angles at nitrogen of 119.3°

show that there is considerable delocalisation within the ring. S-S distances are dependent upon hybridisation as noted earlier (section 2. 2) so that from bond lengths alone it is not possible to deduce the bond order of the S-S bond. A π bond order of 0.35 has been calculated for the S-S bond in $S_3N_2Cl^+$ and of 0.83 for the S-S bond in $S_4N_3^+$ (Adams et al., 1971). Since the S-S bond in $[S_3N_2]_2^{2+}$ is similar in length and environment to those seen in $S_4N_3^+$ and $S_3N_2Cl^+$, it is reasonable to expect substantial π-bonding across this bond.

An isolated $S_3N_2^+$ ring would contain a 7π system using the electron counting rule. (i.e. Each sulphur donates two electrons and nitrogen one electron to the π system, together with the subtraction of one to allow for the positive charge gives 7π electrons). Thus an isolated $S_3N_2^+$ cation will be paramagnetic. However the solution obtained by dissolving $[S_3N_2Cl]_2$ in chlorosulphuric acid was found to contain no paramagnetic ions using n.m.r. techniques. No line broadening or shifts were observed for the proton resonances of tertiary butyl alcohol in chlorosulphuric acid on the addition of $[S_3N_2Cl]_2$. Under these conditions the presence of paramagnetic ions would cause line broadening and shifts to high field of the proton resonances. Hence the S_3N_2 rings are associated in solution sufficiently to allow spin pairing to occur.

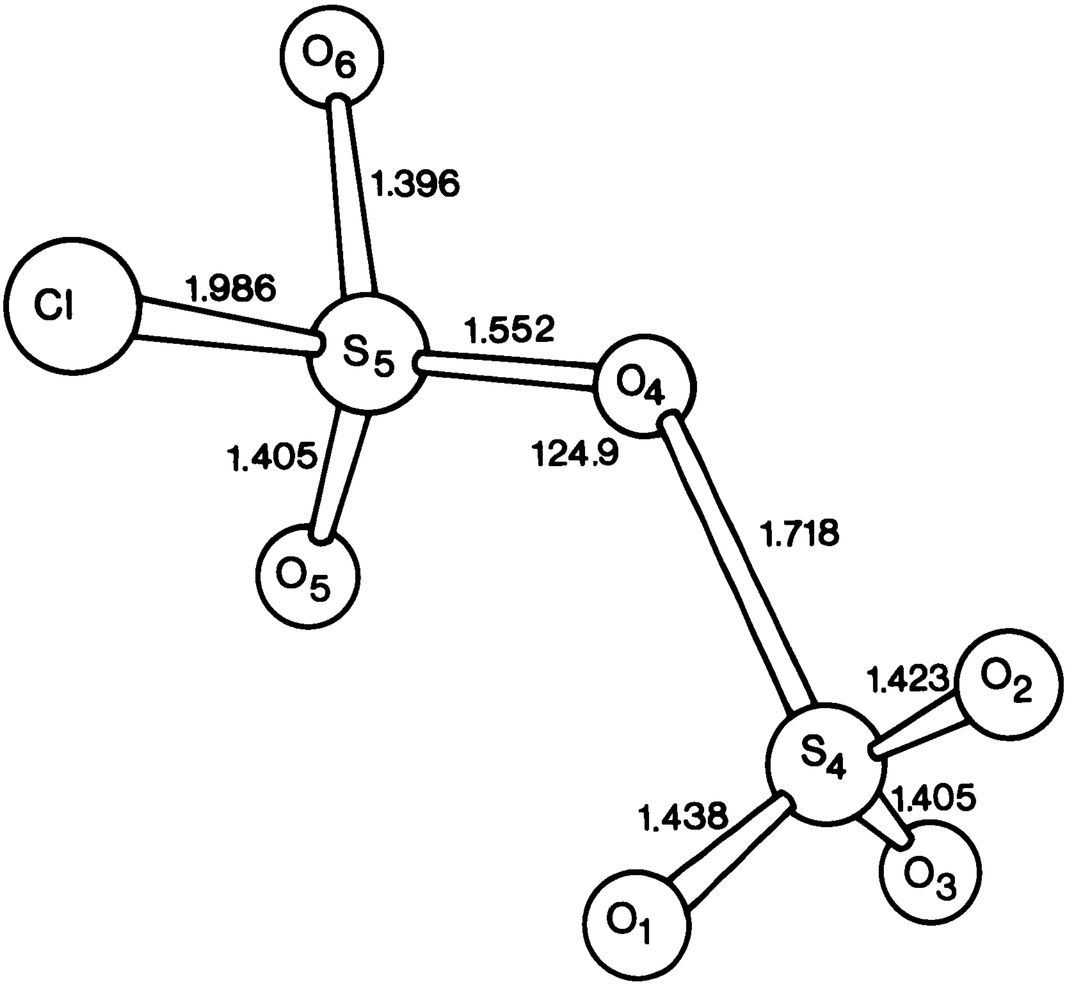
No magnetic measurements were performed on solid $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$ but since spin pairing occurs in solution it is expected to occur also in the solid. The distance between the rings of 3.027Å is far longer than a normal S-S bond distance and yet is considerably shorter than the van der Waals distance for sulphur of 3.60Å (Bondi, 1964). The nature of the association is not clear, yet it must be strong enough to hold two positively charged ions together in solution. The bonding may be described in terms of two S_3N_2 rings each containing an aromatic 6π system held together by a four-centre two electron bond. This cation probably occurs in $[S_3N_2Cl]_2$ also; evidence for this is seen in the similarities of the infrared spectra of $[S_3N_2Cl]_2$ and $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$ and because both compounds give the same electronic spectrum in concentrated sulphuric acid.

Another compound containing an S_3N_2 ring is described in the following chapter so that a discussion of S_3N_2 ring compounds is deferred until then.

3.5.c The $ClS_2O_6^-$ anion.

This is the first structure determination of this anion. It was first observed in infrared and Raman studies on solutions of SO_3 in $ClSO_3H$ (Gillespie and Robinson, 1961). Several alkali metal salts containing this anion have been isolated, (Auger, Wartell and Heubel, 1970) but none has been studied crystallographically.

The anion as shown in figure 3.2 is a chlorine substituted disulphate ion. The most striking feature of the ion is the assymmetry of its S-O-S bridge. The bond distances are 1.552(3)Å for S(5) - O(4) and 1.718(3)Å for S(4) - O(4). The length of



$ClS_2O_6^-$

Figure 3.2

1.718Å is one of the longest S-O distances known. A similar value of 1.72Å has been reported in $(NO_2^+)_2S_3O_{10}^{2-}$ (Cruickshank, 1964b). This distance is longer than the single bond distance of 1.70Å calculated from Pauling's covalent radii (Pauling, 1960) or the value of 1.69Å from the Schomaker Stevenson rule (Schomaker and Stevenson, 1941). The other distance in the bridge (1.552Å) lies between the S-O single bond distance of 1.70Å and the double bond distance of 1.43Å as seen in SO_3 (McDonald and Cruickshank, 1967), and indicates substantial multiple bonding in this bond, as is confirmed by the angle of 124.9° at the bridging oxygen. There is no steric requirement for such a large angle since the nonbonding contacts between terminal atoms on S(4) and S(5) are all greater than the normal van der Waals distances.

This assymmetry is substantially larger than that seen in $HOS_2O_6^-$ in which the bond lengths corresponding to S(5) - O(4) and S(4) - O(4) are 1.59Å and 1.67Å (Brown, Crump and Gillespie, 1971). The S-O-S bridges in these anions may be compared with the symmetrical bridge found in $S_2O_7^{2-}$ in which the S-O distance is 1.645Å (Lynton and Truter, 1960).

The assymmetry of the bridge in $ClS_2O_6^-$ is probably caused by preferential multiple bonding of O(4) to S(5) which carries the chlorine, leaving S(4) - O(4) as essentially a single bond. A chlorine atom bonded to sulphur will lower the energy and contract the orbitals on sulphur more effectively than an oxygen carrying a formal negative charge. Hence O(4) will π bond to S(5) more successfully than to S(4). Further evidence that the length of the S(4) - O(4) bond is due to the chlorine on S(5) rather than the negative charge on S(4) is shown by the S-O bridging length of 1.58Å in $CH_3OSO_3^-$ which is short even though there is a negative charge on the ion (Marsau and Cam, 1973).

The terminal S-O distances lie within the range 1.396 - 1.438Å which are similar to the terminal distances of 1.43Å in $HS_2O_7^-$ (Brown, Crump and Gillespie, 1971) or 1.407Å in $CH_3OSO_3^-$ (Marsau and Cam, 1973) and indicate a high degree of multiple bonding.

The terminal S-O distances to S(5) are, S(5) - O(5) 1.405Å(3) and S(5) - O(6) 1.396(3)Å and are the same within experimental error. Their mean of 1.401Å is shorter than the average terminal S-O distance of 1.422Å in the SO_3^- unit, which is partly due to the presence of chlorine in place of an oxygen carrying a negative charge.

The terminal S-O distances for the SO_3^- part are, S(4) - O(1) 1.438(3)Å, S(4) - O(2) 1.423(4)Å and S(4) - O(3) 1.405(3)Å. This range in bond length is greater than can be ascribed to experimental error, and may be caused by secondary bonding. All the terminal oxygens on the anion participate in short intermolecular contacts (section 3.6) to the sulphur atoms of the $(S_3N_2)_2^{2+}$ cation. The shortest of these involve O(1) and are, S(2) --- O(1) 2.731Å and S(3) ---O(1) 2.680Å. These are well below the normal sulphur-oxygen van der Waal contact of 3.32Å (Bondi, 1964) and the lengthening of S(4) - O(1) may be a consequence of this.

The S(5) - Cl bond distance was found to be 1.986(2)Å which is within the range of S-Cl bond distances observed in sulphur oxyhalides and sulphur halides, eg. 1.99Å in S_2Cl_2 (Palmer, 1950) and

2.011Å in $SOCl_2$ (Hargittai, 1968).

The coordination about S(4) and S(5) is approximately tetrahedral. At S(5) the largest deviations are shown by O(5) - S(5) - O(6), (120.8°) and Cl-S(5) - O(4) (101.7°). The magnitude of O(5) - S(5) - O(6) may be a consequence of the extensive multiple bonding in S(5) - O(5) and S(5) - O(6). This will result in shorter bonds with more s character and hence increase the angle between themselves and decrease the Cl-S(5) -O(4)angle which is observed. The remaining angles would be less affected by this change and range from 107.0° - 111.1°.

At S(4) the angles involving the terminal oxygen atoms are all greater than 109°28', i.e. O(1) - S(4) - O(2) 114.2°, O(1) - S(4) - O(3) 116.2° and O(2) - S(4) - O(3) 117.2°, whereas the angles at S(4) involving the bridging oxygen are all less than 109°28'. The terminal bonds are shorter due to the multiple bonding and hence contain a higher s character, making the angles between themselves larger. The increased proportion of p character in S(4) - O(4) increases the bond length and decreases the angles at S(4) between O(4) and the terminal oxygen atoms. A similar effect is seen in the disulphate ion $S_2O_7^{2-}$ (Lynton and Truter, 1960) in which the average angle between terminal oxygen atoms is 113.9° and the average angle between the terminal and bridging oxygen is 104.5°.

3.6 Intermolecular Contacts.

The packing of $[S_3N_2]_2^{2+}$ and $ClS_2O_6^-$ is characterised by the presence of many short sulphur-oxygen intermolecular contacts. Those less than the normal S---O van der Waals distance of 3.32Å are shown in table 3.7.

The shortest contacts involve O(1) and the basal sulphurs of the S_3N_2 ring as just mentioned. This is shown in figure 3.3

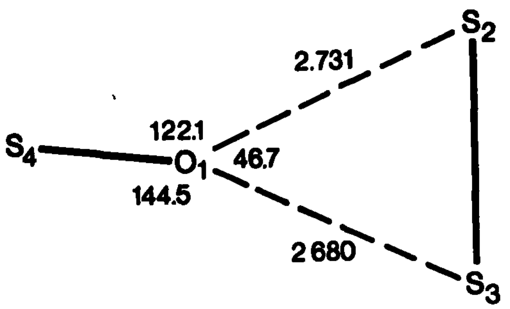


Figure 3.3

In cationic sulphur-nitrogen compounds the sulphur atoms carry a net positive charge, whilst in this compound there is a negative charge spread over the three terminal oxygen atoms attached to S(4); so that part of this interaction could be ionic. However it has been shown that many short intermolecular contacts seen in compounds of the main group elements have a specific orientation with respect to the rest of the molecule (Alcock, 1972) and that they can be explained by the overlap of a lone pair on one atom with vacant orbitals on the other. It is significant therefore that the oxygen atom O(1) lies only 0.06Å away from the plane of the S_3N_2 ring, so that the interaction may involve the overlap of a lone pair orbital on O(1) with a vacant orbital on S(2) and S(3).

Table 3.7 $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$

Sulphur-Oxygen intermolecular contacts < 3.35Å and their Estimated Standard Deviations (Å x 10^3).

Atom A	Atom B	Equivalent	Cell	A---B Å
O(1)	S(1)	2	(0,0,0)	2.980(3)
O(1)	S(2)	1	(0,0,0)	2.731(3)
O(1)	S(3)	1	(0,0,0)	2.680(3)
O(2)	S(1)	2	(0,0,0)	3.251(3)
O(2)	S(2)	2	(0,0,1)	3.043(4)
O(3)	S(1)	2	(1,0,1)	3.030(3)
O(3)	S(3)	1	(0,0,1)	3.071(3)
O(5)	S(1)	2	(1,0,0)	2.996(3)
O(6)	S(1)	1	(0,-1,0)	2.917(3)

This type of interaction is common in compounds in which the sulphur atoms carry a positive charge. The best example is seen in the structure of S_4N_3Cl (Hazel, 1974) which contains three crystallographically independant units of S_4N_3Cl per unit cell. Each of these has a chloride ion situated close to (within 0.4Å) the mean plane of the ring opposite to the S-S bond. The average S---Cl distance of 2.868Å is very short compared with the van der Waals distance of 3.55Å.

Further examples are to be found in a wide range of organic dithiolium compounds of the general formula $[S_2(CR)_3]^+X^-$ which contain an unsaturated five membered cyclic disulphide, where X = I, Br, Cl or N

(Hordvick, 1970). In all of these compounds, X is situated close to the plane of the ring and suggests that the interaction involves orbital overlap.

The other contacts in $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$ are less directional and may be primarily ionic in nature. A projection along c given in figure 3.4, shows the packing of the $[S_3N_2]_2^{2+}$ cations and the $ClS_2O_6^-$ anions and suggests that the shape and size of the cation may be the reason why the chlorodisulphate crystallises out in preference to the chlorosulphate.

Table 3.6. $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$

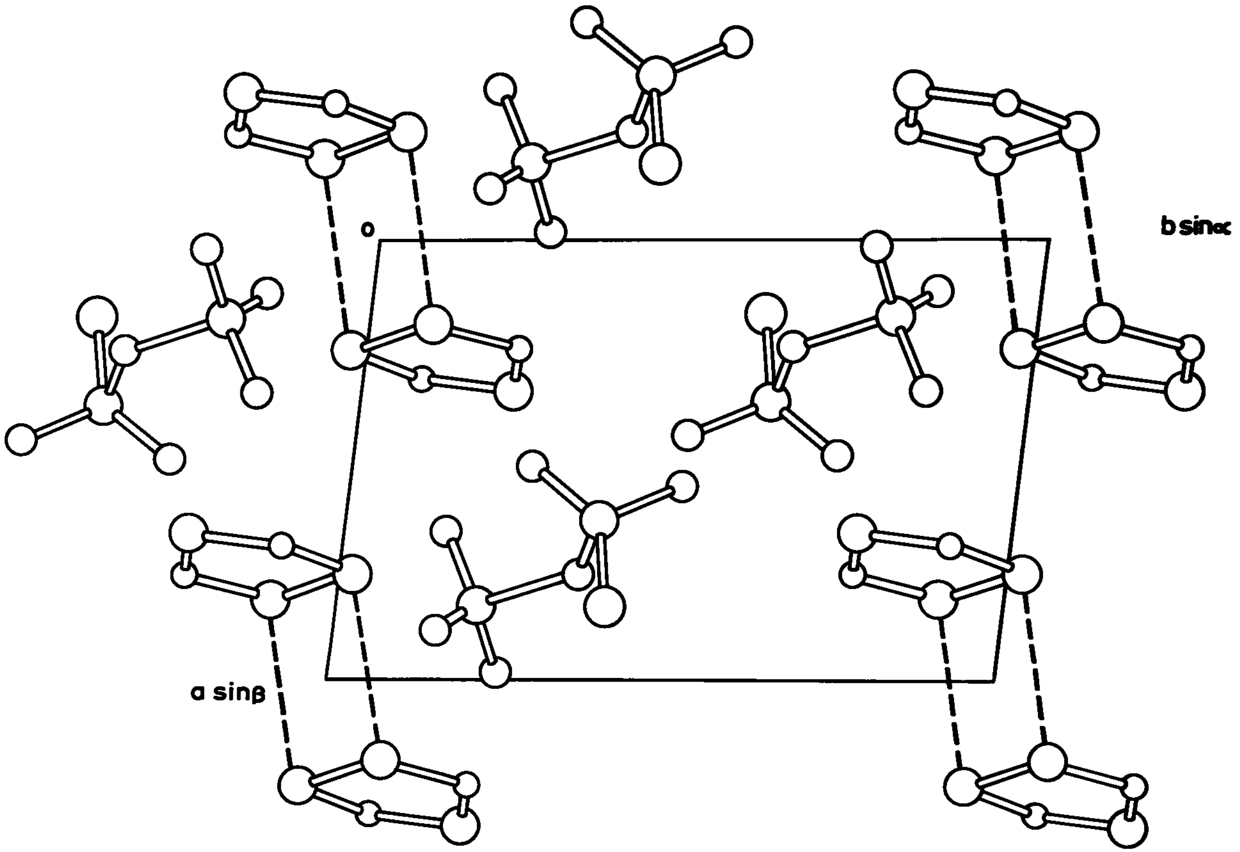
The equation for the weighted mean plane of the S_3N_2 ring.

$$- 0.7411X + 0.1460Y - 0.65532 + 1.4294 = 0$$

Atom	S(1)	S(2)	S(3)	N(1)	N(2)	O(1)†
P	0.0020	0.0014	-0.0003	-0.0224	-0.0081	0.0616
σ(P)	0.0010	0.0010	0.0010	0.0032	0.0031	0.0027

Where P and σ(P) are the distance and its estimated standard deviation of an atom from the mean plane. The plane is calculated with respect to the orthogonal axes X, Y and Z defined such that X lies along a, Z lies along c^*, and Y lies in the plane b^*c^* perpendicular to c^*.

† This atom was not included in the calculation.



$[S_3N_2]_2^{2+}\,(ClS_2O_7^-)_2$

projection on the [001] plane

Figure 3.4

Table 3.8 $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$

Final Calculated and Observed Structure Factors

H	K	L	FO	FC
0	1	0	18.4	19.2
0	2	0	34.2	-37.2
0	3	0	11.7	-11.2
0	4	0	4.8	4.6
0	5	0	35.4	37.5
0	6	0	26.1	-25.9
0	7	0	23.6	-23.9
0	8	0	35.8	35.7
0	9	0	8.1	7.9
0	10	0	10.7	10.9
0	11	0	0.0	-1.1
0	12	0	-3.3	-1.8
0	-12	1	7.6	7.0
0	-11	1	9.2	-8.7
0	-10	1	13.3	13.0
0	-9	1	11.2	-10.9
0	-8	1	-2.7	3.4
0	-7	1	-0.7	0.9
0	-6	1	29.7	-29.7
0	-5	1	36.5	35.9
0	-4	1	9.7	9.9
0	-3	1	48.1	49.6
0	-2	1	83.2	87.8
0	-1	1	15.0	-14.1
0	0	1	44.0	43.6
0	1	1	22.9	23.4
0	2	1	10.6	10.2
0	3	1	16.3	17.0
0	4	1	9.8	9.4
0	5	1	-1.7	1.6
0	6	1	7.7	7.7
0	7	1	14.5	14.2
0	8	1	22.7	22.8
0	9	1	11.1	11.5
0	10	1	11.6	-11.3
0	11	1	-2.4	1.1
0	-12	2	-4.1	-3.3
0	-11	2	14.0	-13.7
0	-10	2	5.7	5.5
0	-9	2	19.2	19.0
0	-8	2	18.1	-18.2
0	-7	2	-1.1	0.0
0	-6	2	18.3	17.8
0	-5	2	56.1	55.2
0	-4	2	34.3	35.1
0	-3	2	11.6	-12.2
0	-2	2	46.6	-45.3
0	-1	2	59.5	59.3
0	0	2	11.4	-10.5
0	1	2	6.4	6.0
0	2	2	19.9	19.1
0	3	2	30.9	31.5
0	4	2	65.3	66.4
0	5	2	14.4	14.4
0	6	2	13.9	-13.8
0	7	2	6.3	6.4
0	8	2	-1.3	1.9
0	9	2	17.8	17.9
0	10	2	15.0	-14.4
0	11	2	9.8	-9.4
0	-12	3	-3.6	-5.0
0	-11	3	7.6	-7.5
0	-10	3	13.6	-13.2
0	-9	3	31.3	31.0
0	-8	3	29.8	31.0
0	-7	3	-1.1	1.1
0	-6	3	9.5	9.2
0	-5	3	19.4	-18.5
0	-4	3	0.0	-0.8
0	-3	3	18.1	17.1
0	-2	3	32.9	-32.8
0	-1	3	41.5	39.8
0	0	3	9.2	8.7
0	1	3	33.3	33.8
0	2	3	42.8	42.7
0	3	3	0.0	-1.0
0	4	3	30.5	31.2
0	5	3	8.3	8.6
0	6	3	5.8	6.4
0	7	3	5.4	3.1
0	8	3	20.0	-19.8
0	9	3	-4.1	2.5
0	10	3	-3.0	2.9
0	-11	4	6.8	7.1
0	-10	4	-2.8	3.0
0	-9	4	4.3	3.6
0	-8	4	8.5	9.4
0	-7	4	17.4	-17.6
0	-6	4	12.6	12.2
0	-5	4	0.0	-0.8

H	K	L	FO	FC
0	-4	4	5.6	5.9
0	-3	4	8.9	-6.8
0	-2	4	-2.6	-2.0
0	-1	4	57.1	56.6
0	0	4	30.7	29.8
0	1	4	5.1	-5.6
0	2	4	-2.8	1.3
0	3	4	8.6	8.2
0	4	4	31.8	33.1
0	5	4	10.5	-10.4
0	6	4	16.0	-16.1
0	7	4	9.2	8.5
0	8	4	17.4	17.8
0	-10	5	-0.8	0.6
0	-9	5	-2.5	0.6
0	-8	5	0.0	-3.1
0	-7	5	15.3	-15.4
0	-6	5	7.7	8.4
0	-5	5	23.8	23.4
0	-4	5	26.9	27.1
0	-3	5	4.7	4.0
0	-2	5	5.6	-5.7
0	-1	5	-3.5	3.8
0	0	5	18.8	18.5
0	1	5	10.2	9.7
0	2	5	12.5	-12.3
0	3	5	-1.3	0.2
0	4	5	6.9	6.6
0	5	5	15.8	15.3
0	6	5	13.1	12.8
0	7	5	-4.3	3.5
0	-9	6	-1.4	-1.1
0	-8	6	4.7	-3.1
0	-7	6	10.9	10.0
0	-6	6	8.9	9.2
0	-5	6	17.6	17.1
0	-4	6	-2.6	1.8
0	-3	6	11.2	-10.8
0	-2	6	19.2	18.7
0	-1	6	-2.4	-1.5
0	0	6	12.4	-11.7
0	1	6	-1.7	-1.0
0	2	6	-2.4	-3.0
0	3	6	37.0	36.8
0	4	6	11.2	10.2
0	-5	7	6.6	6.0
0	-4	7	5.7	6.7
0	-3	7	16.1	-16.0
0	-2	7	5.3	4.9
0	-1	7	7.3	6.9
1	-1	-7	-4.3	-4.1
1	0	-7	18.0	19.3
1	1	-7	8.9	-9.9
1	2	-7	-2.8	2.7
1	3	-7	-2.4	-2.4
1	4	-7	5.5	-4.4
1	5	-7	18.4	18.0
1	6	-7	5.0	3.2
1	-5	-6	10.8	10.6
1	-4	-6	10.4	-10.7
1	-3	-6	-1.0	0.2
1	-2	-6	-2.7	2.8
1	-1	-6	10.0	-9.9
1	0	-6	7.9	7.6
1	1	-6	18.9	-18.5
1	2	-6	0.0	-0.2
1	3	-6	26.9	26.1
1	4	-6	24.7	26.1
1	5	-6	9.7	9.8
1	6	-6	0.0	1.3
1	7	-6	-2.3	-0.6
1	8	-6	13.5	12.5
1	9	-6	-1.8	-1.2
1	-7	-5	6.1	-7.2
1	-6	-5	-3.6	-4.5
1	-5	-5	10.1	10.0
1	-4	-5	0.0	-0.6
1	-3	-5	32.1	-32.0
1	-2	-5	27.9	-28.2
1	-1	-5	17.5	17.8
1	0	-5	20.0	19.8
1	1	-5	23.9	23.6
1	2	-5	-3.2	2.7
1	3	-5	4.1	3.7
1	4	-5	34.4	34.7
1	5	-5	0.0	-0.4
1	6	-5	4.3	-4.0
1	7	-5	-3.2	-2.0
1	8	-5	0.0	-0.6
1	9	-5	13.6	13.5

H	K	L	FO	FC
1	10	-5	0.0	-1.5
1	11	-5	6.5	7.1
1	-9	-4	5.3	5.1
1	-8	-4	12.5	-12.1
1	-7	-4	11.4	-11.5
1	-6	-4	6.0	6.1
1	-5	-4	22.4	-22.3
1	-4	-4	10.0	-10.5
1	-3	-4	-2.2	3.3
1	-2	-4	6.2	-6.5
1	-1	-4	50.8	50.3
1	0	-4	20.0	-19.2
1	1	-4	11.9	11.5
1	2	-4	18.6	18.0
1	3	-4	2.9	-3.1
1	4	-4	7.5	7.4
1	5	-4	18.8	-18.8
1	6	-4	-1.9	1.6
1	7	-4	36.1	35.7
1	8	-4	15.6	16.1
1	9	-4	13.7	13.6
1	10	-4	7.3	-7.6
1	11	-4	6.9	7.8
1	12	-4	15.4	14.9
1	-10	-3	6.4	-6.8
1	-9	-3	-2.5	-1.2
1	-8	-3	20.3	-20.3
1	-7	-3	39.5	-39.1
1	-6	-3	18.6	19.2
1	-5	-3	20.5	21.0
1	-4	-3	16.1	16.2
1	-3	-3	6.6	-6.5
1	-2	-3	11.6	-11.6
1	-1	-3	40.9	40.6
1	0	-3	46.4	-44.1
1	1	-3	50.6	-49.3
1	2	-3	4.1	-4.6
1	3	-3	34.8	32.6
1	4	-3	48.0	47.2
1	5	-3	-2.0	1.1
1	6	-3	10.4	10.1
1	7	-3	26.6	25.8
1	8	-3	15.4	15.1
1	9	-3	13.5	13.2
1	10	-3	4.9	4.7
1	11	-3	9.6	-9.1
1	12	-3	0.0	2.5
1	-11	-2	15.3	-14.3
1	-10	-2	14.6	-14.1
1	-9	-2	9.5	-10.3
1	-8	-2	12.2	12.0
1	-7	-2	-2.7	-0.3
1	-6	-2	3.5	3.9
1	-5	-2	12.1	-12.5
1	-4	-2	27.7	25.9
1	-3	-2	15.2	-14.7
1	-2	-2	32.6	-31.6
1	-1	-2	46.2	-45.3
1	0	-2	0.0	0.8
1	1	-2	0.0	-0.3
1	2	-2	9.3	10.5
1	3	-2	28.4	28.0
1	4	-2	43.0	40.2
1	5	-2	22.5	21.2
1	6	-2	18.8	17.5
1	7	-2	11.9	12.0
1	8	-2	17.8	17.4
1	9	-2	25.8	-26.0
1	10	-2	7.5	6.6
1	11	-2	12.4	12.6
1	12	-2	8.9	8.3
1	-12	-1	14.3	-13.6
1	-11	-1	9.6	-9.0
1	-10	-1	13.7	13.3
1	-9	-1	-3.7	-3.4
1	-8	-1	19.1	-19.4
1	-7	-1	4.4	-3.9
1	-6	-1	6.2	5.7
1	-5	-1	5.1	-4.6
1	-4	-1	57.0	-59.4
1	-3	-1	67.2	-72.2
1	-2	-1	71.0	74.1
1	-1	-1	33.2	33.1
1	0	-1	49.8	47.5
1	1	-1	30.9	-30.0
1	2	-1	57.7	-56.0
1	3	-1	75.7	78.9
1	4	-1	5.9	6.0
1	5	-1	4.7	4.1
1	6	-1	2.8	2.0

H	K	L	FO	FC
1	7	-1	14.4	-14.3
1	8	-1	42.5	42.6
1	9	-1	3.9	3.8
1	10	-1	5.4	-5.5
1	11	-1	19.9	20.1
1	12	-1	12.1	10.9
1	-12	0	-3.1	-2.9
1	-11	0	15.1	-14.1
1	-10	0	4.9	3.7
1	-9	0	-3.0	-0.9
1	-8	0	44.2	-45.1
1	-7	0	19.3	-19.8
1	-6	0	43.6	-44.2
1	-5	0	40.6	39.9
1	-4	0	19.1	19.4
1	-3	0	40.4	-42.4
1	-2	0	44.9	49.6
1	-1	0	3.0	-3.5
1	0	0	5.0	2.8
1	1	0	54.1	54.3
1	2	0	65.2	-67.4
1	3	0	25.3	25.3
1	4	0	34.1	-33.7
1	5	0	18.2	-18.3
1	6	0	28.1	28.8
1	7	0	27.9	28.4
1	8	0	20.3	20.5
1	9	0	22.3	23.0
1	10	0	0.0	0.2
1	11	0	13.6	12.9
1	12	0	5.3	5.0
1	-12	1	-2.7	-2.3
1	-11	1	6.0	-4.7
1	-10	1	11.8	-11.7
1	-9	1	17.0	-17.5
1	-8	1	52.0	-53.6
1	-7	1	6.8	6.1
1	-6	1	22.4	22.3
1	-5	1	8.4	8.0
1	-4	1	19.8	-20.4
1	-3	1	21.3	-21.5
1	-2	1	49.7	51.2
1	-1	1	42.4	42.8
1	0	1	89.0	-90.8
1	1	1	62.0	-66.9
1	2	1	36.9	39.1
1	3	1	30.0	31.3
1	4	1	6.6	-5.8
1	5	1	10.0	-9.9
1	6	1	10.7	11.1
1	7	1	56.9	58.1
1	8	1	7.3	7.9
1	9	1	-4.0	-5.1
1	10	1	0.0	-1.4
1	11	1	-1.2	-0.3
1	-12	2	20.4	-19.6
1	-11	2	-4.0	-4.6
1	-10	2	-3.0	-3.1
1	-9	2	-1.5	2.2
1	-8	2	3.6	3.5
1	-7	2	31.3	-31.8
1	-6	2	-2.3	-0.8
1	-5	2	9.8	-9.4
1	-4	2	15.7	-16.3
1	-3	2	14.0	12.8
1	-2	2	40.4	-41.4
1	-1	2	13.4	-11.6
1	0	2	40.0	39.2
1	1	2	59.0	-58.4
1	2	2	35.0	36.4
1	3	2	15.4	15.4
1	4	2	22.4	23.2
1	5	2	22.6	23.3
1	6	2	16.9	-17.6
1	7	2	5.2	4.4
1	8	2	5.0	-3.7
1	9	2	4.9	-5.5
1	10	2	18.9	18.8
1	-12	3	8.5	-8.1
1	-11	3	5.2	4.4
1	-10	3	4.9	5.4
1	-9	3	24.0	-24.3
1	-8	3	6.5	6.5
1	-7	3	10.3	-10.2
1	-6	3	8.9	-9.1
1	-5	3	26.3	-26.0
1	-4	3	65.8	-65.2
1	-3	3	17.3	17.2
1	-2	3	24.9	24.0
1	-1	3	9.7	-9.3

H	K	L	FO	FC
1	0	3	22.7	21.7
1	1	3	-2.1	-2.5
1	2	3	39.3	39.8
1	3	3	-2.4	-2.2
1	4	3	24.3	-24.7
1	5	3	11.8	-12.1
1	6	3	-3.5	-3.7
1	7	3	15.3	15.3
1	8	3	10.6	10.9
1	9	3	-3.6	-1.7
1	-11	4	-3.0	-3.4
1	-10	4	8.9	9.0
1	-9	4	15.1	-15.0
1	-8	4	26.6	-26.4
1	-7	4	17.1	-17.2
1	-6	4	4.4	-4.1
1	-5	4	10.9	10.9
1	-4	4	23.5	-23.3
1	-3	4	15.4	-15.2
1	-2	4	9.0	8.2
1	-1	4	34.8	34.3
1	0	4	3.7	3.5
1	1	4	17.5	-17.4
1	2	4	15.8	-15.9
1	3	4	5.3	-5.5
1	4	4	-3.4	2.7
1	5	4	-2.9	-0.7
1	6	4	7.8	7.6
1	7	4	9.5	9.3
1	8	4	10.3	10.4
1	-10	5	8.0	-8.2
1	-9	5	7.0	-6.9
1	-8	5	12.9	-12.7
1	-7	5	-3.9	1.8
1	-6	5	-2.2	2.5
1	-5	5	9.0	-8.8
1	-4	5	-2.0	1.5
1	-3	5	-2.8	3.4
1	-2	5	5.9	-6.2
1	-1	5	12.3	-11.9
1	0	5	37.7	-37.7
1	1	5	8.8	9.0
1	2	5	15.2	15.2
1	3	5	6.9	7.7
1	4	5	-3.1	2.4
1	5	5	8.7	-8.2
1	6	5	19.1	18.9
1	-7	6	-3.2	2.7
1	-6	6	11.2	10.7
1	-5	6	17.2	-17.1
1	-4	6	12.2	-12.6
1	-3	6	18.9	-18.9
1	-2	6	5.5	-3.8
1	-1	6	10.7	9.9
1	0	6	16.3	-16.3
1	1	6	7.3	6.3
1	2	6	10.7	9.5
1	3	6	7.9	8.3
2	-2	-7	10.3	10.4
2	-1	-7	24.9	-25.5
2	0	-7	16.9	-17.2
2	1	-7	7.1	-7.0
2	2	-7	8.1	-8.6
2	3	-7	10.6	10.3
2	4	-7	11.1	-10.6
2	5	-7	5.1	-4.4
2	6	-7	15.2	14.5
2	7	-7	4.9	3.4
2	-5	-6	-2.2	-2.2
2	-4	-6	24.0	-24.0
2	-3	-6	29.5	-30.0
2	-2	-6	0.0	-0.9
2	-1	-6	6.5	6.5
2	0	-6	12.0	-11.6
2	1	-6	9.0	-8.2
2	2	-6	4.2	-2.6
2	3	-6	4.5	4.3
2	4	-6	7.0	7.4
2	5	-6	9.6	-9.2
2	6	-6	14.0	-14.5
2	7	-6	0.0	2.5
2	8	-6	9.8	-10.1
2	9	-6	-3.1	2.4
2	-7	-5	17.1	-16.7
2	-6	-5	9.7	-9.8
2	-5	-5	20.0	-19.6
2	-4	-5	24.0	-24.2
2	-3	-5	4.2	3.9
2	-2	-5	15.7	-15.7
2	-1	-5	12.5	12.7

H	K	L	FO	FC
2	0	-5	0.0	0.5
2	1	-5	17.4	-17.7
2	2	-5	32.3	32.4
2	3	-5	24.8	-24.4
2	4	-5	37.9	-37.5
2	5	-5	14.4	-14.8
2	6	-5	9.8	-9.3
2	7	-5	18.9	19.0
2	8	-5	12.4	-13.2
2	9	-5	8.4	-8.1
2	10	-5	19.7	19.6
2	11	-5	10.6	10.4
2	-9	-4	31.1	-30.1
2	-8	-4	8.0	-8.0
2	-7	-4	16.0	-15.6
2	-6	-4	9.8	9.8
2	-5	-4	10.2	-10.2
2	-4	-4	37.9	-38.2
2	-3	-4	26.3	26.2
2	-2	-4	-1.5	1.6
2	-1	-4	22.9	-22.0
2	0	-4	9.1	-8.6
2	1	-4	51.0	-50.1
2	2	-4	22.3	22.1
2	3	-4	9.7	-9.3
2	4	-4	29.4	-28.5
2	5	-4	24.9	-25.3
2	6	-4	6.4	-6.4
2	7	-4	20.3	19.9
2	8	-4	16.8	16.5
2	9	-4	10.2	-10.0
2	10	-4	0.0	1.7
2	11	-4	0.0	1.1
2	-10	-3	5.0	5.2
2	-9	-3	13.5	-14.1
2	-8	-3	-0.7	3.9
2	-7	-3	4.4	-3.4
2	-6	-3	4.6	-4.7
2	-5	-3	-2.0	-3.6
2	-4	-3	19.2	-19.0
2	-3	-3	8.8	-8.4
2	-2	-3	18.6	-18.6
2	-1	-3	47.3	-46.1
2	0	-3	40.9	-38.7
2	1	-3	9.9	-10.3
2	2	-3	-1.9	-1.9
2	3	-3	19.4	-18.8
2	4	-3	8.5	7.9
2	5	-3	12.7	12.7
2	6	-3	16.6	16.5
2	7	-3	21.5	-21.8
2	8	-3	21.9	-22.6
2	9	-3	10.1	-10.1
2	10	-3	6.1	5.8
2	11	-3	7.9	7.5
2	12	-3	8.4	-7.6
2	-11	-2	0.0	0.1
2	-10	-2	-3.5	-1.6
2	-9	-2	-2.2	0.9
2	-8	-2	-2.8	-2.2
2	-7	-2	23.3	23.7
2	-6	-2	7.7	-7.7
2	-5	-2	55.8	-55.2
2	-4	-2	40.2	-40.4
2	-3	-2	14.3	-14.4
2	-2	-2	18.3	-17.0
2	-1	-2	17.5	-18.4
2	0	-2	91.2	-91.7
2	1	-2	37.8	37.7
2	2	-2	19.1	19.6
2	3	-2	17.2	16.9
2	4	-2	14.1	-14.1
2	5	-2	28.3	-28.5
2	6	-2	-1.3	-0.4
2	7	-2	21.0	-20.5
2	8	-2	21.4	-21.1
2	9	-2	5.7	-4.4
2	10	-2	6.8	-7.2
2	11	-2	21.3	21.1
2	12	-2	6.7	6.6
2	-12	-1	-3.5	1.4
2	-11	-1	10.4	10.6
2	-10	-1	0.0	-1.0
2	-9	-1	6.5	6.1
2	-8	-1	30.3	-30.1
2	-7	-1	9.2	-10.2
2	-6	-1	9.5	9.0
2	-5	-1	19.4	-20.1
2	-4	-1	34.7	-33.7
2	-3	-1	77.5	-79.9

H	K	L	FO	FC
2	-2	-1	13.7	-13.6
2	-1	-1	63.3	62.4
2	0	-1	48.8	-48.8
2	1	-1	29.0	27.9
2	2	-1	42.5	-42.7
2	3	-1	25.3	-27.4
2	4	-1	35.8	-33.5
2	5	-1	45.6	-44.4
2	6	-1	21.5	20.8
2	7	-1	-1.4	2.2
2	8	-1	18.8	-19.0
2	9	-1	15.2	14.8
2	10	-1	4.6	3.7
2	11	-1	0.0	1.2
2	12	-1	-1.2	-0.8
2	-12	0	7.0	7.0
2	-11	0	5.8	6.9
2	-10	0	22.4	-22.5
2	-9	0	18.7	-19.0
2	-8	0	5.2	-4.6
2	-7	0	8.1	8.3
2	-6	0	4.9	-4.2
2	-5	0	56.6	-58.2
2	-4	0	40.5	41.0
2	-3	0	17.6	19.3
2	-2	0	12.3	-12.9
2	-1	0	65.2	-68.7
2	0	0	88.7	-91.5
2	1	0	16.0	-16.1
2	2	0	-1.8	-1.2
2	3	0	38.7	-39.6
2	4	0	17.2	-17.2
2	5	0	9.7	-9.5
2	6	0	21.2	21.4
2	7	0	24.0	23.8
2	8	0	15.1	-14.9
2	9	0	21.1	-21.5
2	10	0	9.9	9.6
2	11	0	-4.0	-3.4
2	-12	1	7.3	-7.5
2	-11	1	7.9	8.0
2	-10	1	-3.5	-0.8
2	-9	1	21.2	-20.5
2	-8	1	6.6	-6.9
2	-7	1	6.4	5.7
2	-6	1	30.3	30.1
2	-5	1	12.2	-11.7
2	-4	1	23.0	-24.4
2	-3	1	-1.0	-2.5
2	-2	1	12.4	-13.2
2	-1	1	91.7	-105.3
2	0	1	42.8	-40.7
2	1	1	36.7	-38.2
2	2	1	21.4	21.6
2	3	1	16.5	16.3
2	4	1	19.1	-20.1
2	5	1	22.5	22.4
2	6	1	12.5	-12.1
2	7	1	22.6	-23.2
2	8	1	-3.4	2.2
2	9	1	15.7	-15.2
2	10	1	5.1	4.3
2	11	1	5.9	-5.2
2	-12	2	-2.7	-0.9
2	-11	2	6.2	-6.8
2	-10	2	-1.8	-0.9
2	-9	2	-2.8	-1.8
2	-8	2	24.2	24.2
2	-7	2	11.7	12.1
2	-6	2	49.4	-49.8
2	-5	2	8.6	-8.3
2	-4	2	28.5	-28.9
2	-3	2	6.1	-6.2
2	-2	2	2.9	1.3
2	-1	2	68.3	-68.2
2	0	2	24.4	23.8
2	1	2	19.3	19.5
2	2	2	26.9	-28.3
2	3	2	11.5	-11.4
2	4	2	41.8	-44.2
2	5	2	15.6	15.9
2	6	2	7.6	8.1
2	7	2	27.5	-28.1
2	8	2	12.8	-13.0
2	9	2	-2.9	-1.7
2	10	2	7.9	8.5
2	-11	3	-2.5	2.9
2	-10	3	4.5	1.1
2	-9	3	15.4	-15.5
2	-8	3	18.8	-19.0

H	K	L	FO	FC
2	-7	3	16.0	16.4
2	-6	3	23.2	-23.7
2	-5	3	10.6	-10.6
2	-4	3	19.0	-19.5
2	-3	3	-2.8	-1.6
2	-2	3	32.4	32.3
2	-1	3	4.4	-4.0
2	0	3	25.9	-25.6
2	1	3	18.5	-19.0
2	2	3	18.8	-19.9
2	3	3	12.4	-12.2
2	4	3	21.3	-22.3
2	5	3	12.0	-13.1
2	6	3	0.0	-1.3
2	7	3	-3.7	4.0
2	8	3	-0.5	-0.2
2	-10	4	11.9	-11.1
2	-9	4	-3.4	-4.4
2	-8	4	9.2	-9.0
2	-7	4	7.9	-7.3
2	-6	4	-1.2	-0.3
2	-5	4	-3.6	4.7
2	-4	4	18.2	18.4
2	-3	4	-3.1	3.6
2	-2	4	34.9	-34.5
2	-1	4	16.1	-15.7
2	0	4	4.9	-4.7
2	1	4	12.3	-12.0
2	2	4	7.8	-7.5
2	3	4	31.6	-32.3
2	4	4	-2.5	-2.4
2	5	4	6.0	6.5
2	6	4	-3.3	3.1
2	7	4	-4.3	4.4
2	-9	5	7.5	-8.2
2	-8	5	12.0	12.4
2	-7	5	5.5	4.5
2	-6	5	5.5	4.6
2	-5	5	21.2	-21.0
2	-4	5	13.4	-12.9
2	-3	5	17.3	17.1
2	-2	5	14.5	-14.4
2	-1	5	19.4	-18.9
2	0	5	16.7	-16.7
2	1	5	5.8	-5.6
2	2	5	18.3	17.9
2	3	5	13.0	-13.1
2	4	5	-3.4	-2.2
2	-5	6	5.9	-5.8
2	-4	6	7.2	-6.3
2	-3	6	0.0	0.4
2	-2	6	13.5	-12.9
2	-1	6	4.7	3.3
2	0	6	6.8	6.3
3	-3	-7	-3.3	-3.1
3	-2	-7	-1.5	-0.1
3	-1	-7	8.4	-7.7
3	0	-7	24.2	-24.6
3	1	-7	-2.9	-3.2
3	2	-7	-3.2	3.4
3	3	-7	5.1	4.1
3	4	-7	-2.6	1.1
3	5	-7	5.4	-5.4
3	6	-7	-1.9	-1.7
3	7	-7	0.0	-0.4
3	-6	-6	0.0	1.3
3	-5	-6	-2.9	-2.3
3	-4	-6	-3.0	-2.7
3	-3	-6	4.9	-5.1
3	-2	-6	9.8	-9.7
3	-1	-6	7.9	-7.7
3	0	-6	23.4	23.3
3	1	-6	-2.2	-0.5
3	2	-6	-3.3	-2.7
3	3	-6	19.8	-19.8
3	4	-6	16.2	-16.6
3	5	-6	8.2	8.7
3	6	-6	18.5	-18.9
3	7	-6	16.8	-16.9
3	8	-6	-3.3	-3.8
3	9	-6	5.6	-6.5
3	-8	-5	11.4	11.2
3	-7	-5	7.5	7.5
3	-6	-5	15.6	-15.6
3	-5	-5	0.0	-0.7
3	-4	-5	-4.0	-4.2
3	-3	-5	31.3	31.4
3	-2	-5	24.6	24.6
3	-1	-5	39.8	-40.5
3	0	-5	16.3	16.3

H	K	L	FO	FC
3	1	-5	5.1	-6.0
3	2	-5	7.5	-7.4
3	3	-5	19.9	-20.4
3	4	-5	57.5	-58.4
3	5	-5	-1.3	0.5
3	6	-5	12.8	13.1
3	7	-5	5.6	-5.4
3	8	-5	5.7	5.2
3	9	-5	8.5	-9.4
3	10	-5	0.0	-0.1
3	11	-5	0.0	-0.8
3	-9	-4	8.8	-8.0
3	-8	-4	0.0	-2.9
3	-7	-4	15.8	15.6
3	-6	-4	11.5	-11.7
3	-5	-4	28.3	28.4
3	-4	-4	13.4	12.6
3	-3	-4	14.4	14.4
3	-2	-4	13.1	13.0
3	-1	-4	38.9	-38.8
3	0	-4	18.5	-18.5
3	1	-4	3.5	-3.9
3	2	-4	40.0	-39.0
3	3	-4	12.5	-12.0
3	4	-4	5.4	5.6
3	5	-4	14.1	14.3
3	6	-4	6.3	-6.4
3	7	-4	25.2	-25.7
3	8	-4	8.6	-8.9
3	9	-4	13.9	14.4
3	10	-4	13.6	-13.2
3	11	-4	17.2	-17.5
3	-10	-3	6.4	-6.1
3	-9	-3	22.9	22.5
3	-8	-3	19.3	19.2
3	-7	-3	13.9	14.2
3	-6	-3	13.5	-14.0
3	-5	-3	-2.3	-1.0
3	-4	-3	23.6	23.0
3	-3	-3	5.4	4.8
3	-2	-3	49.1	-48.4
3	-1	-3	2.6	2.3
3	0	-3	13.4	-12.7
3	1	-3	19.7	20.5
3	2	-3	19.7	18.9
3	3	-3	36.1	-35.7
3	4	-3	6.6	-6.3
3	5	-3	0.0	0.3
3	6	-3	10.4	-10.7
3	7	-3	18.5	-18.4
3	8	-3	42.6	-42.2
3	9	-3	-2.0	1.0
3	10	-3	-1.5	3.0
3	11	-3	5.3	-4.7
3	-11	-2	20.8	20.3
3	-10	-2	-2.2	-1.0
3	-9	-2	6.9	7.4
3	-8	-2	22.6	22.3
3	-7	-2	-3.1	-2.6
3	-6	-2	11.2	11.0
3	-5	-2	41.0	-40.3
3	-4	-2	19.6	-19.0
3	-3	-2	25.6	24.7
3	-2	-2	17.0	-16.5
3	-1	-2	59.7	59.6
3	0	-2	51.4	48.6
3	1	-2	26.8	-25.9
3	2	-2	14.6	-12.7
3	3	-2	51.4	-50.1
3	4	-2	8.5	8.8
3	5	-2	30.2	-28.8
3	6	-2	38.0	-38.4
3	7	-2	7.6	-7.7
3	8	-2	5.2	-5.5
3	9	-2	4.1	3.1
3	10	-2	-1.8	-2.0
3	11	-2	8.4	-9.2
3	-11	-1	10.0	9.7
3	-10	-1	5.6	5.9
3	-9	-1	-2.5	0.6
3	-8	-1	14.8	15.9
3	-7	-1	30.3	-30.9
3	-6	-1	4.3	4.4
3	-5	-1	7.2	7.6
3	-4	-1	34.8	35.3
3	-3	-1	34.5	35.0
3	-2	-1	22.7	-23.2
3	-1	-1	10.7	-10.2
3	0	-1	19.6	19.9
3	1	-1	16.5	15.3
3	2	-1	6.3	-6.8
3	3	-1	78.8	-77.5
3	4	-1	11.7	-11.8
3	5	-1	2.7	2.5
3	6	-1	6.9	-7.1
3	7	-1	13.0	-12.7
3	8	-1	4.3	-4.2
3	9	-1	-4.0	1.6
3	10	-1	6.1	4.8
3	11	-1	17.3	-16.9
3	-12	0	10.9	11.0
3	-11	0	4.9	3.9
3	-10	0	6.1	-6.6
3	-9	0	4.4	-4.1
3	-8	0	22.5	22.1
3	-7	0	22.9	23.8
3	-6	0	8.7	9.1
3	-5	0	-0.9	1.7
3	-4	0	17.0	18.1
3	-3	0	21.1	20.5
3	-2	0	24.8	-24.1
3	-1	0	35.8	-35.6
3	0	0	22.3	-21.6
3	1	0	27.6	25.3
3	2	0	0.0	-1.5
3	3	0	-1.9	-1.4
3	4	0	12.3	-11.9
3	5	0	7.3	6.6
3	6	0	4.1	-3.9
3	7	0	23.6	-23.9
3	8	0	-2.4	-0.3
3	9	0	12.7	-12.3
3	10	0	15.5	-16.2
3	11	0	8.6	-7.8
3	-12	1	-3.2	-0.2
3	-11	1	-3.7	-3.1
3	-10	1	15.2	14.3
3	-9	1	35.5	37.0
3	-8	1	15.3	15.9
3	-7	1	6.2	6.2
3	-6	1	19.4	-19.4
3	-5	1	17.7	17.5
3	-4	1	13.2	13.3
3	-3	1	35.7	-37.2
3	-2	1	8.8	-8.9
3	-1	1	6.1	5.3
3	0	1	9.4	9.5
3	1	1	32.4	32.2
3	2	1	43.1	-43.6
3	3	1	24.5	25.1
3	4	1	14.8	15.0
3	5	1	-2.0	-3.3
3	6	1	12.8	-13.1
3	7	1	49.1	-50.1
3	8	1	12.0	-13.1
3	9	1	10.4	10.3
3	10	1	7.6	-7.3
3	-11	2	-1.6	0.2
3	-10	2	0.0	-1.1
3	-9	2	21.4	21.4
3	-8	2	13.0	13.3
3	-7	2	15.0	15.4
3	-6	2	23.9	-24.9
3	-5	2	16.4	-16.4
3	-4	2	37.5	38.8
3	-3	2	15.5	-15.7
3	-2	2	3.2	3.7
3	-1	2	8.3	8.4
3	0	2	10.8	10.9
3	1	2	28.5	30.1
3	2	2	22.4	-24.0
3	3	2	10.5	-10.5
3	4	2	-2.3	-2.4
3	5	2	23.4	-24.5
3	6	2	8.5	-8.7
3	7	2	-3.6	-2.9
3	8	2	-4.4	-3.4
3	9	2	-2.9	1.5
3	-10	3	-1.3	1.8
3	-9	3	6.3	6.1
3	-8	3	6.6	-7.3
3	-7	3	-1.7	1.2
3	-6	3	26.6	27.2
3	-5	3	11.5	11.5
3	-4	3	10.5	10.7
3	-3	3	7.4	-7.7
3	-2	3	-3.4	2.6
3	-1	3	14.6	13.6
3	0	3	11.6	11.3
3	1	3	23.7	-24.5
3	2	3	18.5	-19.2
3	3	3	11.4	-11.6
3	4	3	7.7	8.0
3	5	3	10.7	10.5
3	6	3	12.7	-12.4
3	7	3	-3.4	1.5
3	-9	4	8.5	8.7
3	-8	4	22.1	21.4
3	-7	4	-2.8	-0.9
3	-6	4	0.0	0.0
3	-5	4	23.7	23.8
3	-4	4	10.9	11.2
3	-3	4	11.5	11.3
3	-2	4	18.5	-18.5
3	-1	4	30.3	-29.9
3	0	4	11.3	11.4
3	1	4	6.2	-5.5
3	2	4	6.1	7.0
3	3	4	5.3	4.4
3	4	4	-4.4	-3.3
3	5	4	14.7	15.0
3	-7	5	7.3	7.7
3	-6	5	0.0	-1.3
3	-5	5	12.3	12.7
3	-4	5	11.7	-11.5
3	-3	5	-2.1	-3.2
3	-2	5	-2.0	3.0
3	-1	5	0.0	0.3
3	0	5	12.4	12.2
3	1	5	-4.0	-4.7
3	2	5	-3.0	2.1
4	-3	-7	10.1	-10.3
4	-2	-7	-4.4	3.3
4	-1	-7	15.3	15.0
4	0	-7	16.1	16.4
4	1	-7	5.1	4.7
4	2	-7	-3.6	3.1
4	3	-7	16.2	17.4
4	4	-7	11.0	10.9
4	5	-7	-3.1	-3.0
4	6	-7	13.8	-14.3
4	7	-7	9.1	-9.6
4	-6	-6	12.3	-11.4
4	-5	-6	8.0	8.1
4	-4	-6	18.0	18.2
4	-3	-6	-2.9	1.1
4	-2	-6	12.0	11.6
4	-1	-6	-4.0	3.7
4	0	-6	25.2	25.6
4	1	-6	31.0	31.6
4	2	-6	19.6	-19.9
4	3	-6	-1.0	-2.5
4	4	-6	8.0	-8.5
4	5	-6	8.5	9.8
4	6	-6	7.8	8.8
4	7	-6	16.3	-16.8
4	8	-6	8.5	8.1
4	9	-6	9.9	9.4
4	-8	-5	5.2	-6.0
4	-7	-5	15.0	14.9
4	-6	-5	-2.5	1.5
4	-5	-5	21.9	22.0
4	-4	-5	31.0	31.8
4	-3	-5	-3.3	-4.2
4	-2	-5	22.1	21.8
4	-1	-5	6.1	5.2
4	0	-5	15.4	-15.6
4	1	-5	8.8	8.5
4	2	-5	13.9	-13.9
4	3	-5	29.6	29.6
4	4	-5	14.6	14.2
4	5	-5	11.1	-10.7
4	6	-5	11.7	11.6
4	7	-5	12.8	12.9
4	8	-5	-3.7	4.9
4	9	-5	5.6	5.7
4	10	-5	18.3	-18.3
4	-9	-4	22.1	22.3
4	-8	-4	5.9	5.2
4	-7	-4	5.9	5.8
4	-6	-4	14.6	14.5
4	-5	-4	23.3	23.5
4	-4	-4	36.7	37.0
4	-3	-4	17.0	-17.5
4	-2	-4	27.2	-26.3
4	-1	-4	15.8	15.1
4	0	-4	29.4	29.1
4	1	-4	3.0	-3.2
4	2	-4	6.8	-7.2
4	3	-4	8.3	8.1
4	4	-4	59.4	59.7
4	5	-4	26.8	27.0
4	6	-4	24.9	-25.0
4	7	-4	5.7	-4.4
4	8	-4	4.3	-3.2
4	9	-4	-3.7	-1.3
4	10	-4	5.3	-3.6
4	11	-4	15.0	-15.0
4	-10	-3	-4.6	4.1
4	-9	-3	13.1	13.0
4	-8	-3	25.4	25.0
4	-7	-3	4.8	-5.8
4	-6	-3	10.4	10.4
4	-5	-3	4.3	4.4
4	-4	-3	11.2	-10.8
4	-3	-3	26.4	26.3
4	-2	-3	16.4	15.5
4	-1	-3	12.2	11.4
4	0	-3	47.7	45.9
4	1	-3	31.6	-30.0
4	2	-3	42.1	40.8
4	3	-3	23.8	22.8
4	4	-3	-0.8	0.4
4	5	-3	6.6	6.8
4	6	-3	21.7	-21.4
4	7	-3	7.1	7.1
4	8	-3	12.2	12.7
4	9	-3	14.3	-14.4
4	10	-3	-3.6	1.3
4	11	-3	-2.7	3.2
4	-10	-2	17.6	18.0
4	-9	-2	10.8	-11.0
4	-8	-2	-2.7	-3.1
4	-7	-2	11.0	-10.6
4	-6	-2	12.4	12.5
4	-5	-2	55.2	56.5
4	-4	-2	17.6	-17.6
4	-3	-2	12.1	12.1
4	-2	-2	34.5	32.8
4	-1	-2	32.2	32.2
4	0	-2	62.8	61.6
4	1	-2	17.2	-17.4
4	2	-2	23.1	-22.4
4	3	-2	0.0	1.8
4	4	-2	-0.3	-1.4
4	5	-2	12.4	12.0
4	6	-2	5.4	-5.4
4	7	-2	10.5	10.8
4	8	-2	28.6	28.8
4	9	-2	7.8	7.6
4	10	-2	9.0	-8.8
4	11	-2	6.9	-7.4
4	-11	-1	15.4	-15.3
4	-10	-1	0.0	-0.1
4	-9	-1	5.9	5.0
4	-8	-1	-1.8	2.4
4	-7	-1	6.2	6.5
4	-6	-1	-3.3	-3.7
4	-5	-1	47.3	47.8
4	-4	-1	31.3	31.8
4	-3	-1	25.1	24.8
4	-2	-1	9.1	9.1
4	-1	-1	20.6	19.8
4	0	-1	16.2	-15.6
4	1	-1	-1.2	0.4
4	2	-1	8.1	7.6
4	3	-1	10.6	10.5
4	4	-1	4.5	4.5
4	5	-1	12.5	12.2
4	6	-1	25.7	25.7
4	7	-1	14.7	15.4
4	8	-1	0.0	-1.0
4	9	-1	-3.1	-2.7
4	10	-1	10.0	-9.7
4	-11	0	-0.4	2.7
4	-10	0	7.1	6.2
4	-9	0	11.0	11.5
4	-8	0	-3.4	-3.2
4	-7	0	6.0	5.7
4	-6	0	23.6	24.8
4	-5	0	14.3	14.2
4	-4	0	21.4	22.2
4	-3	0	-2.1	-1.7
4	-2	0	11.7	-12.3
4	-1	0	40.4	39.9
4	0	0	-1.2	2.1
4	1	0	-0.5	-0.3
4	2	0	12.0	11.8
4	3	0	41.9	40.8
4	4	0	48.3	48.3

H	K	L	FO	FC
4	5	0	25.0	-25.1
4	6	0	14.9	-15.5
4	7	0	4.2	4.2
4	8	0	6.7	6.6
4	9	0	6.5	5.3
4	10	0	13.6	-13.3
4	-11	1	0.0	-0.8
4	-10	1	10.7	10.6
4	-9	1	24.2	23.6
4	-8	1	-2.1	3.6
4	-7	1	19.0	-20.0
4	-6	1	13.9	14.4
4	-5	1	6.9	-7.8
4	-4	1	13.1	13.0
4	-3	1	5.8	-5.8
4	-2	1	16.6	11.2
4	-1	1	57.8	57.8
4	0	1	26.5	25.0
4	1	1	22.9	22.6
4	2	1	4.1	4.6
4	3	1	14.5	-14.5
4	4	1	20.5	20.3
4	5	1	11.7	-12.5
4	6	1	4.5	-4.4
4	7	1	6.5	7.4
4	8	1	0.0	0.7
4	9	1	6.9	6.1
4	-10	2	-3.5	-0.7
4	-9	2	-1.6	-4.1
4	-8	2	6.0	-5.2
4	-7	2	0.0	-3.6
4	-6	2	20.5	20.8
4	-5	2	5.4	-6.3
4	-4	2	-2.2	1.0
4	-3	2	19.7	20.2
4	-2	2	33.3	35.7
4	-1	2	37.7	39.5
4	0	2	7.9	-7.2
4	1	2	14.6	-14.2
4	2	2	9.5	9.7
4	3	2	10.4	10.7
4	4	2	-1.7	-1.1
4	5	2	4.6	-4.5
4	6	2	-3.6	2.1
4	7	2	18.5	18.3
4	8	2	13.6	13.5
4	-9	3	-2.4	0.5
4	-8	3	7.3	-7.7
4	-7	3	-2.2	-1.6
4	-6	3	16.7	17.3
4	-5	3	32.6	32.9
4	-4	3	4.1	3.1
4	-3	3	9.3	-9.0
4	-2	3	6.0	5.7
4	-1	3	-0.7	1.5
4	0	3	10.6	10.5
4	1	3	5.1	5.0
4	2	3	-2.0	-0.4
4	3	3	22.8	23.7
4	4	3	-2.9	-0.5
4	5	3	8.4	9.0
4	6	3	7.7	8.5
4	-8	4	6.3	6.3
4	-7	4	17.2	16.3
4	-6	4	6.5	-7.2
4	-5	4	0.0	1.0
4	-4	4	0.0	0.3
4	-3	4	7.4	-6.8
4	-2	4	16.8	16.5
4	-1	4	4.7	-4.4
4	0	4	-1.9	4.7
4	1	4	17.6	16.8
4	2	4	8.7	8.4
4	3	4	20.7	21.9
4	-3	5	6.3	-5.7
4	-2	5	15.6	15.2
5	-3	-7	11.7	-11.9
5	-2	-7	7.8	6.6
5	-1	-7	32.5	33.2
5	0	-7	5.5	6.1
5	1	-7	5.7	6.2
5	2	-7	-2.2	-1.0
5	3	-7	7.7	8.1
5	4	-7	5.1	6.1
5	5	-7	12.9	-13.2
5	6	-7	-4.1	2.0
5	7	-7	8.4	7.9
5	-5	-6	11.5	-11.4
5	-4	-6	15.4	15.7
5	-3	-6	11.4	10.8

H	K	L	FO	FC
5	-2	-6	4.8	3.9
5	-1	-6	17.0	12.2
5	0	-6	9.0	-8.3
5	1	-6	15.6	15.4
5	2	-6	5.6	5.4
5	3	-6	8.9	-9.0
5	4	-6	4.8	3.9
5	5	-6	6.0	-6.1
5	6	-6	19.3	20.1
5	7	-6	22.5	23.1
5	8	-6	0.0	3.7
5	-7	-5	5.4	-5.5
5	-6	-5	23.3	23.7
5	-5	-5	0.0	-1.4
5	-4	-5	-1.3	-2.3
5	-3	-5	11.8	-11.7
5	-2	-5	4.9	5.2
5	-1	-5	16.5	16.8
5	0	-5	15.8	-15.4
5	1	-5	18.5	-18.7
5	2	-5	20.5	20.1
5	3	-5	30.1	30.7
5	4	-5	30.3	31.1
5	5	-5	-3.0	-0.3
5	6	-5	7.3	-7.3
5	7	-5	17.4	17.5
5	8	-5	10.2	10.6
5	9	-5	6.5	-7.3
5	-8	-4	-2.5	1.4
5	-7	-4	6.5	-6.5
5	-6	-4	-2.2	-0.8
5	-5	-4	-2.9	-2.7
5	-4	-4	19.9	-19.8
5	-3	-4	8.2	-7.7
5	-2	-4	-2.5	1.9
5	-1	-4	11.5	-10.6
5	0	-4	20.2	20.7
5	1	-4	19.4	18.8
5	2	-4	29.1	28.4
5	3	-4	28.2	28.3
5	4	-4	12.1	-11.3
5	5	-4	17.9	18.1
5	6	-4	-3.4	2.0
5	7	-4	7.8	-8.3
5	8	-4	6.8	6.2
5	9	-4	6.9	-7.2
5	10	-4	12.9	13.1
5	-9	-3	15.4	-15.0
5	-8	-3	12.5	-12.9
5	-7	-3	14.2	14.0
5	-6	-3	14.1	-13.6
5	-5	-3	-2.2	-1.7
5	-4	-3	45.1	-45.5
5	-3	-3	14.7	-13.9
5	-2	-3	65.9	65.8
5	-1	-3	17.0	16.9
5	0	-3	3.2	-2.7
5	1	-3	0.0	-0.7
5	2	-3	4.0	4.6
5	3	-3	48.9	48.3
5	4	-3	31.6	-31.8
5	5	-3	15.9	-15.9
5	6	-3	27.0	28.0
5	7	-3	17.5	17.7
5	8	-3	10.4	10.5
5	9	-3	0.9	0.2
5	10	-3	-3.0	2.9
5	-10	-2	-0.7	1.1
5	-9	-2	9.6	-9.8
5	-8	-2	26.4	-27.0
5	-7	-2	6.7	7.1
5	-6	-2	10.4	-10.3
5	-5	-2	11.7	12.1
5	-4	-2	22.5	22.6
5	-3	-2	10.4	-10.0
5	-2	-2	4.5	3.3
5	-1	-2	12.1	-11.7
5	0	-2	4.8	-4.3
5	1	-2	13.2	12.9
5	2	-2	8.4	-8.0
5	3	-2	4.4	3.9
5	4	-2	17.8	17.7
5	5	-2	12.1	12.5
5	6	-2	24.3	24.1
5	7	-2	19.6	19.2
5	8	-2	-2.7	-0.3
5	9	-2	7.0	6.2
5	10	-2	-0.8	3.5
5	-10	-1	14.1	-14.3
5	-9	-1	10.3	-9.7

H	K	L	FO	FC
5	-8	-1	-0.6	-3.0
5	-7	-1	10.7	10.9
5	-6	-1	21.8	22.8
5	-5	-1	16.6	-16.8
5	-4	-1	7.4	-8.5
5	-3	-1	7.6	7.8
5	-2	-1	12.6	-12.5
5	-1	-1	25.8	-24.7
5	0	-1	21.5	-21.2
5	1	-1	-1.5	-1.3
5	2	-1	58.0	57.9
5	3	-1	12.2	11.9
5	4	-1	10.6	10.0
5	5	-1	7.5	7.7
5	6	-1	11.5	11.1
5	7	-1	21.5	21.4
5	8	-1	6.0	-5.6
5	9	-1	7.1	-7.8
5	10	-1	-2.3	7.8
5	-10	0	-4.5	5.7
5	-9	0	5.2	-5.6
5	-8	0	0.9	0.6
5	-7	0	15.7	-15.9
5	-6	0	9.8	9.5
5	-5	0	8.9	-8.5
5	-4	0	36.2	-36.3
5	-3	0	6.4	6.2
5	-2	0	0.0	-0.5
5	-1	0	13.6	12.7
5	0	0	10.9	10.8
5	1	0	15.9	-15.4
5	2	0	25.4	25.0
5	3	0	7.6	7.4
5	4	0	13.2	13.3
5	5	0	9.3	9.8
5	6	0	8.2	-8.5
5	7	0	5.4	4.2
5	8	0	-1.6	1.5
5	9	0	6.5	5.8
5	-10	1	5.8	-6.2
5	-9	1	14.8	-15.5
5	-8	1	0.0	-1.6
5	-7	1	9.2	-8.6
5	-6	1	11.1	-11.5
5	-5	1	7.3	-7.0
5	-4	1	14.2	-14.4
5	-3	1	28.2	28.6
5	-2	1	12.3	12.6
5	-1	1	0.0	0.5
5	0	1	12.2	-12.6
5	1	1	0.0	0.1
5	2	1	21.1	20.9
5	3	1	7.6	-7.8
5	4	1	22.3	-22.0
5	5	1	5.7	6.3
5	6	1	21.1	20.9
5	7	1	15.7	14.3
5	8	1	-3.3	2.4
5	-9	2	23.6	-23.8
5	-8	2	12.0	-12.5
5	-7	2	10.0	10.1
5	-6	2	9.5	9.5
5	-5	2	-2.2	-1.1
5	-4	2	7.7	-7.1
5	-3	2	-2.0	3.1
5	-2	2	7.1	6.3
5	-1	2	-0.3	1.0
5	0	2	14.2	-14.0
5	1	2	5.7	-5.2
5	2	2	5.1	-5.7
5	3	2	6.8	6.7
5	4	2	-2.3	3.7
5	5	2	-3.1	4.8
5	6	2	19.9	20.0
5	-8	3	0.0	-3.0
5	-7	3	0.0	0.9
5	-6	3	-3.4	-4.4
5	-5	3	9.8	-9.9
5	-4	3	11.9	12.0
5	-3	3	-4.2	-4.4
5	-2	3	7.7	-8.1
5	-1	3	13.9	-14.2
5	0	3	11.1	-10.7
5	1	3	23.1	23.9
5	2	3	4.9	4.0
5	3	3	0.0	-1.1
5	4	3	8.6	8.0
5	-5	4	20.2	-20.2
5	-4	4	-2.9	-2.1
5	-3	4	-3.3	-1.0

H	K	L	FO	FC
5	-2	4	5.3	6.3
5	-1	4	6.2	5.6
5	0	4	7.2	-6.8
6	-2	-7	12.1	-12.9
6	-1	-7	0.0	-1.5
6	0	-7	5.1	3.9
6	1	-7	9.9	-10.2
6	2	-7	-3.1	-3.9
6	3	-7	25.1	-26.3
6	4	-7	5.6	-6.8
6	5	-7	7.7	7.4
6	-5	-6	5.0	-6.0
6	-4	-6	8.2	-8.5
6	-3	-6	17.6	17.8
6	-2	-6	6.5	-5.9
6	-1	-6	27.8	-27.8
6	0	-6	25.4	-26.3
6	1	-6	8.5	-9.2
6	2	-6	10.3	10.4
6	3	-6	9.3	-9.5
6	4	-6	11.4	-10.7
6	5	-6	8.1	8.4
6	6	-6	9.2	9.4
6	7	-6	6.7	6.4
6	-6	-5	-3.2	-4.2
6	-5	-5	-2.5	-1.2
6	-4	-5	16.7	-16.7
6	-3	-5	19.9	-19.9
6	-2	-5	14.4	-13.9
6	-1	-5	-3.8	-3.7
6	0	-5	10.3	-10.9
6	1	-5	4.7	-4.7
6	2	-5	7.3	-5.7
6	3	-5	9.3	9.8
6	4	-5	5.4	-5.4
6	5	-5	-3.0	0.8
6	6	-5	0.0	0.7
6	7	-5	14.3	-15.1
6	8	-5	-3.7	-3.9
6	9	-5	-0.2	2.2
6	-8	-4	0.0	-0.8
6	-7	-4	-4.4	4.3
6	-6	-4	30.9	-30.8
6	-5	-4	40.0	-39.9
6	-4	-4	-2.6	-1.0
6	-3	-4	4.7	5.1
6	-2	-4	8.0	7.6
6	-1	-4	18.3	-18.6
6	0	-4	14.4	-14.3
6	1	-4	29.7	29.9
6	2	-4	13.6	-14.3
6	3	-4	17.7	-17.7
6	4	-4	23.2	-23.2
6	5	-4	16.1	-15.9
6	6	-4	16.2	17.0
6	7	-4	8.0	-8.6
6	8	-4	9.0	-8.7
6	9	-4	10.0	9.8
6	-9	-3	13.7	-13.1
6	-8	-3	22.4	-22.1
6	-7	-3	0.0	-2.1
6	-6	-3	-2.0	-1.7
6	-5	-3	25.3	-25.4
6	-4	-3	8.8	8.2
6	-3	-3	15.7	-16.2
6	-2	-3	4.8	5.6
6	-1	-3	-1.4	0.9
6	0	-3	20.1	-19.9
6	1	-3	-2.0	2.6
6	2	-3	24.3	-23.5
6	3	-3	33.0	-32.5
6	4	-3	-2.1	-0.2
6	5	-3	7.8	-8.4
6	6	-3	5.3	5.4
6	7	-3	6.4	6.4
6	8	-3	-2.1	-0.1
6	9	-3	10.8	11.3
6	-9	-2	-3.3	0.8
6	-8	-2	-4.0	4.1
6	-7	-2	8.3	-8.2
6	-6	-2	8.5	-8.3
6	-5	-2	18.6	-19.0
6	-4	-2	12.3	12.3
6	-3	-2	3.6	3.6
6	-2	-2	37.9	-38.0
6	-1	-2	39.9	-39.8
6	0	-2	-2.5	-2.5
6	1	-2	7.5	7.0
6	2	-2	-1.6	1.2
6	3	-2	31.4	-31.2

H	K	L	FO	FC
6	4	-2	6.1	-6.0
6	5	-2	28.0	28.0
6	6	-2	-1.6	-2.0
6	7	-2	9.3	-10.5
6	8	-2	8.5	-8.5
6	9	-2	-3.7	-1.6
6	-9	-1	6.8	-6.0
6	-8	-1	8.5	7.2
6	-7	-1	-0.9	-3.4
6	-6	-1	15.6	-16.0
6	-5	-1	5.6	-6.1
6	-4	-1	35.8	-36.7
6	-3	-1	8.1	-7.6
6	-2	-1	5.6	-6.1
6	-1	-1	27.3	-26.9
6	0	-1	0.0	-0.8
6	1	-1	11.8	-11.7
6	2	-1	13.3	13.0
6	3	-1	19.4	19.9
6	4	-1	21.2	-20.8
6	5	-1	-3.4	-3.0
6	6	-1	15.7	-15.6
6	7	-1	13.8	-14.0
6	8	-1	-1.4	-0.1
6	-9	0	-3.4	-2.9
6	-8	0	0.0	1.2
6	-7	0	5.5	-5.2
6	-6	0	36.4	-38.0
6	-5	0	-3.8	-2.7
6	-4	0	8.7	-9.3
6	-3	0	11.4	-10.6
6	-2	0	9.2	-9.6
6	-1	0	14.8	-14.1
6	0	0	23.6	23.1
6	1	0	4.2	4.4
6	2	0	26.0	-25.6
6	3	0	15.9	-15.8
6	4	0	12.6	-12.6
6	5	0	-1.8	2.5
6	6	0	4.9	-3.5
6	7	0	11.1	-11.1
6	-8	1	-1.1	-0.3
6	-7	1	6.9	7.3
6	-6	1	13.1	-13.0
6	-5	1	17.2	-17.4
6	-4	1	0.0	-0.3
6	-3	1	7.2	7.7
6	-2	1	-3.8	-1.9
6	-1	1	20.6	-20.0
6	0	1	16.9	-16.9
6	1	1	7.0	-6.8
6	2	1	8.4	-7.9
6	3	1	17.3	-16.2
6	4	1	-2.1	-2.4
6	5	1	-4.0	2.8
6	6	1	6.4	6.6
6	-7	2	5.7	-6.1
6	-6	2	5.1	5.5
6	-5	2	-2.7	2.0
6	-4	2	0.0	2.3
6	-3	2	13.2	-14.2
6	-2	2	31.8	-33.3
6	-1	2	10.4	-10.4
6	0	2	-3.2	-2.6
6	1	2	-2.1	-1.4
6	2	2	-3.3	-4.1
6	3	2	10.3	-10.8

H	K	L	FO	FC
6	4	2	14.3	14.0
6	-4	3	-4.5	-3.1
6	-3	3	-3.7	-0.5
6	-2	3	18.7	-19.2
6	-1	3	-4.6	-3.8
6	0	3	-2.5	-2.0
7	1	-7	-3.0	-5.0
7	2	-7	16.3	-16.8
7	3	-7	6.3	-6.5
7	-3	-6	9.6	-9.9
7	-2	-6	8.8	-8.7
7	-1	-6	10.9	-10.8
7	0	-6	13.3	-13.5
7	1	-6	7.2	-6.2
7	2	-6	5.7	-5.9
7	3	-6	7.0	7.1
7	4	-6	10.6	10.6
7	5	-6	7.4	-7.1
7	6	-6	11.6	-11.6
7	-5	-5	5.7	-5.3
7	-4	-5	10.1	9.8
7	-3	-5	9.9	-9.2
7	-2	-5	23.5	-23.9
7	-1	-5	5.4	3.9
7	0	-5	8.9	7.9
7	1	-5	5.3	4.3
7	2	-5	10.3	-10.7
7	3	-5	18.9	-19.1
7	4	-5	7.1	8.1
7	5	-5	8.3	-8.8
7	6	-5	13.4	-13.9
7	7	-5	14.8	-15.2
7	-7	-4	-3.9	-3.2
7	-6	-4	-4.5	4.7
7	-5	-4	14.5	-14.9
7	-4	-4	-4.3	5.0
7	-3	-4	15.6	15.6
7	-2	-4	-3.4	-1.9
7	-1	-4	6.2	5.5
7	0	-4	10.4	-9.8
7	1	-4	8.4	-7.5
7	2	-4	12.3	-12.2
7	3	-4	32.8	-33.6
7	4	-4	0.0	-2.6
7	5	-4	-3.0	-4.2
7	6	-4	7.9	-8.0
7	7	-4	0.0	2.2
7	8	-4	0.0	-0.7
7	-7	-3	14.7	-14.7
7	-6	-3	10.8	10.9
7	-5	-3	27.1	27.4
7	-4	-3	13.4	14.0
7	-3	-3	7.6	-8.3
7	-2	-3	25.9	-25.4
7	-1	-3	8.8	7.9
7	0	-3	-2.1	-1.0
7	1	-3	27.6	-27.6
7	2	-3	23.5	-23.5
7	3	-3	7.3	-7.4
7	4	-3	5.9	5.4
7	5	-3	10.8	10.3
7	6	-3	12.3	-12.3
7	7	-3	6.8	-7.2
7	8	-3	5.2	3.2
7	-8	-2	13.5	13.4
7	-7	-2	6.5	6.3
7	-6	-2	6.5	-6.9

H	K	L	FO	FC
7	-5	-2	10.9	11.0
7	-4	-2	7.5	6.5
7	-3	-2	6.0	-5.7
7	-2	-2	14.8	-14.9
7	-1	-2	20.2	-20.4
7	0	-2	4.5	5.0
7	1	-2	-2.6	3.4
7	2	-2	13.4	-13.1
7	3	-2	12.9	12.9
7	4	-2	8.7	-9.0
7	5	-2	10.3	-10.1
7	6	-2	8.6	-8.8
7	7	-2	13.1	-13.1
7	-8	-1	7.4	-7.1
7	-7	-1	-2.6	2.0
7	-6	-1	5.8	-5.5
7	-5	-1	-3.2	3.2
7	-4	-1	-1.6	-1.0
7	-3	-1	23.7	-23.1
7	-2	-1	21.3	22.0
7	-1	-1	15.2	15.0
7	0	-1	-2.0	3.3
7	1	-1	4.6	-4.9
7	2	-1	27.2	-27.2
7	3	-1	5.0	4.5
7	4	-1	-1.6	1.2
7	5	-1	22.2	-22.0
7	6	-1	14.7	-14.2
7	-7	0	-4.3	-4.1
7	-6	0	7.0	-6.7
7	-5	0	-3.0	-1.0
7	-4	0	23.2	23.5
7	-3	0	-2.5	3.1
7	-2	0	-3.5	2.1
7	-1	0	-3.4	1.1
7	0	0	-2.0	-0.6
7	1	0	-2.6	-1.9
7	2	0	16.0	-15.5
7	3	0	20.1	-20.0
7	4	0	-2.5	-3.8
7	5	0	-2.7	-2.5
7	-6	1	15.5	15.9
7	-5	1	10.2	10.3
7	-4	1	7.4	-7.2
7	-3	1	-2.5	-4.3
7	-2	1	-3.5	-2.8
7	-1	1	5.4	5.2
7	0	1	0.0	-1.4
7	1	1	18.8	-18.4
7	2	1	-1.4	-0.4
7	3	1	-3.2	2.2
7	-3	2	7.3	-5.9
7	-2	2	12.1	-12.1
7	-1	2	0.0	1.3
7	0	2	15.0	14.2
8	-1	-6	17.5	17.9
8	0	-6	8.3	9.2
8	1	-6	-1.7	-1.9
8	2	-6	15.5	16.3
8	3	-6	6.8	6.8
8	-3	-5	15.4	15.8
8	-2	-5	7.7	7.9
8	-1	-5	14.1	14.7
8	0	-5	16.9	17.1
8	1	-5	-2.5	-3.6
8	2	-5	9.5	9.6
8	3	-5	-2.3	0.9

H	K	L	FO	FC
8	4	-5	10.4	-10.2
8	5	-5	-3.0	-0.8
8	-5	-4	19.5	19.7
8	-4	-4	5.0	-4.1
8	-3	-4	7.9	7.7
8	-2	-4	13.1	12.9
8	-1	-4	12.5	12.1
8	0	-4	-3.3	2.8
8	1	-4	13.4	-12.9
8	2	-4	0.0	0.3
8	3	-4	15.8	15.5
8	4	-4	0.0	3.9
8	5	-4	-0.6	-0.5
8	6	-4	0.0	-0.1
8	-6	-3	13.6	13.7
8	-5	-3	19.3	18.9
8	-4	-3	8.4	7.5
8	-3	-3	9.5	-9.2
8	-2	-3	-3.2	-2.8
8	-1	-3	-3.9	4.3
8	0	-3	-3.6	4.5
8	1	-3	7.2	6.9
8	2	-3	6.5	5.8
8	3	-3	17.6	17.7
8	4	-3	11.8	11.2
8	5	-3	-1.4	-2.1
8	6	-3	-4.2	4.9
8	-6	-2	14.3	13.9
8	-5	-2	10.0	-10.1
8	-4	-2	0.0	-0.1
8	-3	-2	0.0	3.4
8	-2	-2	20.1	20.2
8	-1	-2	11.2	10.5
8	0	-2	12.7	-13.0
8	1	-2	14.4	14.2
8	2	-2	20.1	19.6
8	3	-2	12.4	12.3
8	4	-2	-4.6	4.3
8	5	-2	17.3	-17.0
8	-5	-1	-4.3	5.0
8	-4	-1	9.1	8.5
8	-3	-1	-4.0	3.3
8	-2	-1	10.9	11.5
8	-1	-1	25.8	25.5
8	0	-1	-2.8	-2.0
8	1	-1	-2.2	-1.7
8	2	-1	-3.8	3.8
8	3	-1	5.0	-3.7
8	4	-1	-1.2	1.6
8	-4	0	5.5	6.5
8	-3	0	18.4	18.1
8	-2	0	7.7	7.8
8	-1	0	-2.2	-1.8
8	0	0	-3.4	-3.2
8	1	0	-4.0	-4.1
8	2	0	5.8	5.8
9	-1	-4	0.0	0.7
9	0	-4	-2.9	-3.0
9	1	-4	6.7	6.5
9	-2	-3	5.2	-4.7
9	-1	-3	-1.3	-0.4
9	0	-3	0.0	1.4
9	1	-3	17.3	17.2
9	2	-3	25.1	25.2
9	-1	-2	10.3	9.8
9	0	-2	5.2	4.7

CHAPTER 4

The Crystal Structure of $P_3N_3F_5$-N-S_3N_2

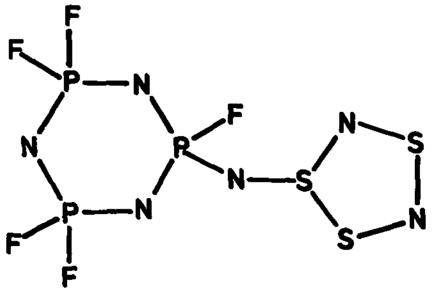
4.1 Introduction.

The $[S_3N_2]_2^{2+}$ cation, as just described, may be considered to consist of two S_3N_2 rings, each containing a 6π system, held together by a four-centre two electron interaction. From this it follows that if the cation $S_3N_2^{2+}$ could be prepared then it would exist as a monomeric planar five-membered ring. On completion of the previous work a report was received of the preparation of various compounds containing the $S_3N_2^{2+}$ cation (Roesky and Dielt, 1973). These were prepared by the action of halosulphuric acids on $S_3N_2Cl_2$ which gave monosubstituted and disubstituted derivatives of the form S_3N_2ClX and $S_3N_2X_2$ where X = SO_3Cl^-, $SO_3F^-$and $SO_3CF_3^-$. These compounds were characterised by elemental analysis and by their infrared spectra, which showed that the $S_3N_2Cl^+$ cation was present in the monosubstituted products and that the S_3N_2 ring was retained in the disubstituted products. An attempt was made to obtain a crystalline derivative (Roesky, 1973) but this work only produced fine powders which could not be recrystallised. A related compound however, $P_3N_3F_5$-N-S_3N_2 was prepared in crystalline form, and was held to contain the same S_3N_2 ring as in the $S_3N_2^{2+}$ derivatives from comparison of their infrared spectra. It was obviously not ionic in nature since the material was soluble in normal organic solvents such as methylene chloride and could also be sublimed.

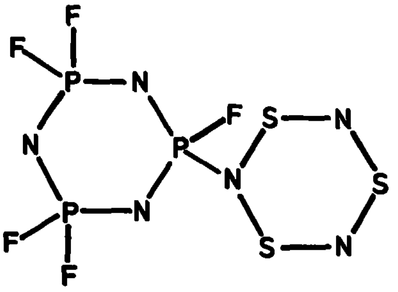
This compound was prepared by the reaction

$$P_3N_3F_5N[Sn(CH_3)_3]_2 + S_3N_2Cl_2 \rightarrow P_3N_3F_5\text{-}N\text{-}S_3N_2 + 2(CH_3)_3SnCl$$

(Roesky and Janβen, 1974). From the infrared spectrum the most likely structure was thought to be (I), although the possibility that it could be II could not be excluded.



I



II

This compound was of interest because it represented a new exocyclic group for sulphur-nitrogen ring systems.

4.2 Crystal data.

The crystals were obtained by sublimation, as well formed . yellow prisms, elongated along c and showing prominent {100} and {010} faces. The crystal used for data collection had dimensions 0.5 x 0.3 x 0.3mm and was sealed in a quartz tube.

Preliminary work using precession and Weissenberg methods showed the unit cell to be orthorhombic and that the conditions limiting reflections were

0 k 1	k = 2n
h 0 1	1 = 2n
h k 0	h = 2n

These uniquely define the space group as Pbca (No. 61). Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections as measured on a four-circle diffractometer.

$P_3N_3F_6$-N-S_3N_2

M = 368.13

a = 15.915(3)Å

b = 14.641(3)Å

c = 6.700(3)Å

U = 2260.2 Å^3

Z = 8

Dm = 2.09g cm^{-3}(by floatation in CH_3I/C_2H_5I)

Dc = 2.16g cm^{-3}

Absorption coefficient for MoKα radiation ($\lambda = 0.7107$Å) = 11.1cm^{-1}.

4.3 Data Collection and Correction.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer using Zr-filtered MoKα radiation. A $2\theta - \omega$ scan technique was used consisting of 80 steps of 0.01° at two seconds per step. The background was measured for 40 seconds at the beginning and end of each scan. Three standard reflections were measured every 40 reflections and showed no systematic changes, indicating that the crystal was stable throughout the experiment. These were used to place the intensities on a common scale. A quarter of the sphere of reflection was measured for $0 < \theta \leq 25°$, giving two equivalent sets of reflections which were averaged if the difference between them was not significant. A total of 1993 independent reflections was recorded; 1528 of these were considered observed having net counts > 2.5 esd's.. The intensities were corrected for Lorentz and polarisation effects, but no corrections were made for absorption.

4.4 Solution and Refinement.

The structure was solved by symbolic addition procedures using a multisolution program (Long, 1968). A set of normalised structure factors were calculated and signs were given to 230 of these with $E > 1.62$. The program initially chose three reflections which were arbitrarily given positive signs and hence defined the origin. A further four reflections were chosen, the signs of which were varied systematically so that each of the sixteen possible combinations was used together with the origin determining reflections as a starting set for the symbolic addition procedure. These reflections together with a summary of the results are shown in table 4.1.

The most self-consistent set corresponds to set 1 which has a consistency index of 0.84. Two other sets have a high consistency index, namely sets 9 and 14 each with a value of 0.79. In set 9 there is a change in sign of one member of the starting set which makes it equivalent to set 1 and in set 14 a change in sign of one of the origin determining planes makes this starting set equivalent to the first by changing the origin.

Table 4.1 $P_3N_3F_5-N-S_3N_2$

The initial reflections used in the Symbolic Addition Procedure.

Origin determing reflections			|E|
4	3	1	2.59
2	6	7	2.84
11	0	4	3.20

Reflections whose signs were varied			|E|
10	1	1	2.56
12	1	1	2.87
8	2	7	2.90
4	1	2	2.10

Results for Symbolic Addition Procedure.

Set No.	Signs	Changes	Cycles	No +	No -	Consistency Index
1	+ + + +		5	130	100	0.837
2	+ + + -		6	113	117	0.534
3	+ + - +	*	16	113	117	0.358
4	+ + - -		9	120	110	0.483
5	+ - + +		16	113	117	0.369
6	+ - + -		8	119	111	0.483
7	+ - - +	- - - +	16	116	114	0.353
8	+ - - -	*	16	115	115	0.369
9	- + + +	+ + + +	7	130	100	0.794
10	- + + -	+ + + -	16	104	126	0.500
11	- + - +		8	119	111	0.414
12	- + - -		16	117	113	0.506
13	- - + +	*	9	116	114	0.491
14	- - + -	*	7	106	124	0.794
15	- - - +		16	110	120	0.542
16	- - - -		8	107	123	0.414

* A sign change occurred for one of the origin determining planes.

An E-map was calculated using the phases estimated from set 1, and revealed the correct positions of all atoms except F(2) and N(3), which were positioned incorrectly due to spurious peaks. In the E-map the heights of the peaks due to the heavier atoms ranged from 3.2 - 5.6 e.$Å^{-3}$, the lighter atoms from 0.9 - 1.1 e.$Å^{-3}$, and with a background fluctuation of $\pm$ 1e.$Å^{-3}$.

All of these atoms were included in two cycles of least squares refinement using the block-diagonal approximation, at the end of which the R value was 0.26. Initially the atoms were given isotropic temperature factors of 3.0$Å^2$ but during the refinement the temperature factors for the atoms taken as F(2) and N(3) increased to about 10$Å^2$ indicating that they had been incorrectly positioned. A difference sysnthesis revealed two peaks of height 5.0e.$Å^{-3}$ and 4.5e.$Å^{-3}$ corresponding to the correct positions for F(2) and N(3). These were included in the subsequent refinement, during which all atoms were refined with anisotropic thermal parameters; after this R fell to 0.045. Further refinement using full matrix least squares methods saw R converge to its final value of 0.0367. The parameter shifts in the last cycle were all $< 0.3\sigma$. A difference synthesis calculated from the final structure factors showed no peaks greater than 0.3e.$Å^{-3}$ and these were associated with the heavier atom positions.

The weighting scheme used in the initial stages of refinement was the same as used previously except that $P_1 = 20.0$ and $P_2 = 0.1$. This was replaced in the final stages of refinement by one based on counting statistics as described earlier. The optimum value for P was 0.06 as determined by an even distribution of $w\Delta^2$ as a function of $|F_o|$. The unobserved reflections were not included in the refinement.

Table 4.2 $P_3N_3F_5$-N-S_3N_2

Least Squares Totals

$\Sigma|Fo|$	$\Sigma|Fc|$	$\Sigma|\Delta|$	R
46932.68	46716.14	1722.88	0.0367

Weighting Analysis

$|Fo|$ Ranges	N	$\Sigma\, w\Delta^2/N$	R
0 - 10	257	0.53	0.152
10 - 20	477	0.45	0.057
20 - 30	257	0.42	0.033
30 - 40	177	0.44	0.029
40 - 50	111	0.32	0.024
50 - 100	194	0.30	0.022
100 - Upwards	54	0.37	0.028

Table 4.3 $P_3N_3F_5\text{-}N\text{-}S_3N_2$

Final Atomic Coordinates with their Estimated Standard Deviations (x 10^5) and their Isotropic Temperature Factors ($Å^2$)†

Atom	x/a	y/b	z/c	B
S(1)	0.08047 (7)	-0.14147 (8)	0.37507 (13)	4.67
S(2)	0.06783 (8)	-0.11637(10)	0.09886 (13)	5.05
S(3)	-0.02359 (6)	-0.04711 (7)	0.32020 (11)	3.63
P(1)	0.07479 (6)	0.11573 (7)	0.29691 (10)	3.16
P(2)	0.24404 (7)	0.08205 (8)	0.29268 (12)	4.01
P(3)	0.18279 (7)	0.21593 (8)	0.45582 (12)	4.14
F(1)	0.03595(16)	0.16244(18)	0.16970 (26)	4.97
F(2)	0.28642(19)	-0.00430(21)	0.34375 (39)	6.75
F(3)	0.30111(17)	0.09890(22)	0.16969 (32)	6.09
F(4)	0.20141(19)	0.31696(20)	0.43801 (36)	6.28
F(5)	0.18409(19)	0.21258(23)	0.61292 (27)	6.28
N(1)	0.11828(23)	-0.15593(26)	0.22052 (39)	4.66
N(2)	0.01408(22)	-0.06874(27)	0.15428 (38)	4.40
N(3)	0.00009(19)	0.05327(23)	0.35541 (35)	3.63
N(4)	0.15333(20)	0.06055(24)	0.24230 (35)	3.82
N(5)	0.25852(21)	0.15912(27)	0.40100 (39)	4.92
N(6)	0.09305(21)	0.19472(22)	0.40413 (37)	3.79

† The temperature factors from the last cycle of Isotropic Refinement.

Table 4.4 $P_3N_3F_5$-N-S_3N_2

Final values of Anisotropic thermal Parameters and their Estimated Standard Deviations (Both $Å^2$ x 10^5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	5861 (67)	5745 (66)	6549 (75)	790 (55)	-48 (56)	702 (55)
S(2)	6099 (73)	8761 (93)	5593 (69)	-2235 (64)	-305 (56)	702 (63)
S(3)	3352 (48)	5415 (61)	5400 (59)	- 145 (48)	329 (43)	-463 (43)
P(1)	3552 (48)	4525 (54)	4168 (53)	290 (44)	84 (40)	297 (41)
P(2)	3807 (53)	6004 (68)	6239 (70)	565 (56)	781 (48)	847 (49)
P(3)	5109 (60)	5695 (66)	5331 (65)	- 514 (53)	-119 (50)	-693 (52)
F(1)	6366(154)	7597(181)	5603(144)	2030(130)	-1157(131)	31(136)
F(2)	7336(188)	7411(194)	13371(284)	1806(195)	-628(191)	2989(166)
F(3)	4542(144)	11903(261)	8078(189)	- 300(176)	2880(138)	-162(141)
F(4)	8354(203)	5750(162)	10825(236)	- 773(157)	- 57(183)	-2114(147)
F(5)	8425(198)	10584(240)	5293(158)	-1492(152)	-810(149)	-621(167)
N(1)	5830(215)	5974(222)	7113(257)	-1381(190)	355(193)	1017(186)
N(2)	4971(197)	7483(248)	5535(217)	- 961(188)	-983(166)	80(189)
N(3)	3769(166)	5103(195)	5489(207)	142(159)	954(143)	121(147)
N(4)	4047(164)	5414(192)	5463(194)	- 806(163)	1089(150)	0(153)
N(5)	4169(184)	7585(251)	6719(230)	- 484(195)	429(176)	-239(180)
N(6)	4312(173)	5048(200)	6233(218)	-1092(166)	508(164)	250(151)

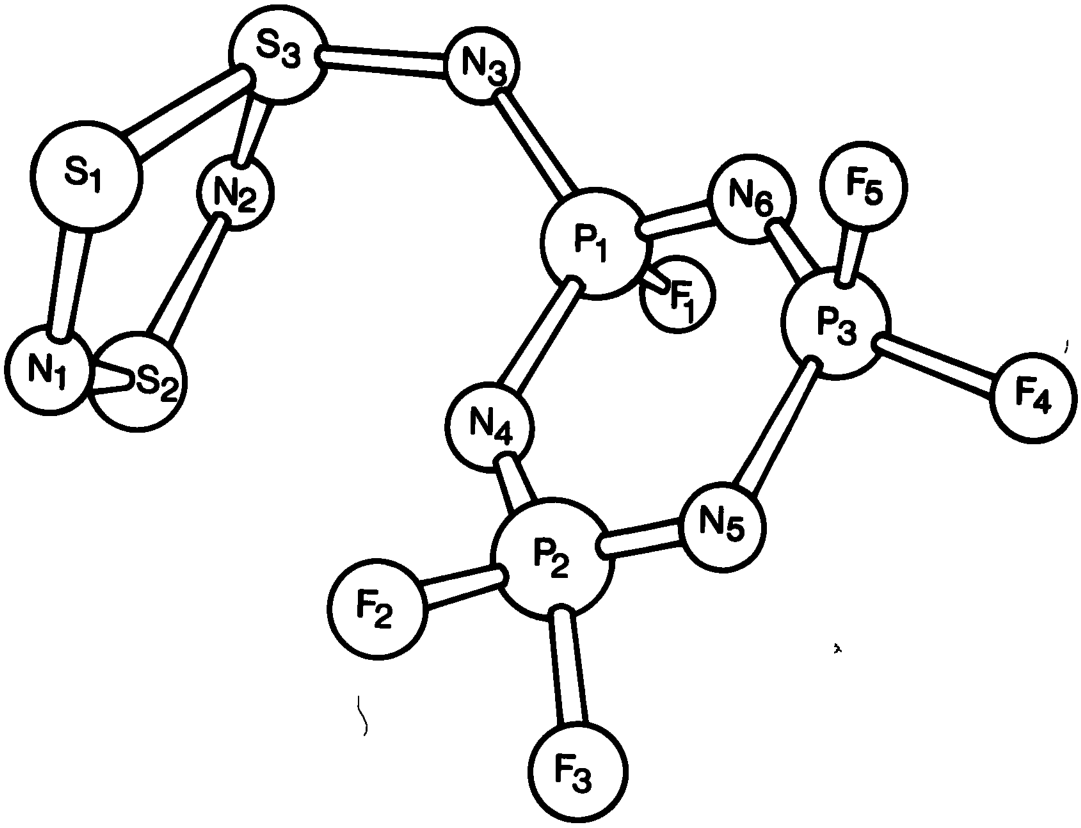
The final least squares totals and weighting analysis are given in table 4.2. The final atomic coordinates and anisotropic thermal parameters are given in tables 4.3 and 4.4. The sulphur and phosphorus atoms were corrected for anomolous dispersion; these correction factors were taken from International Tables Vol. III as were the scattering factors for all atom except fluorine which were those calculated by Freeman (1959). The final calculated and observed structure factors are given in table 4.10.

4.5 The Structure and Bonding in $P_3N_3F_5$-N-S_3N_2.

The molecule consists of a six-membered phosphonitrilic ring bonded through a bridging nitrogen to a five-membered S_3N_2 ring, as shown in figure 4.1, with an angle of 57.0° between the mean planes of these rings. The bond distances and angles are given in tables 4.5 and 4.7. The molecule may be discussed in terms of the phosphonitrilic ring and the N-S_3N_2 fragment.

4.5.a Structure and Bonding in -N-S_3N_2.

This part of the molecule is directly analogous to $S_3N_2Cl^+$ in which formally $\overset{+}{S}$-Cl is replaced by S=N-. The bonding across the bridging nitrogen involves substantial multiple bonding since the S-N and P-N distances are considerably shorter than the corresponding single bond. The S(3) - N(3) bond distance of 1.555Å is very short and approaches the length of an S-N double bond, for example 1.54Å in $S_4N_4F_4$ (Weigers and Vos, 1963) or 1.550Å in R-S-N=S=N-S-R, where R = p-C_6H_4Cl (Olsen and Barrick, 1973). The P(1) - N(3) distance of 1.603Å is also short compared to the P-N single bond distance of 1.77Å



$P_3N_3F_5{-}N{-}S_3N_2$

Figure 4.1

Table 4.5 $P_3N_3F_5$-N-S_3N_2

Final Bond Distances (Å) and their Estimated Standard Deviations (Å x 10^3).

S(1) - S(3)	2.221(2)
S(1) - N(1)	1.629(4)
S(2) - N(1)	1.540(4)
S(2) - N(2)	1.572(4)
S(3) - N(2)	1.647(4)
S(3) - N(3)	1.555(4)
P(1) - N(3)	1.603(3)
P(1) - N(4)	1.579(3)
P(1) - N(6)	1.582(4)
P(2) - N(4)	1.555(3)
P(2) - N(5)	1.559(4)
P(3) - N(5)	1.557(4)
P(3) - N(6)	1.544(4)
P(1) - F(1)	1.540(3)
P(2) - F(2)	1.516(3)
P(2) - F(3)	1.519(3)
P(3) - F(4)	1.518(3)
P(3) - F(5)	1.525(3)

Table 4.6 $P_3N_3F_5$-N-S_3N_2

Some Mean Planes

$$-0.6182X - 0.7844Y - 0.0512Z - 0.6296 = 0$$

Atom	S(1)	S(2)	S(3)	N(1)	N(2)	N(3)†
P	0.018	-0.009	-0.016	-0.111	0.222	-1.419
σ(P)	0.001	0.001	0.001	0.004	0.004	0.003

$$-0.4978X - 0.8635Y - 0.0810Z - 0.8569 = 0$$

Atom	S(1)	S(2)	S(3)†	N(1)	N(2)	N(3)†
P	-0.0003	-0.0006	-0.326	0.005	0.002	-1.810
σ(P)	0.0012	0.0014	0.001	0.004	0.004	0.003

$$0.1098X + 0.6564Y - 0.7464Z + 0.9056 = 0$$

Atom	P(1)	P(2)	P(3)	N(4)	N(5)	N(6)
P	-0.001	0.002	0.000	0.001	-0.017	0.014
σ(P)	0.001	0.001	0.001	0.004	0.004	0.004

$$0.1157X + 0.6577Y - 0.7443Z + 0.8755 = 0$$

Atom	P(1)†	P(2)	P(3)	N(4)	N(5)	N(6)
P	-0.016	0.002	0.000	-0.009	-0.012	0.004
σ(P)	0.001	0.001	0.001	0.003	0.004	0.003

Where P and σ(P) represent the distance and its e.s.d. of an atom from the mean plane

X, Y and Z refer to orthogonal coordinates in Å whose directions lie along $\underline{a}$, $\underline{b}$ and $\underline{c}$.

† this atom was not included in calculation of the mean plane.

Table 4.7 $P_3N_3F_5$-N-S_3N_2

Final Bond Angles (degrees) with their Estimated Standard Deviations (deg. x 10^2)

S(3) - S(1) - N(1)	97.78(15)
N(1) - S(2) - N(2)	109.66(21)
S(1) - S(3) - N(2)	92.65(14)
S(1) - S(3) - N(3)	110.78(14)
N(2) - S(3) - N(3)	111.97(19)
N(3) - P(1) - N(4)	114.40(18)
N(3) - P(1) - N(6)	108.69(18)
N(4) - P(1) - N(6)	116.69(18)
N(3) - P(1) - F(1)	103.86(16)
N(4) - P(1) - F(1)	106.00(17)
N(6) - P(1) - F(1)	106.01(17)
N(4) - P(2) - N(5)	119.68(20)
N(4) - P(2) - F(2)	110.27(19)
N(4) - P(2) - F(3)	109.90(18)
N(5) - P(2) - F(2)	108.52(20)
N(5) - P(2) - F(3)	108.87(19)
F(2) - P(2) - F(3)	97.26(18)
N(5) - P(3) - N(6)	119.77(20)
N(5) - P(3) - F(4)	109.31(19)
N(5) - P(3) - F(5)	108.27(19)
N(6) - P(3) - F(4)	109.84(19)
N(6) - P(3) - F(5)	109.30(19)
F(4) - P(3) - F(5)	98.18(18)
S(1) - N(1) - S(2)	117.64(24)
S(2) - N(2) - S(3)	119.69(24)
S(3) - N(3) - P(1)	129.86(22)
P(1) - N(4) - P(2)	121.65(22)
P(2) - N(5) - P(3)	120.16(24)
P(1) - N(6) - P(3)	122.01(22)

in $NH_3PO_3^-$ (Cruickshank, 1964a)and approaches the P(1) - N(4) and P(1) - N(6) ring distances of 1.579Å and 1.582Å. As with S-N bonds, the P-N single bond distance varies with the electronegativity of its ligands and also with the hybridisation, so that the shortness will in part be due to the fluorine and nitrogen atoms attached to P(1). In addition the angle at N(3) is 129.9°, which indicates essentially sp^2 hybridisation at this nitrogen. The increase in this angle may be a steric requirement since its decrease would result in short contacts between the two parts of the molecule, (table 4.8.) The shortness of these bonds and the size of the angle at nitrogen suggest that there is substantial multiple bonding in both bridge bonds.

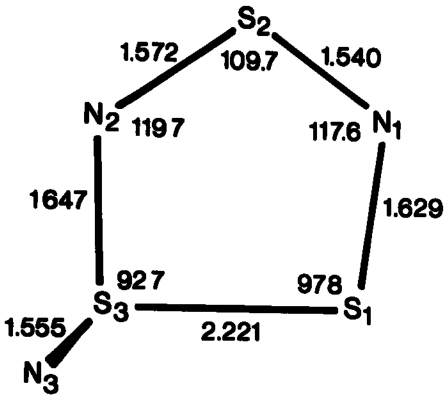
The S_3N_2 ring is not planar; S(3) which carries the exocyclic nitrogen lies 0.33Å above the mean plane of the remaining ring atoms. For these atoms the maximum deviation from their mean plane is 0.005Å as given in table 4.6. The S-N bond lengths within the ring are all shorter than the normal S-N single bond distance of 1.73Å as seen in S_7NH (Weiss and Neubert, 1965) and indicate substantial multiple bonding around the ring. The S(2) - N(1) bond distance of 1.540Å is particularly short and is the length normally associated with S-N double bonds eg. 1.54Å in $S_4N_4F_4$. The S(1) - S(3) distance of 2.221Å is similar to that of 2.066Å in $S_4N_3^+$ or 2.136Å in $S_3N_2Cl^+$, although as noted in section 3.5.b, the length of S-S bonds depends markedly on the hybridisation; so that it is not possible to estimate bond orders from bond lengths alone.

4.5.b A Comparison of the Structures of $(S_3N_2)_2^{2+}$, $N-S_3N_2$, and $S_3N_2Cl^+$.

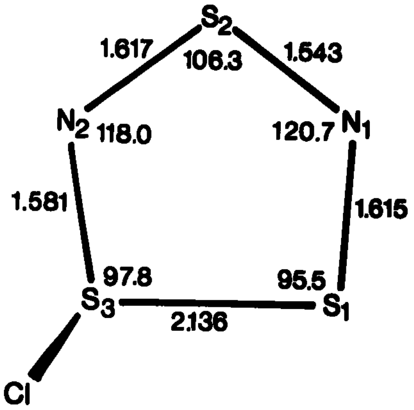
The bonding in $N-S_3N_2$ may be discussed by comparison with the analogous $S_3N_2Cl^+$ ion, but the structure of $[S_3N_2]_2^{2+}$ has just been described in chapter 3, and it is meaningful to correlate the structures of all three. The dimensions of these three compounds are shown in figure 4.2. This task is not simple since it is impossible to describe the bonding in any one of these compounds without resorting to molecular orbital calculations, but it is possible to make several qualitative observations.

The dimensions of these three rings are all very similar, since the maximum difference between corresponding bond lengths in any of these rings is less than 0.09Å. Likewise the bond angles in the rings are very similar, particularly those at nitrogen which are all close to 120°. Angles of 120° or greater at nitrogen are a characteristic feature of π-bonded sulphur-nitrogen compounds since nitrogen requires sp^2 hybridisation in order to participate effectively in the π-system, whereas for sulphur the π-bonding is less dependent on angle because of the larger number of orbitals available.

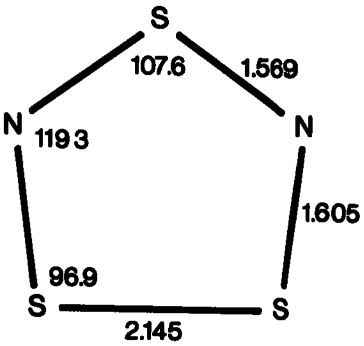
Calculations have shown that $S_3N_2Cl^+$ contains a pseudo 6π system (Adams et al., 1971) where the term pseudo refers to the lack of planarity of the S_3N_2 ring. In view of the similarities between these three ring compounds it is reasonable to conclude that $[S_3N_2]_2^{2+}$ and $-N-S_3N_2$ contain 6π systems. These calculations also suggested that the majority of the positive charge in $S_3N_2Cl^+$, i.e. + 0.76e. resides on the apical sulphur, whereas they suggest that there is only a charge of + 0.12e. on the sulphur attached to chlorine and + 0.24e. on the remaining sulphur. By comparison the charge distribution in the



$N-S_3N_2$



$S_3N_2Cl^+$



$[S_3N_2]_2^{2+}$

Figure 4.2

S_3N_2 rings of $[S_3N_2]_2^{2+}$ is expected to be more even. This is shown by the smaller variation in the mean S-N distances of 1.569 - 1.605Å as compared to 1.543 - 1.617Å in $S_3N_2Cl^+$. In comparing these compounds it is convenient to consider the effects produced by attaching a chlorine or nitrogen atom to the S_3N_2 ring in $[S_3N_2]_2^{2+}$.

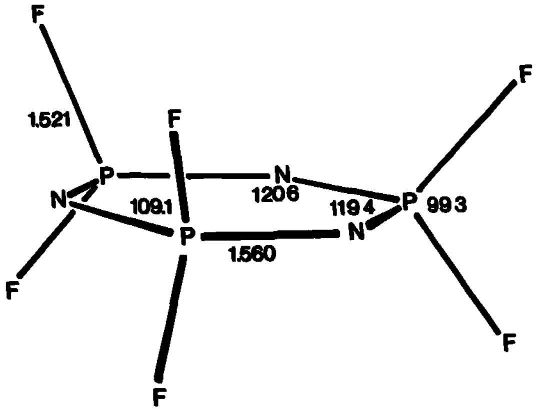
It is reasonable to suggest that the S-Cl bond in $S_3N_2Cl^+$ is essentially a single bond so that since most of the positive charge does not reside on S(3), this sulphur must be involved in the multiple bonding to S(1) and N(2). Compared to $[S_3N_2]_2^{2+}$, the attachment of a chlorine atom produces a decrease in the S(3) - N(2) bond distance which is presumably due to the contraction of the orbitals on S(3) by the electronegative chlorine atom. This change does not appear to affect the S-S bond distance significantly. Conversely because N(2) is more involved in the π-bonding with S(3) there is an increase in the S(2) - N(2) distance to 1.617Å and a decrease in the S(2) - N(1) distance to 1.543Å compared to the mean of 1.569Å in $[S_3N_2]_2^{2+}$.

The attachment of a nitrogen atom to the S_3N_2 ring formally removes the positive charge, and results in a larger variation in the S-N bond lengths i.e. 1.540 - 1.647Å. The length of the S(3) - N(3) bond external to the ring shows that there is considerable multiple bonding in this bond, and so S(3) is not able to participate as effectively in the π-bonding of the S_3N_2 ring. This accounts for the increase in the S(3) - N(2) bond from 1.605Å in $[S_3N_2]_2^{2+}$ to 1.647Å and the increase in the S-S distance from 2.145Å to 2.221Å. From the foregoing discussion it would be expected that removal of the positive charge would result in an increase in all the S-N distances in the ring, because the sulphur atoms will carry less positive charge and hence the orbitals should be less contracted. However both S(2) - N(1) and S(2) - N(2) are still very short i.e. 1.540Å and 1.572Å compared to 1.569Å in $[S_3N_2]_2^{2+}$, and suggest that the bonding across N(1) - S(2) - N(2) is approaching that of a sulphur diimide. Strong π-bonding is possible in this part of the ring because S(2) is attached to two nitrogen atoms which contract its orbitals. Conversely the orbitals on S(1) are contracted by only one nitrogen and more affected by the loss of the positive charge, resulting in an increase in the S(1) - N(1) distance to 1.629Å. Further confirmation that S(3) is less involved in the π-bonding in the S_3N_2 ring is shown by S(3) being further from the mean plane of the other ring atoms than S(3) in $S_3N_2Cl^+$ i.e. 0.33Å as compared to 0.24Å, (Shearer, 1972).

4.5.c The Structure and Bonding in $P_3N_3F_5$-

This part of the molecule as shown in figure 4.4 is a derivative of $P_3N_3F_6$ in which one fluorine has been replaced by a nitrogen. The most interesting aspects of this part are the changes in the structure caused by this substitution. The parent molecule, $P_3N_3F_6$ shows 3mm symmetry within experimental error and its dimensions are shown in figure 4.3.

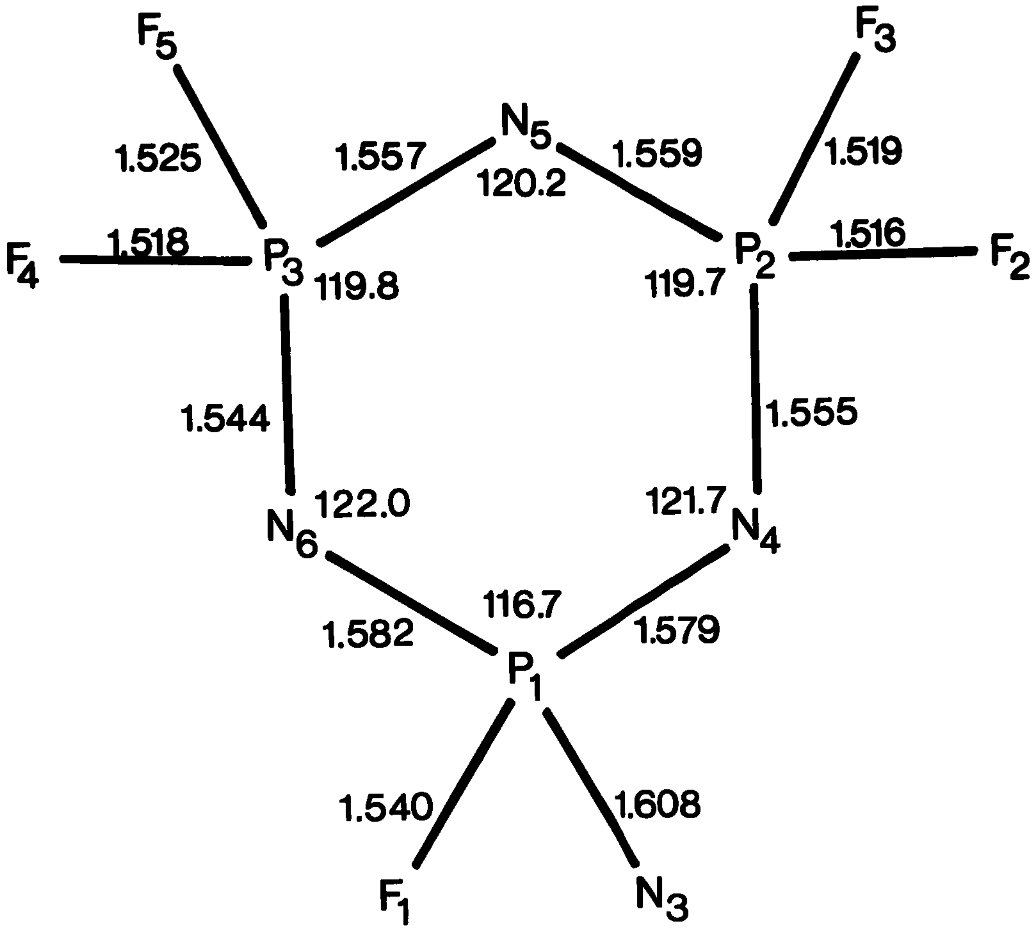
Substitution of a fluorine by nitrogen causes a loss of the planarity in the P_3N_3 ring. The mean planes given in table 4.6 show that the atoms in the P_3N_3 ring deviate from their mean plane by as much as 0.017Å. Removal of P(1) from the calculation shows that the remaining ring atoms are coplanar to within 0.012Å.



$P_3N_3F_6$

Figure 4.3

The bond distances may be considered in two parts, those involving P(1) and those which do not. The P-N distances not involving P(1) are all the same within experimental error, i.e. P(2) - N(4) 1.555(4)Å, P(2) - N(5) 1.559(4)Å, P(3) - N(5) 1.557(4)Å and P(3) - N(6) 1.544(4)Å, and the mean value of 1.553(2)Å does not differ significantly from that of 1.560(6)Å found in $P_3N_3F_6$ (Dougill, 1963). The P-N distances involving P(1) are substantially longer i.e. P(1) - N(4) 1.579(4)Å and P(1) - N(6) 1.582(4)Å. A similar effect is seen in the P-F distances. Except for P(1) - F(1) they are the same within experimental error and their mean of 1.520(2)Å does not differ significantly from the P-F distance of 1.521(5)Å seen in $P_3N_3F_6$; conversely P(1) - F(1) has a bond distance of 1.540(3)Å and is significantly longer. This effect is caused by the smaller electronegativity of nitrogen as compared to fluorine, resulting in less orbital contraction and longer bonds.



$P_3N_3F_5-N$

Figure 4.4

The theories of the bonding in phosphonitrilic compounds have been reviewed extensively (Craig and Paddock, 1971). It is impossible to describe the bonding in phosphonitrilic derivatives without invoking d-orbital participation, since the alternative ionic model which does not require d-orbital participation cannot explain the geometry observed for these compounds. For example the ionic model is not able to explain the angles at nitrogen in these compounds being close to or larger than 120°. The nature of the delocalisation however has been the subject of considerable controversey.

It has been argued that because of the equalisation of bond lengths within the ring and the planarity or near planarity of some of the phosphonitrilic compounds, such as $P_3N_3F_6$, the π-bonding should be viewed in terms of molecular orbitals which encompass the entire ring as in organic aromatic compounds (Craig et al, 1961). An alternative interpretation considers that the π-system should be viewed in terms of P-N-P islands of delocalisation because π molecular orbitals involving d orbitals must have a node at phosphorus. (Dewar, Lucken and Whitehead, 1960). These two theories have been compared (Craig and Mitchell, 1965) and it has been shown that the two theories are capable of explaining most structural features but that cyclic delocalisation is necessary to explain the observed ionisation potentials. It is not easy to estimate the extent of d orbital participation from bond lengths alone because of the variation in the P-N distance with hybridisation. However it has been estimated that $\approx 60\%$ of the shortening of these bonds can be ascribed to π-bonding (Craig and Paddock, 1971).

The most important prerequisite for d-orbital participation in any phosphorus compound is orbital contraction, so that the shortest bond lengths are found when phosphorus is bound to highly electronegative ligands such as fluorine. Thus substitution of a fluorine atom by a less electronegative element or group produces an increase in the associated P-N distances. This is best illustrated by the series: $P_3N_3F_6$, $P_3N_3Cl_6$ and $P_3N_3Ph_6$ which have P-N bond lengths of 1.560Å, 1.583Å and 1.597Å (Craig and Paddock, 1971). In $P_3N_3F_4Ph_2$ the geminal replacement of two fluorine atoms by phenyl groups increases the adjacent P-N distances to 1.618Å (Allen et al., 1969) and as expected this effect is far greater than the replacement of one fluorine atom by a nitrogen atom.

The decrease in π-bonding in the ring with substitution of a less electronegative atom is also reflected in a reduction in the ring angle at that phosphorus. The angle at P(1) is 116.7° as compared to 119.7° at the unsubstituted phosphorus atoms. The angles at the nitrogen atoms adjacent to P(1) are both larger than that at N(5), i.e. P(1) - N(4) - P(2) and P(1) - N(6) - P(3) have values of 121.7° and 122.0° as compared to the value of 120.2° for P(2) - N(5) - P(3). The coordination at P(2) and P(3) is very similar to that seen in $P_3N_3F_6$, the average N-P-F angle of 109.2° being close to the value of 109.1° in $P_3N_3F_6$. The attachment of the bridging nitrogen to P(1) is not symmetrical since the angle N(3) - P(1) - N(4) of 114.4° is substantially greater than N(3) - P(1) - N(6) of 108.7°. This distortion increases the separation between N(4) in the phosphonitrilic ring and the atoms in the S_3N_2 ring (table 4.8). The average N(3) - P - N angle of 111.6° external to the ring is larger than the N-P-F angles at P(2) and P(3) as a consequence of some multiple bonding in the P(1) - N(3) bond.

There are many similarities between the π-bonding in sulphur-nitrogen and phosphorus-nitrogen ring compounds. In both cases contraction of the orbitals is necessary for effective delocalisation. In phosphorus compounds, this is provided by highly electronegative ligands giving rise to $(PNX_2)_n$ species, whereas in sulphur-nitrogen chemistry it is provided both by electronegative ligands, giving rise to $(SNX)_n$ and $(SNOX)_n$ type compounds and also by the presence of positive charges as in $S_4N_3^+$, $S_3N_2Cl^+$ or $S_5N_5^+$.

Table 4.8 $P_3N_3F_5$-N-S_3N_2

Intramolecular Contacts between N(4) and the S_3N_2 ring Å.

S(2) - N(4)	3.239
S(3) - N(4)	3.313
N(1) - N(4)	3.225
N(2) - N(4)	3.377

4.6 Intermolecular Contacts and Packing.

In view of the large number of short contacts seen in $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$ described earlier, it is of interest to see if short contacts occur with this molecule. The van der Waals radii for the atoms in this structure are S = 1.80Å, P = 1.80Å, F = 1.47Å and N = 1.55Å (Bondi, 1964).

Any secondary bonding present will be between sulphur and nitrogen or fluorine, since it is known that in these compounds the sulphur atoms carry a slight positive charge and the nitrogen and fluorine atoms a slight negative charge. The only S---N contacts less than 3.35Å are those of 3.185Å for $S(1)---N(3^{I})$, and 3.170Å for $S(3)---N(3^{I})$ whereas the only S---F contact less than 3.27Å is that of 3.157Å for $S(2)---F(1^{II})$, as given in table 4.9.

Table 4.9 $P_3N_3F_5\text{-}N\text{-}S_3N_2$

Some Intermolecular Contacts < 3.35Å

$S(1) - N(3^{I})$	3.185
$S(2) - F(1^{II})$	3.157
$S(3) - N(3^{I})$	3.170
$F(1) - F(5^{III})$	3.034
$F(2) - F(4^{IV})$	2.779
$F(3) - F(4^{III})$	3.014
$F(4) - F(5^{III})$	3.195

The superscripts refer to the following equivalent positions with reference to the molecule at x, y, z

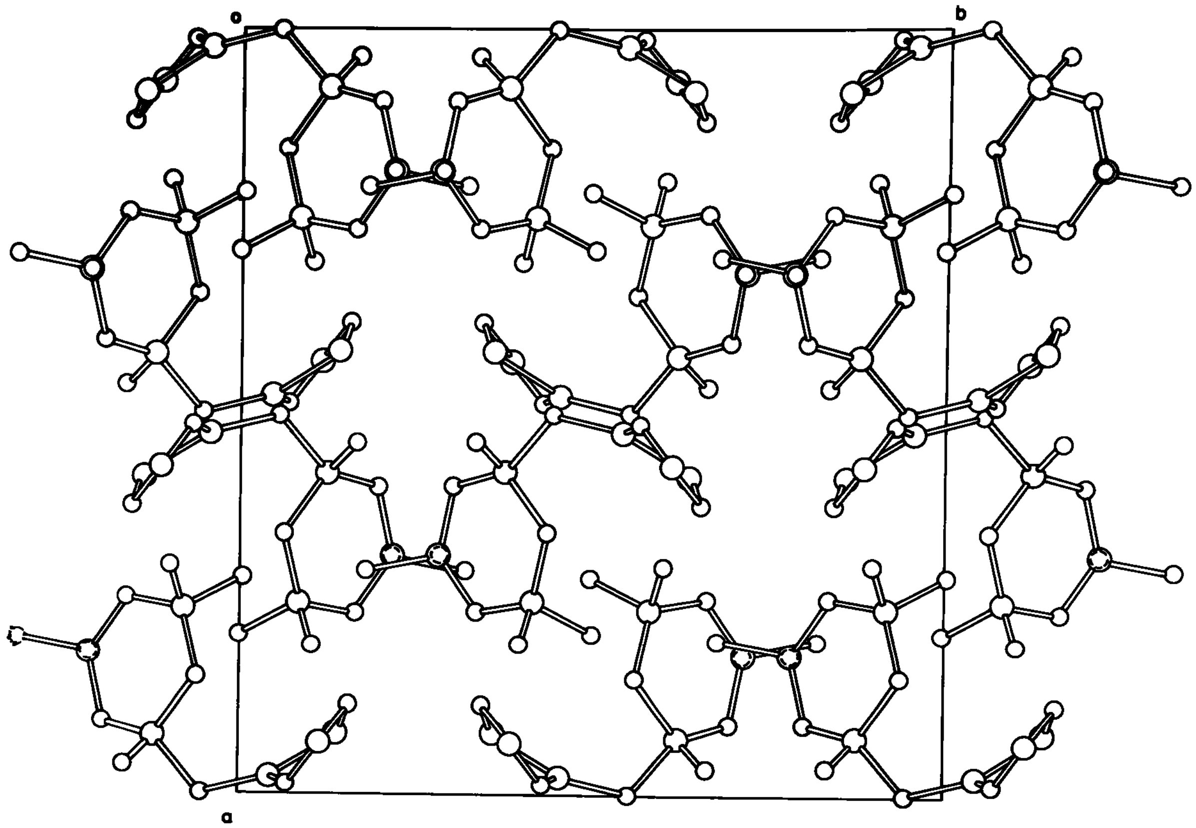
I	$\bar{x}, \bar{y}, 1-z$	III	$x, \frac{1}{2}-y, -\frac{1}{2}-z$
II	$\bar{x}, \bar{y}, \bar{z}$	IV	$\frac{1}{2}-x, -\frac{1}{2}-y, z$

There are no short contacts involving phosphorus because of its fourfold coordination.

In contrast to S---F and S---N contacts, interactions between nitrogen and fluorine are not expected to lower the potential energy of the packing. Consequently, there are no N---F contacts less than

3.02Å and there is only one F---F distance less than 2.94Å namely F(2)---F(4^{IV}) of length 2.779Å thus it is clear that there are no very strong intermolecular contacts involved in the packing of these molecules. This might have been expected because the compound may be sublimed.

A projection on the [001] plane of the contents of the unit cell is shown in figure 4.5.



$P_3N_3F_5$-N-S_3N_2

projection on the [001] plane

Figure 4.5

Table 4.10 $P_3N_3F_5$-N-S_3N_2

Final Calculated and Observed Structure Factors

H	K	L	FO	FC
2	0	0	39.2	40.2
4	0	0	211.2	208.0
6	0	0	93.6	-93.1
8	0	0	121.6	-126.3
10	0	0	50.6	50.3
12	0	0	105.5	107.4
14	0	0	8.5	4.3
16	0	0	38.3	37.8
18	0	0	64.9	-65.0
2	1	0	122.2	-121.5
4	1	0	156.0	159.5
6	1	0	133.4	-130.5
8	1	0	75.9	-76.3
10	1	0	10.6	10.0
12	1	0	69.5	-69.7
14	1	0	15.8	-18.3
16	1	0	7.3	5.9
18	1	0	13.2	-12.5
0	2	0	40.1	40.3
2	2	0	133.1	135.1
4	2	0	193.4	192.9
6	2	0	17.7	12.0
8	2	0	141.7	136.7
10	2	0	35.9	-35.5
12	2	0	-3.1	3.0
14	2	0	30.9	32.4
16	2	0	21.6	-20.6
18	2	0	11.7	-10.8
2	3	0	117.2	121.6
4	3	0	126.1	-128.3
6	3	0	32.3	32.2
8	3	0	89.0	-86.2
10	3	0	113.7	-115.8
12	3	0	29.8	29.0
14	3	0	72.1	-74.8
16	3	0	13.3	-13.9
18	3	0	13.2	-15.0
0	4	0	232.9	-251.1
2	4	0	137.7	-144.8
4	4	0	47.3	46.3
6	4	0	254.6	259.1
8	4	0	52.5	51.4
10	4	0	48.0	49.8
12	4	0	67.7	-69.3
14	4	0	54.7	-55.2
16	4	0	30.2	-31.5
18	4	0	24.6	24.4
2	5	0	158.8	-162.8
4	5	0	30.1	-26.2
6	5	0	34.8	-35.6
8	5	0	22.0	-21.1
10	5	0	24.8	-24.2
12	5	0	18.1	-16.8
14	5	0	52.8	-54.0
16	5	0	-5.1	-7.4
18	5	0	29.8	-30.6
0	6	0	0.0	-11.1
2	6	0	10.0	11.8
4	6	0	53.7	-53.9
6	6	0	40.4	-37.6
8	6	0	30.5	-30.4
10	6	0	34.0	35.4
12	6	0	56.9	-56.5
14	6	0	8.6	7.6
16	6	0	28.7	-29.0
2	7	0	68.4	-68.1
4	7	0	0.0	2.1
6	7	0	94.5	-96.3
8	7	0	39.7	-39.1
10	7	0	47.1	-45.5
12	7	0	42.3	-43.7
14	7	0	-5.9	-5.8
16	7	0	14.2	-14.9
0	8	0	42.4	-39.8
2	8	0	28.3	29.4
4	8	0	94.2	-96.5
6	8	0	125.9	-127.4
8	8	0	101.5	-105.5
10	8	0	8.2	-6.6
12	8	0	13.7	12.5
14	8	0	52.7	53.1
16	8	0	11.1	11.0
2	9	0	80.8	81.2
4	9	0	0.0	-2.8
6	9	0	-5.9	5.9
8	9	0	50.6	-52.2
10	9	0	30.5	-30.3
12	9	0	10.1	-9.8
14	9	0	-6.9	7.1
16	9	0	9.0	-4.2
0	10	0	0.0	1.1
2	10	0	109.8	-112.8
4	10	0	19.2	-18.6
6	10	0	41.4	-44.3
8	10	0	60.3	-61.6
10	10	0	8.9	11.3
12	10	0	-5.6	1.4
14	10	0	-3.5	5.0
2	11	0	41.4	-42.1
4	11	0	0.0	0.6
6	11	0	-5.8	4.6
8	11	0	40.4	42.7
10	11	0	39.9	39.3
12	11	0	7.4	-5.8
14	11	0	-6.7	4.9
0	12	0	51.5	-53.4
2	12	0	74.7	-75.1
4	12	0	32.4	31.2
6	12	0	19.2	-19.8
8	12	0	57.3	56.3
10	12	0	25.8	-28.1
12	12	0	16.7	-15.6
2	13	0	12.8	12.2
4	13	0	35.8	-35.8
6	13	0	10.5	11.3
8	13	0	29.2	28.5
10	13	0	-5.9	6.3
12	13	0	23.2	24.2
0	14	0	21.8	21.2
2	14	0	38.0	-38.5
4	14	0	-1.1	-2.9
6	14	0	7.0	7.2
8	14	0	-5.8	5.9
10	14	0	-3.8	3.6
2	15	0	20.8	21.1
4	15	0	44.9	41.7
6	15	0	-2.8	2.1
8	15	0	-5.3	-4.4
0	16	0	7.2	5.3
2	16	0	22.7	20.1
4	16	0	-4.8	-4.1
6	16	0	10.6	-8.9
2	17	0	12.8	10.2
4	17	0	7.8	7.9
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3	1	1	13.6	-13.8
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6	1	1	111.9	103.8
7	1	1	25.5	-25.1
8	1	1	58.5	59.4
9	1	1	9.6	-9.7
10	1	1	114.3	112.5
11	1	1	46.7	-46.9
12	1	1	95.3	98.5
13	1	1	-4.1	-2.2
14	1	1	-4.5	-6.2
15	1	1	-3.9	7.7
16	1	1	11.3	12.5
17	1	1	12.8	11.9
18	1	1	12.5	-14.2
0	2	1	87.3	-88.0
1	2	1	72.9	74.3
2	2	1	167.5	170.7
3	2	1	20.5	21.8
4	2	1	94.8	-91.4
5	2	1	49.0	47.6
6	2	1	49.3	49.1
7	2	1	23.0	-20.7
8	2	1	15.6	-15.2
9	2	1	10.9	12.6
10	2	1	52.8	51.7
11	2	1	50.6	-51.7
12	2	1	41.7	-43.0
13	2	1	18.6	18.9
14	2	1	8.9	9.8
15	2	1	19.9	-21.0
16	2	1	25.4	-24.6
17	2	1	20.5	19.5
18	2	1	14.5	14.3
1	3	1	12.5	11.8
2	3	1	186.8	193.0
3	3	1	109.5	-110.7
4	3	1	223.0	223.4
5	3	1	43.9	-41.9
6	3	1	73.3	73.3
7	3	1	47.6	-46.9
8	3	1	19.3	-18.7
9	3	1	10.8	-12.5
10	3	1	-1.6	-2.5
11	3	1	60.8	61.1
12	3	1	13.9	14.1
13	3	1	7.8	7.2
14	3	1	25.0	25.3
15	3	1	-5.5	3.2
16	3	1	34.3	34.1
17	3	1	-6.6	-5.2
18	3	1	16.1	16.6
0	4	1	72.3	-72.2
1	4	1	52.1	-50.0
2	4	1	188.2	195.5
3	4	1	42.8	44.9
4	4	1	67.2	69.3
5	4	1	81.9	82.5
6	4	1	92.1	95.7
7	4	1	5.6	-5.5
8	4	1	0.0	-0.4
9	4	1	36.5	36.7
10	4	1	16.3	16.1
11	4	1	-3.8	-1.8
12	4	1	41.7	-41.9
13	4	1	13.0	-14.4
14	4	1	19.3	-21.2
15	4	1	24.6	25.0
16	4	1	38.9	-38.8
17	4	1	-4.5	5.5
18	4	1	7.3	-6.1
1	5	1	57.5	-59.0
2	5	1	80.5	84.4
3	5	1	12.7	13.8
4	5	1	43.3	45.9
5	5	1	19.8	17.6
6	5	1	47.1	47.1
7	5	1	18.8	-18.9
8	5	1	52.4	-52.9
9	5	1	55.4	55.6
10	5	1	34.9	-36.4
11	5	1	42.1	-41.3
12	5	1	60.4	-62.4
13	5	1	13.2	13.7
14	5	1	21.0	21.9
15	5	1	-6.1	2.9
16	5	1	13.4	13.8
17	5	1	14.3	-15.5
18	5	1	21.0	21.5
0	6	1	33.9	35.3
1	6	1	60.1	63.9
2	6	1	15.8	17.1
3	6	1	-2.0	-2.3
4	6	1	89.0	88.1
5	6	1	50.4	-49.1
6	6	1	23.1	24.5
7	6	1	55.9	56.1
8	6	1	6.4	-6.2
9	6	1	25.1	-25.7
10	6	1	-4.9	5.4
11	6	1	35.7	37.0
12	6	1	16.7	-17.9
13	6	1	50.1	51.2
14	6	1	7.6	-7.9
15	6	1	-4.0	-6.2
16	6	1	12.4	-12.8
17	6	1	-5.3	4.8
1	7	1	42.9	42.7
2	7	1	61.3	-61.8
3	7	1	63.1	-66.0
4	7	1	120.9	-121.5
5	7	1	94.9	97.7
6	7	1	23.7	-23.5
7	7	1	0.0	-1.5
8	7	1	14.9	-14.6
9	7	1	10.9	-9.8
10	7	1	21.3	19.0
11	7	1	11.9	12.2
12	7	1	27.2	-27.8
13	7	1	29.6	-30.1
14	7	1	-5.5	-1.4
15	7	1	9.3	-9.1
16	7	1	35.4	-35.1
17	7	1	19.0	17.7
0	8	1	116.4	119.0
1	8	1	74.6	-78.2
2	8	1	23.3	-22.7
3	8	1	35.3	-33.9
4	8	1	7.0	8.4
5	8	1	-2.0	-1.3
6	8	1	57.3	-57.4
7	8	1	30.0	-31.3
8	8	1	-5.5	4.7
9	8	1	59.3	61.5
10	8	1	0.0	-0.4
11	8	1	31.0	31.2
12	8	1	21.7	22.7
13	8	1	12.5	-11.6
14	8	1	11.9	-10.4
15	8	1	14.5	13.2
16	8	1	7.3	7.4
1	9	1	5.6	2.6
2	9	1	14.7	-14.8
3	9	1	74.3	75.9
4	9	1	80.9	-82.8
5	9	1	36.2	-37.2
6	9	1	31.1	-31.3
7	9	1	-4.4	6.5
8	9	1	-4.6	-4.7
9	9	1	19.3	18.3
10	9	1	25.5	26.6
11	9	1	25.3	-24.2
12	9	1	7.8	-8.9
13	9	1	22.3	22.5
14	9	1	19.7	-19.7
15	9	1	-4.8	5.2
16	9	1	26.6	-26.5
0	10	1	43.3	43.0
1	10	1	38.8	40.9
2	10	1	28.6	-28.4
3	10	1	14.1	12.6
4	10	1	40.6	40.4
5	10	1	11.3	-10.4
6	10	1	23.8	-24.2
7	10	1	64.4	63.0
8	10	1	34.8	33.9
9	10	1	29.8	-30.1
10	10	1	35.7	-36.8
11	10	1	-6.2	5.0
12	10	1	-5.2	6.4
13	10	1	0.0	-3.9
14	10	1	20.8	-19.8
15	10	1	10.2	-7.6
1	11	1	48.9	49.7
2	11	1	31.0	31.6
3	11	1	17.5	-15.5
4	11	1	16.9	-16.5
5	11	1	35.4	34.9
6	11	1	8.4	-7.8
7	11	1	13.2	-13.7
8	11	1	37.1	-37.9
9	11	1	7.1	-3.2
10	11	1	42.1	-40.8
11	11	1	25.9	24.4
12	11	1	17.6	-17.2
13	11	1	0.0	-0.5
14	11	1	15.6	-15.9
0	12	1	32.8	-31.8
1	12	1	14.0	-12.2
2	12	1	39.2	-40.5
3	12	1	53.6	54.2
4	12	1	12.7	13.6
5	12	1	26.2	25.4
6	12	1	29.1	28.6
7	12	1	23.7	-22.2
8	12	1	16.1	14.7
9	12	1	14.9	-14.3
10	12	1	14.3	-14.2
11	12	1	19.1	-19.6
12	12	1	9.4	-10.0
13	12	1	6.9	-3.5
1	13	1	-3.8	5.5
2	13	1	-5.9	7.2
3	13	1	17.5	17.2
4	13	1	17.7	17.9
5	13	1	-1.1	2.1
6	13	1	-4.6	-3.6
7	13	1	13.2	13.3
8	13	1	25.1	-25.1
9	13	1	15.1	15.0
10	13	1	36.4	-36.2
11	13	1	0.0	-2.0
12	13	1	17.1	-15.8
0	14	1	13.0	-13.5
1	14	1	-3.4	3.0
2	14	1	-5.8	6.9
3	14	1	24.8	-25.1
4	14	1	39.0	-39.3
5	14	1	12.4	-11.5
6	14	1	-3.5	-4.6
7	14	1	9.5	-10.0
8	14	1	13.1	-13.5
9	14	1	-0.9	4.0
10	14	1	12.9	12.8
11	14	1	-1.9	-4.1
1	15	1	10.7	-10.2
2	15	1	10.5	-9.4
3	15	1	0.0	1.9
4	15	1	-4.2	-3.3
5	15	1	12.6	11.7
6	15	1	0.0	1.2
7	15	1	7.2	8.6
8	15	1	-5.9	3.4
9	15	1	-1.8	-0.5
0	16	1	-4.0	2.3
1	16	1	0.0	0.1
2	16	1	13.0	12.3
3	16	1	20.6	-21.2
4	16	1	21.9	-20.5
5	16	1	14.6	-14.5
6	16	1	9.9	-11.1
7	16	1	-4.1	0.8
1	17	1	8.4	6.4
2	17	1	-6.2	-5.2
3	17	1	9.1	-10.1
0	0	2	236.7	-242.4
1	0	2	150.5	152.0
2	0	2	114.1	-108.9
3	0	2	85.9	-82.2
4	0	2	89.0	-88.2
5	0	2	50.3	51.1
6	0	2	50.5	53.5
7	0	2	183.5	-171.8
8	0	2	109.8	-103.1
9	0	2	73.6	-73.8
10	0	2	55.6	55.0
11	0	2	76.9	-75.7
12	0	2	23.3	-23.4
13	0	2	33.4	34.3
14	0	2	7.0	-9.5
15	0	2	-5.3	4.2
16	0	2	11.4	10.3
17	0	2	15.1	16.2

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10	0	2	28.3	28.9	8	6	2	28.6	29.0	11	12	2	-4.8	5.7	2	4	3	52.0	-52.8
1	1	2	46.9	45.9	9	6	2	70.2	-70.5	12	12	2	-5.6	-1.5	3	4	3	41.9	-40.9
2	1	2	52.3	-47.6	10	6	2	23.2	-25.1	13	12	2	7.1	5.7	4	4	3	32.0	-28.7
3	1	2	55.8	-54.0	11	6	2	10.8	8.4	1	13	2	13.5	12.2	5	4	3	93.1	-92.4
4	1	2	184.1	170.7	12	6	2	37.5	38.3	2	13	2	0.0	1.8	6	4	3	61.2	-60.0
5	1	2	-3.1	3.4	13	6	2	19.1	-19.1	3	13	2	-4.8	-1.6	7	4	3	31.8	-29.8
6	1	2	9.2	9.1	14	6	2	0.0	-2.6	4	13	2	11.6	-11.1	8	4	3	33.2	32.5
7	1	2	46.7	-46.7	15	6	2	25.1	25.1	5	13	2	10.5	-10.9	9	4	3	51.0	-52.1
8	1	2	21.8	19.6	16	6	2	11.5	11.2	6	13	2	0.0	6.5	10	4	3	40.3	-40.9
9	1	2	9.2	8.4	17	6	2	-2.6	1.2	7	13	2	14.8	-15.5	11	4	3	9.7	10.2
10	1	2	18.1	19.4	1	7	2	86.4	-88.3	8	13	2	-6.3	-6.2	12	4	3	42.6	42.0
11	1	2	26.2	27.1	2	7	2	44.3	-42.2	9	13	2	-2.9	2.9	13	4	3	48.2	-47.8
12	1	2	61.3	-60.6	3	7	2	47.1	-45.8	10	13	2	10.9	-12.5	14	4	3	21.4	-20.9
13	1	2	-5.3	4.6	4	7	2	37.3	-38.7	11	13	2	0.0	0.8	15	4	3	-3.2	0.5
14	1	2	38.5	38.8	5	7	2	0.0	-1.3	12	13	2	0.0	0.8	16	4	3	17.5	16.9
15	1	2	30.5	30.6	6	7	2	12.7	12.0	0	14	2	14.7	13.4	17	4	3	21.6	-22.6
16	1	2	19.7	16.9	7	7	2	43.2	43.7	1	14	2	21.1	20.7	1	5	3	49.6	-50.6
17	1	2	14.9	15.4	8	7	2	68.7	69.6	2	14	2	16.5	15.8	2	5	3	-3.4	3.0
18	1	2	7.5	6.2	9	7	2	43.1	43.9	3	14	2	11.5	10.5	3	5	3	53.1	54.1
0	2	2	262.0	-273.4	10	7	2	52.4	52.4	4	14	2	-5.7	-5.1	4	5	3	-4.6	4.1
1	2	2	7.3	-6.7	11	7	2	13.7	13.4	5	14	2	19.9	19.8	5	5	3	27.0	-27.8
2	2	2	96.8	95.5	12	7	2	33.5	33.0	6	14	2	8.8	9.0	6	5	3	28.1	27.6
3	2	2	77.7	-73.9	13	7	2	-6.3	-5.9	7	14	2	-5.2	5.2	7	5	3	73.9	74.6
4	2	2	83.5	-79.1	14	7	2	9.4	9.8	8	14	2	23.4	-22.8	8	5	3	0.0	-2.0
5	2	2	7.0	-7.2	15	7	2	-1.0	-6.1	9	14	2	-5.9	-2.7	9	5	3	-3.1	2.0
6	2	2	64.4	-60.4	16	7	2	9.5	-8.4	10	14	2	-5.6	7.2	10	5	3	-1.5	6.0
7	2	2	18.2	-19.0	17	7	2	-6.0	6.8	1	15	2	19.8	-19.5	11	5	3	15.9	-15.8
8	2	2	19.5	20.5	0	8	2	11.0	10.7	2	15	2	31.3	-29.1	12	5	3	8.1	-8.6
9	2	2	17.2	16.7	1	8	2	-5.3	-2.6	3	15	2	0.0	-2.8	13	5	3	9.2	-9.4
10	2	2	13.4	-13.0	2	8	2	19.2	19.4	4	15	2	14.1	-14.3	14	5	3	17.4	-19.2
11	2	2	18.0	-17.6	3	8	2	28.4	29.8	5	15	2	26.3	25.6	15	5	3	12.5	-10.4
12	2	2	25.7	-26.6	4	8	2	39.8	39.4	6	15	2	11.1	-8.8	16	5	3	-4.6	6.0
13	2	2	25.6	-26.4	5	8	2	7.5	7.3	7	15	2	28.2	27.2	17	5	3	-6.7	-3.5
14	2	2	25.8	25.0	6	8	2	34.2	34.1	8	15	2	11.0	-9.2	0	6	3	118.4	-120.5
15	2	2	13.9	-13.5	7	8	2	12.2	13.3	9	15	2	10.3	9.0	1	6	3	7.5	7.7
16	2	2	-4.7	-6.4	8	8	2	56.4	57.6	0	16	2	10.3	-11.0	2	6	3	107.6	-106.2
17	2	2	10.7	-11.6	9	8	2	-6.1	-5.6	1	16	2	-4.3	0.3	3	6	3	0.0	3.5
18	2	2	19.6	19.7	10	8	2	34.7	-35.4	2	16	2	0.0	-0.3	4	6	3	25.9	26.3
1	3	2	66.3	65.4	11	8	2	11.6	11.1	3	16	2	-6.8	8.1	5	6	3	20.5	-19.6
2	3	2	153.4	156.5	12	8	2	6.7	4.3	4	16	2	8.3	5.8	6	6	3	75.9	75.7
3	3	2	9.6	7.5	13	8	2	9.0	9.9	5	16	2	0.0	1.5	7	6	3	24.8	-24.1
4	3	2	27.1	28.6	14	8	2	23.6	-21.9	6	16	2	10.8	-9.5	8	6	3	74.7	75.8
5	3	2	36.3	31.8	15	8	2	26.5	27.0	1	17	2	-6.8	4.0	9	6	3	42.3	-43.2
6	3	2	78.6	77.8	16	8	2	-6.1	-7.4	2	17	2	0.0	2.6	10	6	3	18.8	-19.7
7	3	2	46.9	-47.3	1	9	2	62.4	-61.3	1	1	3	107.7	110.0	11	6	3	54.5	-55.2
8	3	2	14.1	12.8	2	9	2	22.0	22.9	2	1	3	-1.9	-1.7	12	6	3	43.9	-44.6
9	3	2	0.0	-3.1	3	9	2	6.2	-5.2	3	1	3	56.0	54.2	13	6	3	24.1	-24.6
10	3	2	25.9	-29.4	4	9	2	-5.6	-3.7	4	1	3	114.4	-107.5	14	6	3	17.8	-16.8
11	3	2	8.2	-0.7	5	9	2	-5.5	-3.5	5	1	3	11.9	11.7	15	6	3	18.6	-20.9
12	3	2	9.7	-8.9	6	9	2	30.5	31.3	6	1	3	19.3	-17.9	16	6	3	13.5	-13.9
13	3	2	37.0	38.2	7	9	2	29.4	28.6	7	1	3	24.4	-22.3	17	6	3	-5.8	5.5
14	3	2	40.6	41.5	8	9	2	0.0	-2.2	8	1	3	7.0	-5.4	1	7	3	11.1	-10.2
15	3	2	39.3	42.1	9	9	2	16.3	-15.8	9	1	3	9.3	9.2	2	7	3	9.5	-10.4
16	3	2	10.7	10.2	10	9	2	12.8	-13.5	10	1	3	38.3	37.1	3	7	3	21.2	-21.3
17	3	2	25.2	24.9	11	9	2	19.3	-19.8	11	1	3	38.4	36.9	4	7	3	25.7	-26.5
18	3	2	31.5	31.7	12	9	2	19.6	21.2	12	1	3	24.4	-24.9	5	7	3	55.8	-56.7
0	4	2	126.1	126.8	13	9	2	-5.1	-4.6	13	1	3	24.7	25.5	6	7	3	9.1	-8.0
1	4	2	10.7	11.6	14	9	2	-6.4	-5.3	14	1	3	9.3	10.4	7	7	3	14.0	-14.2
2	4	2	30.3	-33.4	15	9	2	11.4	10.0	15	1	3	-4.6	1.8	8	7	3	7.4	7.5
3	4	2	35.5	-36.6	0	10	2	46.7	44.8	16	1	3	12.7	-12.1	9	7	3	40.1	-39.2
4	4	2	28.9	-28.0	1	10	2	12.5	12.5	17	1	3	13.7	-16.0	10	7	3	7.6	5.2
5	4	2	28.1	-28.7	2	10	2	28.4	29.2	18	1	3	-3.2	1.5	11	7	3	42.9	42.8
6	4	2	26.6	-27.2	3	10	2	10.3	-9.5	0	2	3	198.5	196.0	12	7	3	36.0	36.7
7	4	2	60.2	59.7	4	10	2	-5.3	-4.9	1	2	3	30.4	-31.2	13	7	3	9.4	11.2
8	4	2	31.8	-32.2	5	10	2	11.7	11.5	2	2	3	42.8	42.2	14	7	3	11.7	-12.7
9	4	2	11.5	-11.4	6	10	2	49.8	50.2	3	2	3	-4.7	3.1	15	7	3	12.3	12.1
10	4	2	-3.8	3.5	7	10	2	22.4	21.3	4	2	3	14.9	-12.0	16	7	3	0.0	-4.2
11	4	2	36.4	37.5	8	10	2	-2.7	2.6	5	2	3	58.3	-58.1	0	8	3	45.3	-43.6
12	4	2	32.7	33.2	9	10	2	35.8	35.7	6	2	3	106.7	-105.2	1	8	3	6.5	6.2
13	4	2	45.1	-46.1	10	10	2	14.2	14.6	7	2	3	71.0	66.0	2	8	3	6.2	6.4
14	4	2	8.1	-7.1	11	10	2	33.4	34.1	8	2	3	102.3	-97.7	3	8	3	20.3	20.4
15	4	2	23.5	-23.0	12	10	2	13.7	-14.5	9	2	3	38.8	-39.0	4	8	3	36.6	-38.0
16	4	2	25.8	25.9	13	10	2	15.4	15.1	10	2	3	32.0	-33.1	5	8	3	55.9	56.6
17	4	2	20.4	-21.0	14	10	2	8.2	-9.6	11	2	3	48.0	46.2	6	8	3	42.6	43.7
18	4	2	12.1	-12.3	15	10	2	-3.9	2.8	12	2	3	59.5	58.5	7	8	3	59.8	-60.4
1	5	2	30.6	28.2	1	11	2	55.6	53.4	13	2	3	18.5	-17.7	8	8	3	40.4	-40.6
2	5	2	25.6	22.6	2	11	2	8.0	8.6	14	2	3	46.4	47.9	9	8	3	-5.1	-3.8
3	5	2	27.0	23.8	3	11	2	-3.8	1.6	15	2	3	0.0	0.5	10	8	3	30.1	31.3
4	5	2	18.2	-17.9	4	11	2	56.9	57.5	16	2	3	18.3	18.5	11	8	3	54.7	-56.2
5	5	2	8.6	5.8	5	11	2	28.7	-30.5	17	2	3	23.6	-23.9	12	8	3	-6.2	-6.5
6	5	2	16.9	-15.7	6	11	2	13.2	-13.6	18	2	3	16.2	-16.2	13	8	3	9.2	-8.2
7	5	2	9.8	-9.5	7	11	2	53.2	-55.5	1	3	3	37.5	37.2	14	8	3	0.0	0.5
8	5	2	25.2	25.5	8	11	2	23.4	-22.8	2	3	3	41.5	42.0	15	8	3	0.0	1.9
9	5	2	23.7	23.0	9	11	2	23.3	-24.0	3	3	3	100.0	100.3	16	8	3	10.3	-10.1
10	5	2	71.0	70.3	10	11	2	20.6	-20.6	4	3	3	70.7	67.8	1	9	3	9.1	-8.7
11	5	2	15.7	18.3	11	11	2	-6.2	5.2	5	3	3	58.6	56.2	2	9	3	36.0	-37.5
12	5	2	7.8	10.1	12	11	2	16.1	-16.3	6	3	3	8.6	-8.2	3	9	3	-5.1	-2.4
13	5	2	29.4	30.2	13	11	2	15.2	16.0	7	3	3	105.7	101.7	4	9	3	34.5	35.6
14	5	2	22.6	23.3	14	11	2	-3.6	-5.8	8	3	3	14.6	-13.1	5	9	3	57.8	-61.3
15	5	2	-5.6	-3.3	0	12	2	19.3	-20.0	9	3	3	-5.5	-6.1	6	9	3	-4.4	-3.9
16	5	2	-5.0	1.1	1	12	2	15.4	14.6	10	3	3	57.1	-55.9	7	9	3	24.9	-25.0
17	5	2	15.1	15.9	2	12	2	52.0	53.3	11	3	3	25.5	-24.7	8	9	3	-5.2	-4.7
0	6	2	74.8	72.6	3	12	2	29.2	-30.1	12	3	3	11.7	-10.2	9	9	3	14.5	-15.1
1	6	2	75.7	73.4	4	12	2	9.8	-9.8	13	3	3	43.3	-42.2	10	9	3	-4.8	6.9
2	6	2	69.2	-64.1	5	12	2	27.0	26.8	14	3	3	7.0	7.7	11	9	3	6.8	-8.6
3	6	2	9.2	-9.2	6	12	2	-5.8	3.0	15	3	3	26.8	-28.3	12	9	3	-3.3	-1.5
4	6	2	62.2	62.5	7	12	2	7.6	6.8	16	3	3	-4.4	2.3	13	9	3	11.3	10.0
5	6	2	5.9	5.2	8	12	2	10.0	-7.8	17	3	3	9.5	9.2	14	9	3	-6.7	7.2
6	6	2	33.2	-34.4	9	12	2	36.2	35.9	0	4	3	99.8	94.5	15	9	3	11.5	9.9
7	6	2	8.4	-5.6	10	12	2	-6.6	5.4	1	4	3	25.7	-26.7	0	10	3	7.1	6.1

H	K	L	FO	FC
1	10	3	27.6	28.9
2	10	3	64.9	67.1
3	10	3	60.6	-63.1
4	10	3	32.6	-33.7
5	10	3	15.2	-16.1
6	10	3	53.7	-53.2
7	10	3	24.8	-24.1
8	10	3	25.0	-24.0
9	10	3	-3.0	4.8
10	10	3	-4.0	5.2
11	10	3	-6.2	-4.1
12	10	3	10.6	10.1
13	10	3	15.3	15.1
14	10	3	28.4	27.0
1	11	3	45.3	-46.4
2	11	3	25.0	24.7
3	11	3	47.6	-49.4
4	11	3	0.0	-1.2
5	11	3	-3.7	-3.2
6	11	3	31.3	31.8
7	11	3	-5.9	-7.5
8	11	3	6.7	-7.0
9	11	3	14.6	-15.3
10	11	3	-2.3	-4.1
11	11	3	0.0	-5.4
12	11	3	7.4	5.5
13	11	3	7.3	-8.7
0	12	3	18.4	18.7
1	12	3	14.9	-16.6
2	12	3	-1.8	-1.9
3	12	3	31.5	-30.5
4	12	3	10.0	12.0
5	12	3	9.1	-10.1
6	12	3	-5.2	4.1
7	12	3	0.0	-1.2
8	12	3	13.5	-12.7
9	12	3	28.3	28.4
10	12	3	-2.1	0.9
11	12	3	21.4	21.3
12	12	3	-6.6	-3.7
1	13	3	40.4	-41.4
2	13	3	0.0	-0.5
3	13	3	13.2	-13.1
4	13	3	0.0	2.5
5	13	3	16.0	-17.8
6	13	3	0.0	-4.2
7	13	3	-4.7	-1.0
8	13	3	-1.3	1.5
9	13	3	-2.9	-1.0
10	13	3	22.2	20.5
11	13	3	-5.7	-6.0
0	14	3	16.0	-15.8
1	14	3	-5.5	4.6
2	14	3	-2.0	-3.8
3	14	3	32.1	30.1
4	14	3	17.5	16.9
5	14	3	16.7	16.7
6	14	3	-6.0	5.3
7	14	3	25.9	24.3
8	14	3	18.5	16.8
9	14	3	-4.8	-5.6
10	14	3	0.0	1.6
1	15	3	-4.8	1.2
2	15	3	7.6	-8.4
3	15	3	0.0	0.2
4	15	3	12.8	-13.0
5	15	3	8.1	-11.2
6	15	3	-5.0	2.1
7	15	3	0.0	-2.7
8	15	3	11.0	10.1
0	16	3	0.0	0.3
1	16	3	-4.4	5.8
2	16	3	-4.9	-5.3
3	16	3	26.9	25.0
4	16	3	11.9	11.6
5	16	3	13.9	11.9
0	0	4	201.4	-197.8
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2	0	4	118.5	-115.7
3	0	4	16.0	-16.1
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6	0	4	49.3	45.2
7	0	4	143.0	139.1
8	0	4	48.8	48.4
9	0	4	26.9	26.7
10	0	4	51.8	-50.3
11	0	4	135.8	132.2
12	0	4	13.6	-13.6
13	0	4	35.2	36.5
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17	0	4	14.8	-14.7
1	1	4	93.0	92.6
2	1	4	93.9	-93.8
3	1	4	9.0	-11.0
4	1	4	49.3	-46.6
5	1	4	60.9	55.8
6	1	4	37.1	-34.2
7	1	4	-1.7	4.2
8	1	4	44.0	43.4
9	1	4	32.5	-31.2
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11	1	4	15.9	·16.4
12	1	4	39.2	39.5
13	1	4	40.0	-37.7
14	1	4	10.8	-10.1
15	1	4	13.0	-13.8
16	1	4	11.7	-12.9
17	1	4	0.0	-4.9
0	2	4	9.9	9.5
1	2	4	116.5	-117.0
2	2	4	40.0	-36.4
3	2	4	49.7	49.3
4	2	4	51.1	-45.9
5	2	4	12.7	-12.0
6	2	4	50.1	-48.0
7	2	4	23.6	22.9
8	2	4	11.8	-11.6
9	2	4	45.6	44.8
10	2	4	37.0	-37.1
11	2	4	35.3	34.6
12	2	4	16.2	16.8
13	2	4	-3.5	-1.5
14	2	4	7.0	-7.1
15	2	4	33.9	32.3
16	2	4	-6.1	-6.8
17	2	4	-6.3	-2.8
1	3	4	27.7	-26.3
2	3	4	102.8	-102.5
3	3	4	88.0	88.3
4	3	4	35.2	-35.4
5	3	4	30.3	-29.4
6	3	4	19.3	-19.9
7	3	4	58.2	59.2
8	3	4	53.6	52.9
9	3	4	9.1	-7.1
10	3	4	44.5	45.6
11	3	4	38.3	-36.5
12	3	4	44.3	46.9
13	3	4	15.5	-16.5
14	3	4	11.0	-10.2
15	3	4	13.2	-14.0
16	3	4	8.4	-9.4
17	3	4	22.0	-21.2
0	4	4	57.7	57.5
1	4	4	26.9	29.5
2	4	4	53.1	53.0
3	4	4	79.7	79.0
4	4	4	13.0	-15.5
5	4	4	65.0	63.3
6	4	4	46.0	-44.3
7	4	4	-4.4	2.2
8	4	4	51.4	-50.8
9	4	4	22.7	-23.5
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11	4	4	59.1	-57.4
12	4	4	14.7	14.7
13	4	4	23.1	22.6
14	4	4	10.0	11.3
15	4	4	7.3	9.0
16	4	4	-1.4	1.6
17	4	4	30.5	30.7
1	5	4	29.0	31.9
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4	5	4	80.2	80.1
5	5	4	10.1	-10.2
6	5	4	34.6	34.3
7	5	4	14.3	15.7
8	5	4	37.0	-36.4
9	5	4	7.7	-9.2
10	5	4	34.7	-34.2
11	5	4	15.5	14.9
12	5	4	7.0	-5.1
13	5	4	9.5	-8.3
14	5	4	14.7	15.5
15	5	4	-4.2	-6.1
16	5	4	24.4	24.8
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3	6	4	13.0	13.5
4	6	4	12.8	-12.2
5	6	4	77.9	80.1
6	6	4	56.9	57.4
7	6	4	42.7	-44.3
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9	6	4	31.3	29.7
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11	6	4	35.2	-36.0
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13	6	4	15.9	15.8
14	6	4	7.6	4.7
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16	6	4	0.0	2.5
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2	7	4	53.2	52.4
3	7	4	17.4	18.2
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6	7	4	25.5	26.1
7	7	4	24.7	-24.7
8	7	4	21.1	-21.7
9	7	4	-2.1	0.6
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12	7	4	0.0	-4.3
13	7	4	8.2	-6.7
14	7	4	-6.2	4.0
15	7	4	-3.6	-3.1
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6	9	4	-1.4	-0.6
7	9	4	20.5	20.4
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9	9	4	-4.1	2.5
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4	10	4	25.4	25.9
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6	10	4	13.0	-12.4
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8	10	4	0.0	-2.4
9	10	4	36.4	-37.6
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9	12	4	30.3	-29.1
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11	12	4	16.4	-17.6
12	12	4	-6.7	8.6
1	13	4	7.8	-6.6
2	13	4	22.0	21.9
3	13	4	7.6	8.6
4	13	4	6.7	6.5
5	13	4	17.7	-18.2
6	13	4	0.0	-1.2
7	13	4	-4.9	-4.0
8	13	4	-5.4	-6.3
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1	14	4	7.4	4.9
2	14	4	18.9	-18.1
3	14	4	20.7	20.1
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5	14	4	10.8	-8.7
6	14	4	17.0	15.8
7	14	4	-3.3	1.7
8	14	4	8.5	8.5
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1	16	4	-5.0	-7.7
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14	1	5	15.5	-16.2
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2	2	5	18.0	-16.9
3	2	5	19.4	18.8
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6	2	5	10.1	10.9
7	2	5	53.0	-51.9
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12	2	5	42.7	-42.4
13	2	5	30.6	28.6
14	2	5	-4.1	3.4
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1	3	5	37.7	-35.6
2	3	5	25.9	-26.4
3	3	5	18.7	-19.8
4	3	5	60.0	-57.5
5	3	5	-0.8	-4.4
6	3	5	46.5	-45.8
7	3	5	43.3	-41.0
8	3	5	0.0	-2.1
9	3	5	25.2	-26.2
10	3	5	24.7	-23.2
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13	3	5	23.5	24.5
14	3	5	22.8	-21.9
15	3	5	26.2	27.0
16	3	5	16.1	-16.8
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1	4	5	49.4	48.9
2	4	5	34.4	-35.4
3	4	5	23.0	-23.6
4	4	5	34.3	-35.3
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6	4	5	-5.7	-4.1
7	4	5	10.4	-10.9
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12	4	5	18.1	18.0
13	4	5	45.4	44.5
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2	5	5	19.9	-19.0
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1	6	5	21.6	-22.9

H	K	L	FO	FC
2	6	5	27.1	28.4
3	6	5	35.1	-36.6
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15	6	5	11.6	-11.1
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3	7	5	9.5	8.6
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8	7	5	22.7	22.2
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2	8	5	29.1	-28.8
3	8	5	51.5	54.7
4	8	5	-4.7	-0.2
5	8	5	24.1	-23.9
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8	8	5	8.3	-8.2
9	8	5	22.9	-23.0
10	8	5	-4.4	3.4
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12	8	5	0.0	1.5
13	8	5	0.0	-3.7
14	8	5	20.4	-19.7
1	9	5	41.7	-42.0
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4	9	5	31.5	30.6
5	9	5	51.7	53.3
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7	9	5	44.4	45.2
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9	9	5	31.5	31.4
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12	9	5	-4.0	-2.6
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0	10	5	37.1	-37.3
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2	10	5	7.4	6.6
3	10	5	47.5	47.9
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5	10	5	0.0	-1.1
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8	10	5	29.1	29.0
9	10	5	19.9	-19.3
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13	10	5	-6.2	2.3
1	11	5	14.4	15.4
2	11	5	0.0	1.2
3	11	5	26.8	26.6
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12	11	5	19.6	18.7
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5	13	5	13.4	-12.8
6	13	5	-5.2	3.5
7	13	5	17.6	-17.6
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1	14	5	-1.8	2.6
2	14	5	12.1	11.3
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5	0	6	21.8	21.8
6	0	6	64.3	62.1
7	0	6	20.6	20.0
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9	0	6	45.2	-44.2
10	0	6	24.7	24.6
11	0	6	61.6	-60.5
12	0	6	21.6	-21.9
13	0	6	-3.1	-1.9
14	0	6	9.4	-10.3
15	0	6	36.2	-33.9
16	0	6	12.8	-12.6
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2	1	6	0.0	-2.6
3	1	6	91.2	-89.5
4	1	6	76.6	-77.0
5	1	6	12.4	13.2
6	1	6	17.8	-16.7
7	1	6	60.4	-58.5
8	1	6	23.4	-22.9
9	1	6	24.2	-22.9
10	1	6	10.9	-11.9
11	1	6	41.1	41.0
12	1	6	12.2	11.6
13	1	6	-6.6	5.3
14	1	6	7.4	-7.2
15	1	6	0.0	4.2
16	1	6	0.0	-2.7
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2	2	6	8.3	6.3
3	2	6	15.2	14.4
4	2	6	49.5	49.4
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7	2	6	83.9	-83.9
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9	2	6	20.3	20.1
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13	2	6	8.3	-10.0
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15	2	6	-4.7	3.4
16	2	6	-3.7	-1.8
1	3	6	9.4	-10.2
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3	3	6	14.4	15.3
4	3	6	68.6	-68.3
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6	3	6	36.1	-37.0
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8	3	6	12.5	-10.7
9	3	6	9.2	9.2
10	3	6	0.0	-1.2
11	3	6	14.3	-13.4
12	3	6	11.8	-14.2
13	3	6	35.8	35.0
14	3	6	16.3	-15.2
15	3	6	0.0	-0.4
0	4	6	17.9	19.2
1	4	6	7.5	7.3
2	4	6	19.0	19.0
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4	4	6	8.4	7.6
5	4	6	68.8	-70.1
6	4	6	20.0	-20.8
7	4	6	21.2	20.5
8	4	6	-4.8	3.8
9	4	6	16.4	-15.3
10	4	6	10.5	-10.9
11	4	6	27.2	28.1
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13	4	6	14.6	14.8
14	4	6	8.3	7.9
15	4	6	12.0	-12.6
1	5	6	62.3	-65.3
2	5	6	24.3	25.2
3	5	6	38.5	-40.4
4	5	6	-3.3	-6.6
5	5	6	30.9	32.0
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7	5	6	-5.0	3.5
8	5	6	12.6	-13.2
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3	7	6	26.3	-27.0
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5	7	6	6.4	6.3
6	7	6	20.1	-19.9
7	7	6	-3.7	3.4
8	7	6	31.8	-31.2
9	7	6	-3.1	5.1
10	7	6	43.4	-43.2
11	7	6	14.3	-13.8
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14	7	6	-6.4	-5.9
0	8	6	14.5	-17.2
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4	8	6	29.3	-30.9
5	8	6	19.5	19.6
6	8	6	12.8	-14.0
7	8	6	17.4	17.7
8	8	6	6.8	-5.9
9	8	6	-4.9	-3.7
10	8	6	-4.0	2.9
11	8	6	9.1	-8.3
12	8	6	0.0	-2.5
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2	9	6	19.6	-20.1
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7	9	6	7.9	-6.6
8	9	6	-3.3	4.4
9	9	6	0.0	0.7
10	9	6	7.2	-7.2
11	9	6	11.8	11.7
12	9	6	-1.8	-2.1
0	10	6	30.1	-29.7
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3	10	6	21.2	21.4
4	10	6	19.6	-18.3
5	10	6	25.7	26.2
6	10	6	-5.4	-5.5
7	10	6	6.6	3.7
8	10	6	0.0	-1.2
9	10	6	8.5	-10.2
10	10	6	-5.7	-8.3
11	10	6	11.3	-9.1
1	11	6	16.9	16.6
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3	11	6	8.0	-8.2
4	11	6	8.3	-7.3
5	11	6	12.0	15.0
6	11	6	0.0	1.2
7	11	6	-6.3	-3.1
8	11	6	-1.2	6.4
9	11	6	14.1	-12.5
10	11	6	17.9	18.1
0	12	6	0.0	-1.5
1	12	6	10.7	-11.6
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3	12	6	20.7	-20.5
4	12	6	8.6	-8.9
5	12	6	11.0	9.9
6	12	6	9.7	-9.8
7	12	6	18.6	-18.7
8	12	6	12.8	-12.5
9	12	6	31.4	32.0
1	13	6	-5.1	-3.1
2	13	6	0.0	-2.5
3	13	6	18.4	19.1
4	13	6	-2.8	4.3
5	13	6	-3.2	2.2
6	13	6	-6.8	7.6
7	13	6	11.3	11.6
0	14	6	-3.2	-0.5
1	14	6	-6.3	3.5
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3	14	6	30.6	-29.9
4	14	6	0.0	-3.3
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3	1	7	7.9	6.9
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6	1	7	30.7	29.7
7	1	7	18.0	-18.2
8	1	7	18.4	18.0
9	1	7	-5.2	-4.7
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7	2	7	35.4	34.2
8	2	7	70.8	69.3
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11	2	7	39.4	37.6
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2	3	7	7.2	6.6
3	3	7	19.4	-18.3
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5	3	7	6.3	1.0
6	3	7	36.3	35.4
7	3	7	-6.0	-8.5
8	3	7	44.2	43.7
9	3	7	11.9	13.1
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13	3	7	-4.8	-3.6
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10	4	7	7.7	4.7
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12	4	7	9.4	-8.4
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3	5	7	10.6	-9.6
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12	5	7	8.6	-10.1
13	5	7	14.7	-15.3
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H	K	L	FO	FC
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3	7	7	10.9	11.2
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3	10	8	-7.2	-5.7
4	10	8	12.2	12.7
5	10	8	-1.1	3.1
6	10	8	23.6	21.9
7	10	8	21.2	20.1
8	10	8	11.9	13.2
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3	11	8	14.7	-15.0
4	11	8	-2.1	2.8
5	11	8	19.3	19.3
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3	12	8	19.0	18.5
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0	4	9	13.5	-14.4
1	4	9	6.7	7.7
2	4	9	32.0	-35.3
3	4	9	15.2	-16.0
4	4	9	-5.0	2.4
5	4	9	-4.4	0.8
6	4	9	7.3	-7.1
7	4	9	11.7	-10.2
8	4	9	-5.6	-3.3
9	4	9	14.5	-15.1
10	4	9	-5.1	-3.3
11	4	9	15.8	-15.2
1	5	9	-3.3	1.8
2	5	9	24.2	-24.4
3	5	9	0.0	0.4
4	5	9	15.6	-14.3
5	5	9	-1.9	-0.8
6	5	9	17.5	-17.3
7	5	9	-1.7	1.4
8	5	9	9.0	9.1
9	5	9	7.6	1.1
10	5	9	20.3	18.2
0	6	9	42.2	-42.8
1	6	9	16.4	-13.1
2	6	9	9.6	-11.2
3	6	9	12.8	-15.7
4	6	9	-4.5	-3.4
5	6	9	13.2	-12.3
6	6	9	0.0	-4.0
7	6	9	22.2	-21.4
8	6	9	9.4	11.1
9	6	9	0.0	-1.5
1	7	9	11.8	-12.2
2	7	9	-5.1	7.4
3	7	9	-5.6	0.8
4	7	9	12.1	-12.1
5	7	9	-6.6	-7.8
6	7	9	-4.4	5.9
7	7	9	6.9	-1.7
8	7	9	10.9	11.4
9	7	9	-6.7	7.7
0	8	9	0.0	-1.6
1	8	9	-4.5	-2.5
2	8	9	6.7	-3.0
3	8	9	-5.3	-7.9
4	8	9	14.9	-14.6
5	8	9	19.0	-17.6
6	8	9	-2.4	-0.5
7	8	9	9.4	7.0
8	8	9	18.0	-16.4
1	9	9	-3.2	-4.7
2	9	9	19.4	20.3
3	9	9	8.7	-9.1
4	9	9	29.9	30.3
5	9	9	8.3	6.7
6	9	9	9.4	9.1
0	10	9	-3.8	-4.2
1	10	9	9.2	-10.9
2	10	9	11.4	10.4
3	10	9	15.2	14.0
4	10	9	13.8	-12.8
0	0	10	34.3	34.4
1	0	10	16.8	16.8
2	0	10	16.1	16.1
3	0	10	18.1	18.0
4	0	10	0.0	0.5
5	0	10	32.8	32.8
6	0	10	63.6	-62.2
7	0	10	12.9	13.1
8	0	10	8.2	-7.8
9	0	10	-4.1	1.2
1	1	10	0.0	3.2
2	1	10	-6.0	5.1
3	1	10	10.3	9.6
4	1	10	16.1	-15.6
5	1	10	11.7	9.8
6	1	10	7.0	7.5
7	1	10	9.7	9.3
8	1	10	13.5	12.0
9	1	10	-3.0	1.2
0	2	10	12.0	10.8
1	2	10	0.0	5.5
2	2	10	9.6	-9.7
3	2	10	0.0	1.1
4	2	10	-3.9	2.3
5	2	10	12.8	10.7
6	2	10	-3.0	-3.0
7	2	10	-3.9	4.1
8	2	10	10.9	-11.5
9	2	10	11.2	9.4
1	3	10	6.9	6.5
2	3	10	-2.0	-5.4
3	3	10	14.6	15.1
4	3	10	7.0	6.2
5	3	10	11.5	11.0
6	3	10	9.4	-8.8
7	3	10	8.0	7.7
8	3	10	6.9	7.0
0	4	10	44.0	-46.2
1	4	10	8.2	-8.6
2	4	10	7.6	-5.7
3	4	10	11.1	-9.3
4	4	10	-5.2	4.2
5	4	10	10.0	-9.2
6	4	10	28.2	27.5
7	4	10	-5.5	6.2
8	4	10	19.9	20.1
1	5	10	15.6	15.0
2	5	10	-3.5	5.3
3	5	10	9.2	10.6
4	5	10	9.9	-6.9
5	5	10	8.2	6.6
6	5	10	-4.6	-6.3
7	5	10	0.0	-2.4
0	6	10	9.9	-10.5
1	6	10	10.2	-8.5
2	6	10	-4.3	2.4
3	6	10	7.3	6.5
4	6	10	-2.7	-4.2
5	6	10	-3.0	-2.7
6	4	10	21.8	20.2
1	7	10	15.9	15.7
2	7	10	0.0	1.9
3	7	10	12.9	13.0
4	7	10	-4.8	-3.0
5	7	10	9.5	9.8
0	8	10	23.1	24.4
1	8	10	0.0	1.4
2	8	10	18.4	18.6
3	8	10	7.3	6.9
1	1	11	-2.7	-0.8
2	1	11	14.2	-16.6
3	1	11	-4.6	-5.6
4	1	11	20.1	-19.4
5	1	11	7.4	-8.5
0	2	11	-5.0	-7.1
1	2	11	-6.2	4.1
2	2	11	-3.2	9.2
3	2	11	21.6	21.1
4	2	11	7.7	-8.9
5	2	11	18.9	18.0
1	3	11	16.9	-18.3
2	3	11	15.0	15.7
3	3	11	-4.7	-4.6
4	3	11	16.8	15.8
0	4	11	16.8	-15.9
1	4	11	-6.7	6.6
2	4	11	-2.1	-2.7
3	4	11	7.3	6.8
1	5	11	7.0	-4.9

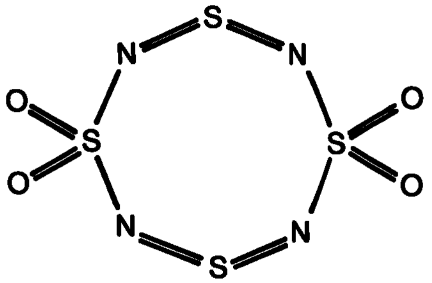
CHAPTER 5

The Crystal Structure of $S_5N_5^+S_3N_3O_4^-$

5.1 Introduction.

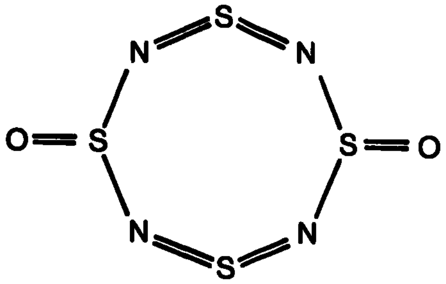
S_4N_4 has been known since 1835 (Gregory, 1835) and constitutes the most well known and studied sulphur-nitrogen compound. As mentioned in section 2.2 it is a very reactive compound and is the starting point for the preparation of many other cyclic sulphur-nitrogen species. Many compounds have been prepared in which the S_4N_4 ring is retained; the simplest of these are derivatives such as $S_4N_4F_4$, described earlier or $S_4N_4H_4$ which contains a puckered S_4N_4 ring and shows 4m symmetry (Sabine and Cox, 1967). S_4N_4 also forms a wide range of adducts with Lewis acids such as $SbCl_5$, which coordinates to a nitrogen in the ring to give $SbCl_5.S_4N_4$.

In contrast, the first oxide of S_4N_4 has only been prepared quite recently (Roesky and Petersen, 1972), and corresponds to $S_4N_4O_4$. This has been assigned the structure shown below from infrared and mass spectral studies.



In the course of further investigation of inorganic ring systems, Roesky and Grosse Böwing (1973) succeeded in isolating two compounds which they formulated as $S_4N_4O_2$. Both compounds were prepared by the reaction between $Me_3Si-N=S=N-SiMe_3$ and $FSO_2-N=S=O$ in methylene chloride. The reaction proceeded readily at room temperature, and when the reaction was complete the solvent and volatile products were removed in vacuo. The residues were redissolved in methylene chloride and after several days violet-black crystals of compound I were deposited. When a small amount of solvent was removed yellow crystals of compound II were produced. Cryoscopic molecular weight measurements and elemental analysis yielded results in good agreement with the formulation of both compounds as $S_4N_4O_2$.

Compound I was thought to be



and its crystal structure is described in this chapter. The crystal structure of compound II is discussed in chapter 7.

5.2 Crystal Data.

The crystals were obtained as violet-black prisms, elongated along a with prominent {011} faces. The crystal used for data collection had dimensions 0.6 x 0.2 x 0.2mm and was sealed in a quartz tube.

Precession photographs showed the unit cell to be monoclinic with space group $P2_1/c$. Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections as measured on a four-circle diffractometer.

$S_8N_8O_4$ M = 432.53
a = 8.874(1)Å α = 90°
b = 11.299(2)Å β = 97.27°
c = 13.112(2)Å γ = 90°
U = 1314.7Å^3
Z = 4
Dm = 2.14g cm^{-3} (by floatation in CH_3I/C_2H_5I)
Dc = 2.185g cm^{-3}

Absorption coefficient for MoKα radiation (λ = 0.7107Å) = 13.3cm^{-1}.

5.3 Data Collection and Correction.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer (described before) using Zr-filtered MoKα radiation. A $2\theta-\omega$ scan was used consisting of 80 steps of 0.01° with a counting time of 2 seconds per step. The background was measured for 40 seconds at the beginning and end of each scan. Three standard reflections were measured every 40 reflections, and showed no systematic changes indicating that the crystal was stable throughout the experiment. The standard reflections were used to place the reflections on a common scale.

Half the sphere of reflection was recorded for $0 < \theta \leq 26^{o}$. This yielded two sets of equivalent reflections which on averaging gave a total of 2563 independent reflections, and of these 1915 were taken as observed having net counts > 3 e.s.d's.

The intensities were corrected for Lorentz and polarisation effects but not for absorption.

5.4 Solution and Refinement.

The structure was solved by the symbolic addition procedure using a multisolution program (Long, 1968). A set of normalised structure factors were calculated and 214 of these with $E \geq 1.7$ were phased. Seven reflections were chosen by the program (Table 5.1); the first three were arbitrarily given positive signs and hence determined the origin. The phases of the remainder were varied to form, together with the origin determining reflections, 16 starting sets for the reiterative application of Sayre's relationship. The results are shown in table 5.1.

The most self-consistent phases were obtained from starting set 15 which has a consistency index of 0.97. The only other set with a high consistency index is set 13 however this shows a sign change in the starting set that leaves it equivalent to set 15.

An E-map was computed using the phases estimated from set 15 which revealed the positions of all the sulphur atoms and most of the lighter atoms. The structure was very different from that expected and did not contain the $S_4N_4O_2$ molecules originally proposed, so that only the positions of the sulphur atoms were included in the first stages of refinement. The sulphur atoms were refined with isotropic temperature factors of $3.0Å^2$ using least squares methods with the block-diagonal approximation and after two cycles this resulted in an R value of 0.37. An electron density map was calculated based on the phases obtained from the sulphur atoms and this revealed positions for all the lighter atoms except for one nitrogen. Because the anion was new it was not certain which atoms were oxygen so that all the lighter atoms were included as nitrogen. Further refinement and the calculation of difference syntheses revealed the remaining nitrogen atom and indicated which atoms were oxygen (R = 0.081). All atoms were then given anisotropic thermal parameters and with further refinement, using full matrix least squares methods, R converged on its final value of 0.0300. During the last cycle all the parameter shifts were $< 0.2\sigma$. A difference synthesis calculated from the final structure factors showed no peaks $> 0.3e.\text{Å}^{-3}$.

The initial weighting scheme used was the same as that described earlier except that $P_1 = 20$ and $P_2 = 0.15$. This was replaced in the final stages of refinement by one based on counting statistics as described in section 3.4 and took the form

$$\sqrt{w} = 2.N/(Fo.[T + B.G + (PN)^2]^{\frac{1}{2}})$$

The optimum value of P as determined by a uniform distribution of $w\Delta^2$ over the whole range of Fo, was 0.05. The unobserved reflections were not included in the refinement. The final least squares totals and weighting analysis are given in table 5.2. The final structure factors are shown in table 5.9. The sulphur atoms were corrected

Table 5.1 $S_5N_5^+S_3N_3O_4^-$

The reflections used in the starting sets.

Origin determining reflections			E	Reflections whose signs were varied			|E|
6	2	$\bar{7}$	3.48	4	2	$\bar{9}$	3.45
3	3	10	3.16	4	5	4	2.98
2	3	9	3.14	7	6	$\bar{6}$	2.87
				0	3	3	2.84

Results for Symbolic Addition Procedure

Set No	Signs	Changes	Cycles	No +	No -	Consistency Index
1	+ + + +		10	124	90	0.766
2	+ + + -		11	107	107	0.580
3	+ + - +		9	110	104	0.568
4	+ + - -		12	110	104	0.529
5	+ - + +		11	113	101	0.518
6	+ - + -		11	111	103	0.690
7	+ - - +	+ - + +	10	103	111	0.601
8	+ - - -		9	105	109	0.720
9	- + + +		10	119	95	0.633
10	- + + -	- + - +	15	100	114	0.723
11	- + - +		10	119	95	0.667
12	- + - -		9	110	104	0.757
13	- - + +	- - - +	12	111	103	0.941
14	- - + -		11	105	109	0.548
15	- - - +		7	111	103	0.972
16	- - - -		16	109	105	0.599

Table 5.2 $S_5N_5^+S_3N_3O_4^-$

Final Least Squares Totals

$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	R
48031.63	48009.02	1442.51	0.0300

Weighting Analysis

$\|F_o\|$ Ranges	N	$\Sigma w\Delta^2/N$	R
0 - 7	84	0.39	0.160
7 - 9	169	0.27	0.102
9 - 15	516	0.29	0.051
15 - 20	282	0.32	0.030
20 - 45	636	0.32	0.021
45 - 70	143	0.27	0.018
70 Upwards	85	0.57	0.028

Table 5.3 $S_5N_5^+S_3N_3O_4^-$

Final Atomic Coordinates with their Estimated Standard Deviations(x 10^5) and their Isotropic Temperature Factor† (Å^2)

Atom	$^x/a$	$^y/b$	$^z/c$	B
S(1)	0.71855 (11)	0.00867 (8)	0.07288 (7)	3.82
S(2)	0.48780 (10)	0.15440 (8)	0.17082 (7)	3.70
S(3)	0.61041 (10)	0.33077 (8)	0.31946 (7)	3.47
S(4)	0.93756 (10)	0.30549 (8)	0.33504 (7)	3.38
S(5)	0.99551 (10)	0.12928 (8)	0.18528 (7)	3.57
S(6)	0.30339 (8)	0.35385 (7)	-0.07419 (6)	2.95
S(7)	0.20910 (8)	0.42751 (7)	0.10532 (6)	2.66
S(8)	0.24056 (10)	0.59349 (7)	-0.04941 (6)	3.26
O(1)	0.24664 (29)	0.28272 (24)	-0.16087 (19)	4.26
O(2)	0.45972 (25)	0.33688 (25)	-0.03526 (20)	4.16
O(3)	0.07676 (27)	0.41551 (24)	0.15577 (18)	4.01
O(4)	0.35186 (26)	0.41959 (23)	0.16846 (17)	3.76
N(1)	0.57104 (34)	0.06471 (26)	0.10682 (22)	4.06
N(2)	0.60484 (30)	0.22946 (25)	0.23939 (20)	3.31
N(3)	0.78213 (33)	0.35791 (24)	0.36117 (21)	3.55
N(4)	0.90270 (30)	0.21067 (24)	0.24873 (20)	3.29
N(5)	0.88328 (34)	0.05109 (26)	0.11102 (22)	3.96
N(6)	0.19020 (28)	0.34203 (23)	0.00840 (20)	2.96
N(7)	0.20125 (29)	0.56562 (23)	0.05822 (19)	3.01
N(8)	0.28947 (30)	0.49364 (26)	-0.11704 (20)	3.19

† The temperature factors obtained from the last cycle of isotropic refinement.

Table 5.4 $S_5N_5^+S_3N_3O_4^-$

Final Anisotropic Thermal Parameters and their Estimated Standard Deviations (Both $Å^2$ x 10^5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	6948(61)	4157(48)	3968(45)	-750(38)	221(41)	-356(43)
S(2)	3929(44)	5250(54)	5236(51)	-475(42)	3(37)	-609(39)
S(3)	4510(46)	4392(46)	4830(48)	-811(39)	1128(37)	386(37)
S(4)	4229(46)	4239(47)	4602(47)	-385(37)	325(37)	-611(36)
S(5)	4269(45)	4675(50)	5042(50)	-469(39)	827(38)	552(38)
S(6)	3193(39)	4695(48)	3793(41)	-901(36)	634(31)	- 91(35)
S(7)	3259(38)	4250(44)	3034(37)	246(32)	586(29)	- 31(33)
S(8)	4576(47)	4138(47)	3966(44)	611(35)	307(36)	-158(36)
O(1)	6066(160)	6520(167)	4736(144)	2423(125)	406(126)	-143(131)
O(2)	3221(120)	7562(181)	6226(157)	-923(139)	823(111)	799(120)
O(3)	4703(136)	7166(176)	4695(133)	298(127)	2192(111)	-623(125)
O(4)	4480(131)	6410(160)	4295(130)	520(117)	-648(107)	447(117)
N(1)	6309(189)	4354(162)	4294(155)	- 11(133)	188(139)	-754(144)
N(2)	4310(154)	4263(158)	4158(154)	75(122)	248(126)	104(122)
N(3)	5491(171)	3909(156)	4078(149)	-640(120)	829(128)	-274(131)
N(4)	4359(151)	3874(145)	4187(152)	217(118)	986(123)	119(120)
N(5)	6207(190)	4569(165)	4361(160)	-211(132)	472(138)	526(143)
N(6)	3736(139)	3928(147)	4118(142)	-297(117)	830(113)	-607(117)
N(7)	4201(144)	3846(142)	3761(141)	-132(117)	360(114)	368(120)
N(8)	4444(151)	5713(179)	3520(143)	273(127)	1051(120)	-755(133)

for anomolous dispersion. These correction factors as well as the scattering factors for all atoms were taken from International tables Vol III. The final atomic coordinates and anisotropic thermal parameters are given in tables 5.3 and 5.4 respectively.

5.5 Results and Discussion.

The structure consists of $S_5N_5^+$ cations and $S_3N_3O_4^-$ anions, and does not contain molecules of $S_4N_4O_2$ as was originally suggested. It is of interest that the average molecular weight and atomic composition for these two ions does correspond to $S_4N_4O_2$. The bond distances and angles for these ions are shown in tables 5.5 and 5.6 respectively.

5.5a The Structure of the $S_5N_5^+$ cation.

This is the second determination of the structure of this cation. As seen in figure 5.1, it consists of a ten-membered ring with alternating sulphur and nitrogen atoms. The ring is roughly planar with the maximum deviation from the mean plane being 0.06Å as shown on figure 5.2 and in table 5.7. The deviations are systematic and

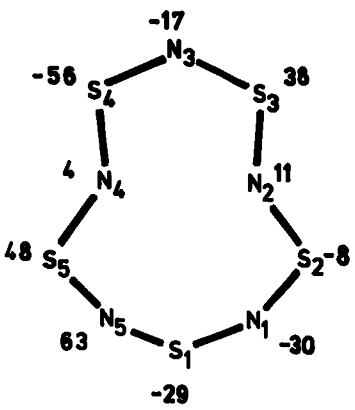


Figure 5.2

Deviations of the atoms from their mean plane (Å x 10^3)

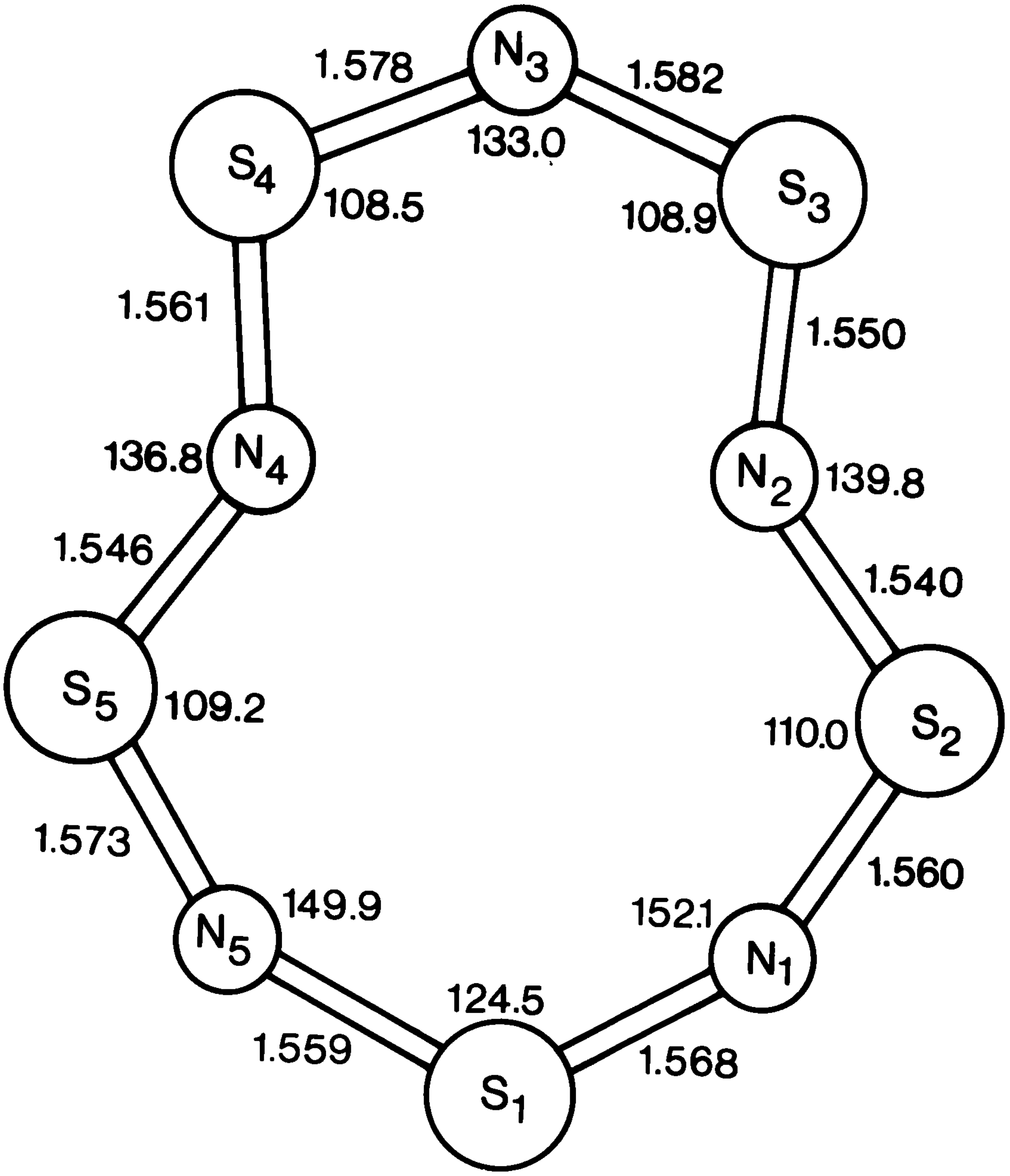
indicate that the S_5N_5 ring is slightly buckled along the line S(4) to N(1). This buckling is greater than that found in medium sized aromatic hydrocarbons, such as pyrene $C_{16}H_{10}$ which shows deviations of up to 0.02Å from its mean plane (Hazell, Larsen and Lehmann, 1972) and suggests that the heterocyclic ring is more flexible than its organic counterparts. This might be expected because π bonding involving d orbitals is less sensitive to deviations from planarity than that involving only p orbitals. The bond lengths on either side of the ring are the same within experimental error, for example the length of 1.568(3)Å for S(1)-N(1) does not differ significantly from that of 1.559(3)Å for S(1)-N(5). Likewise the corresponding angles are equal within experimental error except for S(2)-N(2)-S(3) and S(4)-N(4)-S(5) which have values of 139.8(2)° and 136.8(2)° respectively. Thus the shape of the ion approaches mm symmetry. A similar divergence in the angles in the S_5N_5 ring is found in the $S_5N_5^+$ ion described in chapter 6 and will be discussed there.

The bond distances which vary from 1.540-1.582Å are characteristic of multiple bonds in aromatic sulphur-nitrogen compounds, and may be compared with the range of 1.548-1.566Å seen in $S_4N_3^+$ (Kruss and Zeigler, 1972b). The bond angles at nitrogen which vary from 133° to 151° are also characteristic of these compounds and are similar to the angles of 138° and 148° found in $S_4N_3^+$. As mentioned in section 2.5 theoretical calculations have shown that the $S_5N_5^+$ cation found originally in $S_5N_5^+AlCl_4^-$ is a 14π electron inorganic aromatic species. In view of the bond distances and angles found in the present determination it is reasonable to assume that this also contains a 14π electron system.

The $S_5N_5^+$ ion reported here differs markedly from the heart-shaped cation first reported in $S_5N_5^+AlCl_4^-$ (Hazell and Hazell, 1972) which is shown in figure 5.3. However closer examination shows that the sulphur atoms in both structures have approximately the same distribution and that the main difference is in the position of two nitrogen atoms. There is also a far greater variation in the S-N bond distances and angles at nitrogen in $S_5N_5^+AlCl_4^-$ than in the present structure, i.e. 1.465-1.590Å and 129-177°. In view of these differences another derivative of $S_5N_5^+$ has been studied and is described in the following chapter, so that further discussion on these ions is deferred until then.

5.5b The Structure and Bonding in the $S_3N_3O_4^-$ anion.

This is the first time that this anion has been observed although the preparation of $HS_3N_3O_4$ has been reported (Roesky and Kuhtz, 1974). As seen in figure 5.4 it consists of an S_3N_3 ring with two terminal oxygen atoms on two of the sulphur atoms. The bond distances on either side of the ring are the same within experimental error. In the case of S(6)-N(6) and S(7)-N(6) of length 1.573(3)Å and 1.588(3)Å it is necessary to allow for the dependance of their lengths on the common position of N(6). Likewise corresponding angles on either side of the ring are the same within experimental error at the 0.1% level, so that the molecule shows m symmetry within experimental error.



$S_5N_5^+$

Figure 5.1

The $S_5N_5^+$ Cation found in $S_5N_5^+S_3N_3O_4^-$

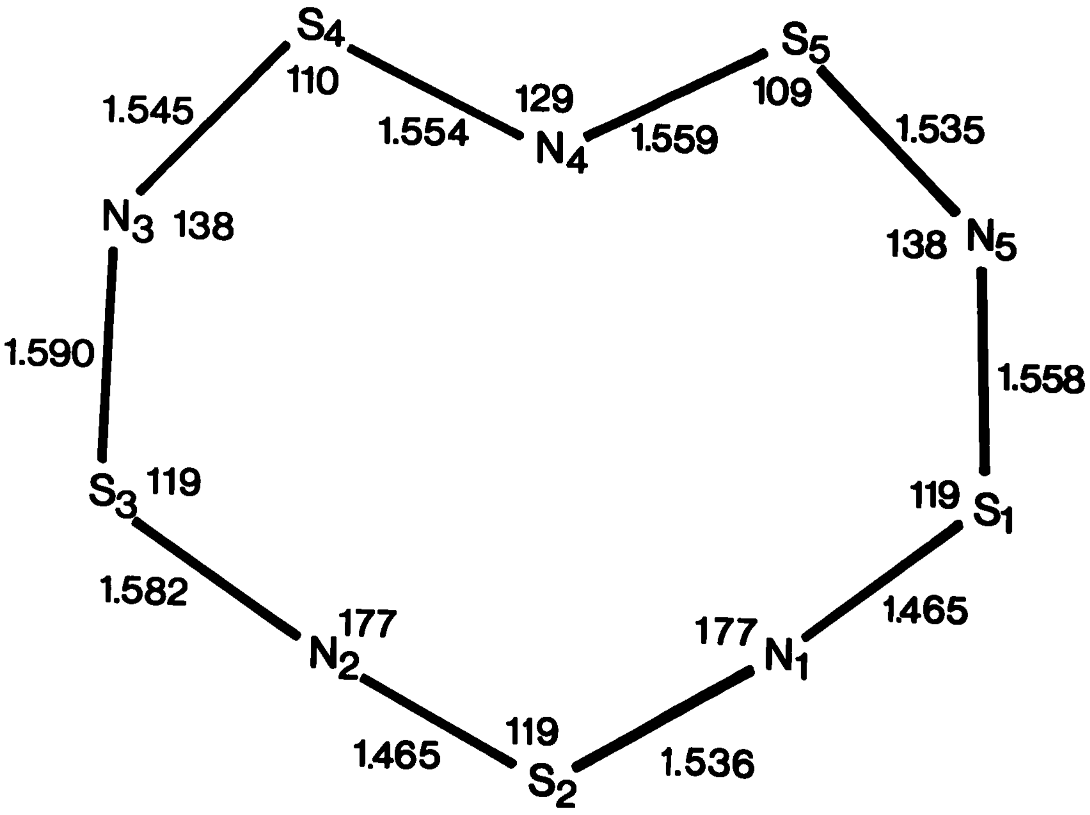


Figure 5.3

The $S_5N_5^+$ Cation found in $S_5N_5^+AlCl_4^-$

Table 5.5 $S_5N_5^+S_3N_3O_4^-$

Final Bond Distances (Å) with their Estimated Standard Deviations (Å x 10^3)

S(1) - N(1)	1.568 (3)
S(1) - N(5)	1.559 (3)
S(2) - N(1)	1.560 (3)
S(2) - N(2)	1.540 (3)
S(3) - N(2)	1.550 (3)
S(3) - N(3)	1.582 (3)
S(4) - N(3)	1.578 (3)
S(4) - N(4)	1.561 (3)
S(5) - N(4)	1.546 (3)
S(5) - N(5)	1.573 (3)
S(6) - O(1)	1.431 (3)
S(6) - O(2)	1.429 (3)
S(6) - N(6)	1.573 (3)
S(6) - N(8)	1.676 (3)
S(7) - O(3)	1.425 (3)
S(7) - O(4)	1.426 (2)
S(7) - N(6)	1.588 (3)
S(7) - N(7)	1.677 (3)
S(8) - N(7)	1.529 (3)
S(8) - N(8)	1.532 (3)

Table 5.6 $S_5N_5^+S_3N_3O_4^-$

Final Bond Angles (degrees) and their Estimated Standard Deviations (deg. x 10^2)

N(1) - S(1) - N(5)	124.53(17)
N(1) - S(2) - N(2)	109.99(16)
N(2) - S(3) - N(3)	108.91(15)
N(3) - S(4) - N(4)	108.47(15)
N(4) - S(5) - N(5)	109.20(16)
S(1) - N(1) - S(2)	152.11(22)
S(2) - N(2) - S(3)	139.81(20)
S(3) - N(3) - S(4)	133.00(19)
S(4) - N(4) - S(5)	136.77(19)
S(1) - N(5) - S(5)	149.92(21)
O(1) - S(6) - O(2)	115.88(16)
N(6) - S(6) - O(1)	107.94(15)
N(6) - S(6) - O(2)	114.71(15)
N(8) - S(6) - O(1)	105.05(15)
N(8) - S(6) - O(2)	105.86(15)
N(6) - S(6) - N(8)	106.53(14)
O(3) - S(7) - O(4)	116.62(15)
N(6) - S(7) - O(3)	107.69(14)
N(6) - S(7) - O(4)	115.00(14)
N(7) - S(7) - O(3)	105.15(14)
N(7) - S(7) - O(4)	105.36(14)
N(6) - S(7) - N(7)	106.03(14)
N(7) - S(8) - N(8)	119.82(15)
S(6) - N(6) - S(7)	119.16(17)
S(7) - N(7) - S(8)	121.88(17)
S(6) - N(8) - S(8)	120.97(18)

Table 5.7 $S_5N_5^+S_3N_3O_4^-$

Some mean planes

$$0.0863X + 0.6869Y - 0.7217Z + 0.0486 = 0$$

Atom	S(1)	S(2)	S(3)	S(4)	S(5)
P.	-0.0286	-0.0076	0.0386	-0.0556	0.0484
σ(P)	0.0009	0.0009	0.0009	0.0009	0.0009

Atom	N(1)	N(2)	N(3)	N(4)	N(5)
P	-0.0300	0.0111	-0.0168	0.0043	0.0633
σ(P)	0.0029	0.0028	0.0027	0.0027	0.0029

$$-0.9095X - 0.1548Y - 0.3858Z + 2.8057 = 0$$

Atom	S(6)	S(7)	S(8)	N(6)†	N(7)	N(8)
P	-0.0011	0.0011	-0.0002	0.6431	-0.0119	0.0171
σ(P)	0.0007	0.0007	0.0009	0.0025	0.0026	0.0025

Where P and σ(P) are the distance and its e.s.d. of an atom from the mean plane.

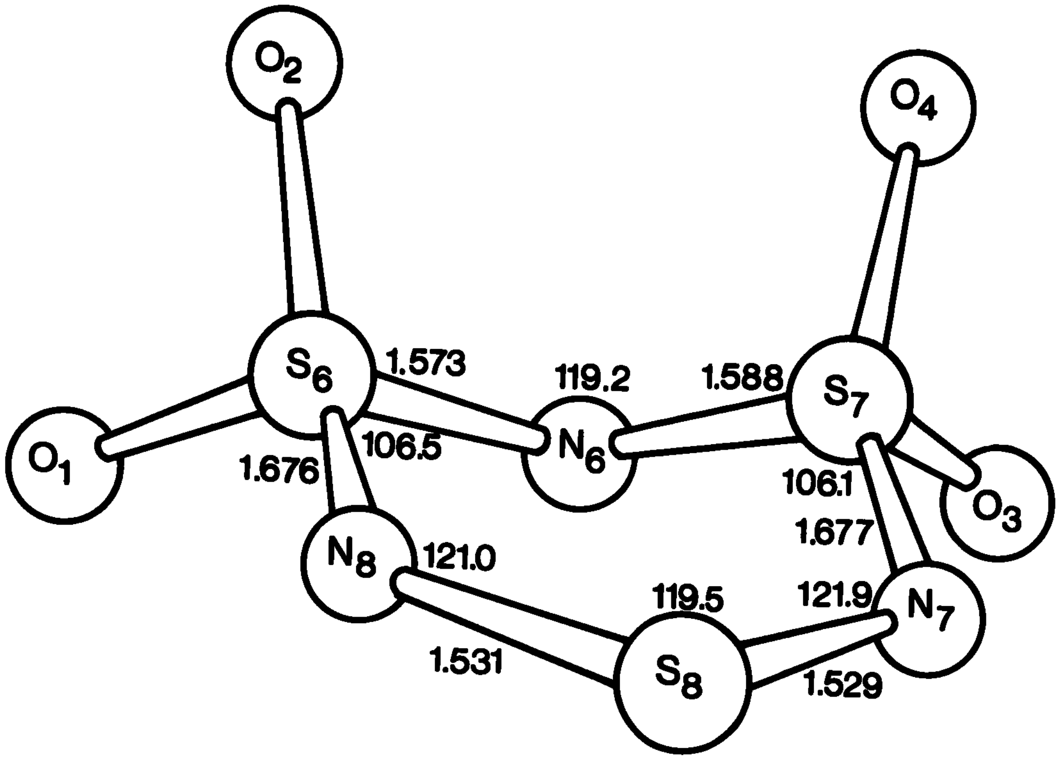
X, Y, and Z are orthogonal coordinates in Å oriented in the direction of a, b and c* respectively.

† this atom was not included in the calculation of the mean plane.

The S_3N_3 ring is not planar; however for five of the atoms the maximum deviation from their mean plane is 0.017Å, whereas the remaining nitrogen atom, N(6) lies 0.64Å away from this plane as shown in table 5.7. This is caused by the approximately tetrahedral coordination at S(6) and S(7), and by the other angles in the ring being close to 120°.

The bonding in this molecule may be considered in two sections; the SO_2-N-SO_2 part and the N-S-N part. This may be done because the bonds lengths of S(6)-N(8) and S(7)-N(7) of 1.676Å and 1.677Å approach those expected for single S-N bonds (cf. 1.73Å in S_7NH). Some shortening is expected because of the contraction of the orbitals on S(6) and S(7) due to the terminal oxygen atoms and also because of the sp^2 hybridisation at N(7) and N(8).

The negative charge on this anion resides on the SO_2-N-SO_2 part and is situated mostly on the oxygen atoms rather than on N(6). This is shown by the S-O distances being equal within experimental error and also by the length of the S-N bonds involving the bridging nitrogen atom N(6). The mean S-N distance of 1.581Å is considerably shorter than the normal single bond distance of 1.73Å and, together with the angle at N(6) of 119.2°, indicates that there is substantial multiple bonding in this region. This implies that the negative charge does not reside on N(6). The magnitude of the angle S(6)-N(6)-S(7) may in part be due to the steric requirements of the ring since a reduction in this angle would result in a decrease in the angles at S(8), N(7) and N(8) whereas angles of approximately 120° are normally found in sulphur diimides. The mean S-O distance of



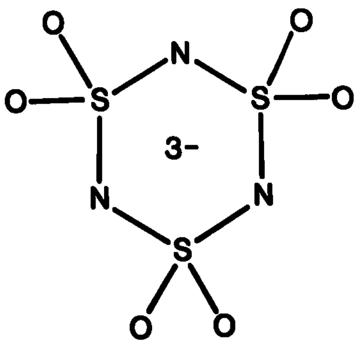
$S_3N_3O_4^-$

Figure 5.4

1.428 is close to that expected for a double bond eg. 1.43Å in SO_3 (Mcdonald and Cruickshank, 1967) and as expected indicates substantial multiple bonding in these bonds.

As mentioned earlier the coordination about S(6) and S(7) is approximately tetrahedral. The mean value of 116.3° for the angle between the terminal oxygen atoms is significantly larger than the tetrahedral angle and may be attributed to the effects of multiple bonding. The S-O bonds will contain more s character than those not involved in multiple bonding so that the angle between these bonds will be larger than 109°28'. Conversely the angles between the S-O multiple bonds and single bonds will be smaller which is seen in the values of 105.1° for N(8)-S(6)-O(1) and 105.9° for N(8)-S(6)-O(2), and similarly in the corresponding angles at S(7).

This part of the molecule may be compared with the $(NSO_2)_3^{3-}$ anion (Dalgaard, Hazell and Hazell, 1974) shown below

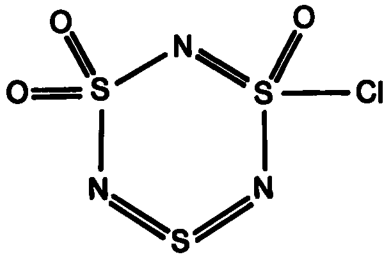


The S-N distances in this anion are all the same within experimental error and their mean value of 1.636Å is longer than that of 1.581Å seen in $S_3N_3O_4^-$. Likewise the mean S-O distance of 1.446Å is longer than that of 1.428Å in $S_3N_3O_4^-$. These differences may be accounted for by the presence of a full negative charge per SO_2 group in $(NSO_2)_3^{3-}$ as compared to formally half in $S_3N_3O_4^-$.

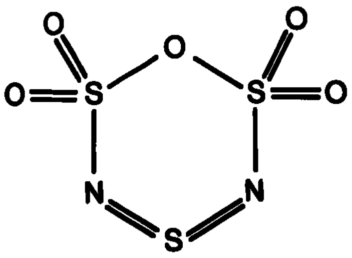
The remainder of the ring consists of a sulphur diimide fragment connected by two single bonds to the SO_2-N-SO_2 part. The S-N bonds within the diimide group are very short, i.e. S(8)-N(7) 1.529Å and S(8)-N(8) 1.532Å, with a mean of 1.531Å, and are close to the length of 1.54Å normally ascribed to S-N double bonds, eg. 1.54Å in $S_4N_4F_4$ (Wiegers and Vos, 1963). This is supported by the angle of 119.8° at S(8) and the mean of 121.4° for the angles at N(7) and N(8) which all indicate sp^2 hybridisation. This diimide fragment is similar to that seen in R-S-N=S=N-S-R, where R = p-C_6H_4Cl (Olsen and Barrick, 1973) in which the mean S=N bond distance was found to be 1.550(12)Å with an N=S=N angle of 124°.

The structure of $HS_3N_3O_4$ has not been studied crystallographically but spectroscopic studies suggested that the hydrogen is located on the nitrogen atom between the SO_2 groups (Roesky and Kuhtz, 1974). Thus it is expected that in this compound the S-O bonds will be shorter and the S-N bonds to the N-H group will be longer with a smaller angle at this nitrogen atom than is seen in $S_3N_3O_4^-$.

There are two other analogues of $S_3N_3O_4^-$ neither of which has been studied crystallographically, namely $S_3N_3O_3Cl$ (Roesky, 1971) and $S_3N_2O_5$ (Goehring et al., 1954). $S_3N_3O_3Cl$ has been assigned the structure III from spectroscopic evidence and is expected to contain an assymmetric SO_2-N-SOCl bridge.



III



IV

$S_3N_2O_5$ has been assigned the structure IV from spectroscopic and chemical evidence and in this compound the oxygen bridge is expected to be symmetric with a bridge angle less than 120^o.

5.6 Molecular Packing.

The structure involves the packing together of positive and negative ions and it is of interest to see whether examples of secondary bonding may be found similar to those seen in $[S_3N_2]_2^{2+}$ $(ClS_2O_6^-)_2$ described earlier. As noted before the intermolecular interactions which are most likely to give a decrease in the potential energy of the structure will involve sulphur atoms with either oxygen or nitrogen atoms; Whereas S---S, N---N, O---O or O---N interactions are expected to be destabilising. Thus it is not surprising that there are no contacts less than the appropriate van der Waals distance for these last four types of interaction. Conversely there are a significant number of S---O and S---N contacts less than their respective van der Waals distances of 3.32Å and 3.35Å, as shown in table 5.8.

Two of the shortest contacts are found between S(8) in the sulphur diimide fragment and O(2) at 1-x, 1-y, -z and O(3) at -x, 1-y, -z with distances of 2.860Å and 2.982Å respectively. The oxygen atoms lie 2.84Å and 2.51Å away from the mean plane of S(6), S(7), S(8), N(7) and N(8) and are almost directly below and above S(8). This interaction may involve the overlap of a lone pair on each of the oxygen atoms with unfilled π orbitals on the sulphur atom. The shortest contacts involving the $S_5N_5^+$ cation are associated with S(4) and S(5) to O(1) situated at 1+x, $\frac{1}{2}$-y, $\frac{1}{2}$+z with distances of 2.912Å and 2.981Å so that the oxygen atom bridges these two sulphur atoms. The oxygen atom lies 0.54Å away from the plane of the ring and is similar to the interaction seen in $[S_3N_2]_2^{2+}$ (section 3.6) but is probably not as strong. This may be interpreted as the overlap of a vacant orbital on each of the two sulphur atoms with the lone pairs on the oxygen atom. The other contacts between the ions are less specific in their orientation and may be primarily ionic in nature. It may be concluded that secondary bonding is an important feature in ionic sulphur-nitrogen compounds.

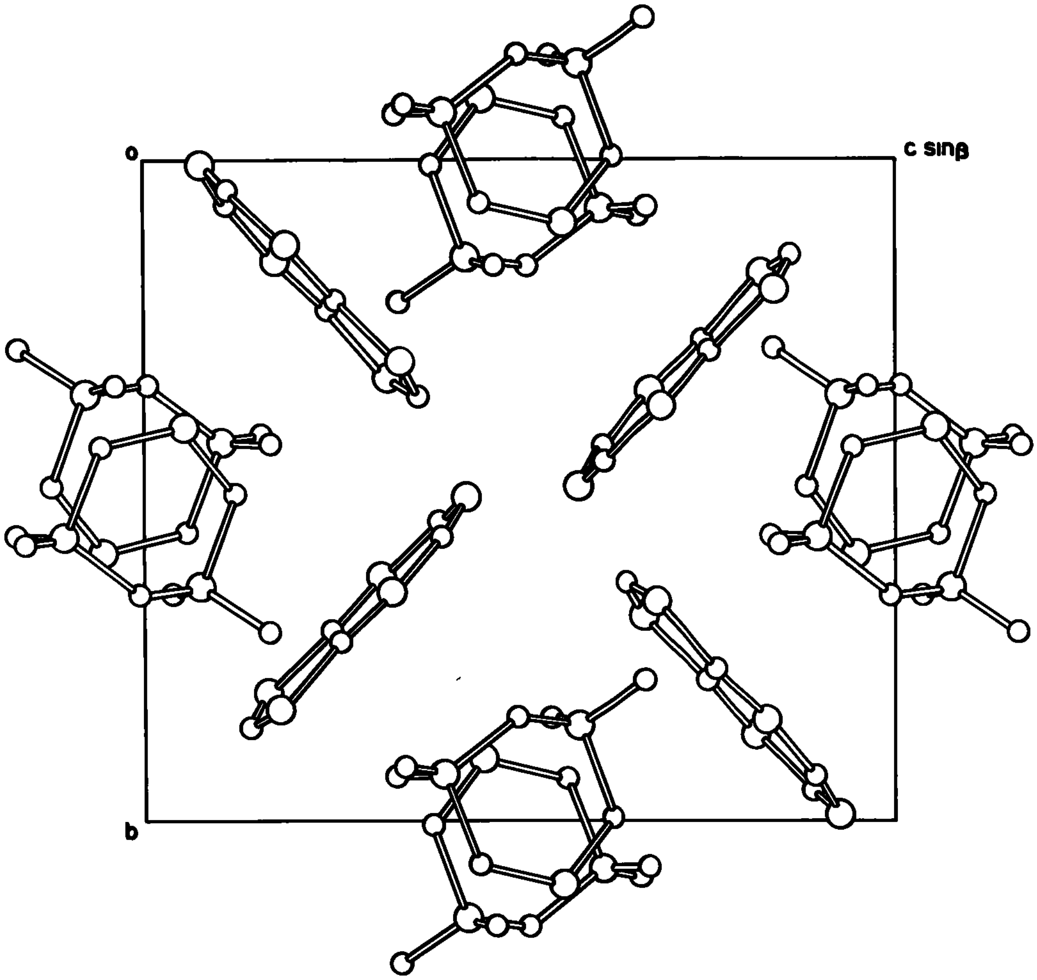
A projection on the [100] plane of the contents of the unit cell is shown in figure 5.5.

Table 5.8 $S_5N_5^+S_3N_3O_4^-$

S---O and S---N Intermolecular Contacts ≤ 3.5Å

Atom A	Atom B	Equivalent Posn. of B	Cell	A-B Å
S(1)	O(1)	2	(1, 0, 0)	3.490
S(1)	N(1)	2	(1, 0, 0)	3.363
S(2)	O(1)	4	(0, 0, 0)	3.339
S(3)	O(2)	4	(0, 0, 0)	3.107
S(3)	N(1)	3	(1, 0, 0)	3.303
S(4)	O(1)	4	(1, 0, 0)	2.912
S(4)	O(3)	1	(1, 0, 0)	3.055
S(4)	N(5)	3	(2, 0, 0)	3.232
S(4)	N(6)	4	(1, 0, 0)	3.418
S(4)	N(7)	3	(1,-1, 0)	3.356
S(5)	O(1)	4	(1, 0, 0)	2.981
S(5)	O(3)	1	(0, 0, 0)	3.347
S(5)	O(3)	3	(1,-1, 0)	3.306
S(8)	O(2)	2	(1, 1, 0)	2.860
S(8)	O(3)	2	(0, 1, 0)	2.982

Equivalent Position		
	1	x, y, z
	2	$-x, -y, -z$
	3	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
	4	$x, \frac{1}{2}-y, \frac{1}{2}+z$



$S_5N_5^+ S_3N_3O_4^-$

projection on the [100] plane

Figure 5.5

Table 5.9 $S_5N_5^+S_3N_3O_4^-$

Final Calculated and Observed Structure Factors

H	K	L	FO	FC
0	0	2	14.9	-15.6
0	0	4	143.6	-149.6
0	0	6	39.4	39.8
0	0	8	92.9	-92.1
0	0	10	23.0	-23.1
0	0	12	52.3	52.1
0	0	14	29.9	-30.2
0	0	16	13.5	12.9
0	1	1	71.6	-67.8
0	1	2	21.6	21.0
0	1	3	104.7	-106.4
0	1	4	5.0	4.7
0	1	5	44.0	45.9
0	1	6	-1.4	-0.4
0	1	7	0.0	-2.5
0	1	8	22.9	22.8
0	1	9	14.3	-14.1
0	1	10	26.0	-26.5
0	1	11	31.4	31.6
0	1	12	18.6	-19.3
0	1	13	9.2	9.0
0	1	14	8.6	7.3
0	1	15	7.8	7.3
0	1	16	14.7	13.8
0	2	0	6.9	8.3
0	2	1	6.9	-7.2
0	2	2	132.6	137.8
0	2	3	8.5	9.7
0	2	4	84.0	-80.8
0	2	5	61.3	-58.1
0	2	6	97.2	-97.3
0	2	7	11.2	10.2
0	2	8	0.0	1.6
0	2	9	36.4	36.4
0	2	10	30.0	28.1
0	2	11	15.1	14.3
0	2	12	26.6	-28.0
0	2	13	-2.0	1.0
0	2	14	6.5	6.0
0	2	15	-5.4	-5.9
0	3	1	38.2	36.8
0	3	2	170.0	-181.4
0	3	3	196.8	213.3
0	3	4	43.8	42.3
0	3	5	92.1	-94.0
0	3	6	15.6	13.8
0	3	7	62.6	-61.3
0	3	8	30.1	-29.8
0	3	9	25.6	24.9
0	3	10	16.2	16.8
0	3	11	23.4	-23.3
0	3	12	26.0	-26.1
0	3	13	28.0	28.0
0	3	14	0.0	-0.3
0	3	15	24.2	23.9
0	4	0	116.5	-121.4
0	4	1	33.2	31.9
0	4	2	8.6	-7.8
0	4	3	11.7	15.3
0	4	4	0.0	10.8
0	4	5	40.6	40.1
0	4	6	72.2	-69.1
0	4	7	10.4	-10.1
0	4	8	56.3	55.8
0	4	9	10.5	10.3
0	4	10	6.9	-6.9
0	4	11	-5.4	-5.7
0	4	12	0.0	0.1
0	4	13	-2.7	3.0
0	4	14	14.2	14.0
0	4	15	-4.9	-4.0
0	5	1	94.1	95.3
0	5	2	85.1	-83.3
0	5	3	25.4	-25.8
0	5	4	65.2	-65.5
0	5	5	16.7	-16.1
0	5	6	17.8	17.6
0	5	7	27.1	-27.5
0	5	8	34.2	35.4
0	5	9	47.9	-48.3
0	5	10	-1.1	-0.3
0	5	11	-3.3	2.9
0	5	12	-3.9	1.6
0	5	13	15.1	15.2
0	5	14	-4.9	0.3
0	6	0	51.8	50.1
0	6	1	21.4	22.0
0	6	2	9.4	-9.8
0	6	3	5.5	-5.5
0	6	4	-3.6	-1.0
0	6	5	45.5	-44.8
0	6	6	41.7	41.9
0	6	7	36.5	37.1
0	6	8	44.6	-44.9
0	6	9	36.7	-38.1
0	6	10	-4.3	5.6
0	6	11	-4.3	-4.4
0	6	12	32.4	32.7
0	6	13	19.8	18.3
0	6	14	14.6	14.0
0	7	1	45.8	45.2
0	7	2	46.4	45.7
0	7	3	59.0	-58.3
0	7	4	28.4	-28.1
0	7	5	15.2	15.4
0	7	6	37.1	37.8
0	7	7	9.6	-9.7
0	7	8	27.2	27.0
0	7	9	30.5	-31.5
0	7	10	17.2	-16.8
0	7	11	14.2	12.9
0	7	12	-4.8	4.9
0	7	13	13.0	-12.6
0	8	0	21.2	-20.4
0	8	1	27.0	-27.8
0	8	2	8.3	8.1
0	8	3	67.6	-69.1
0	8	4	21.1	20.9
0	8	5	14.0	-13.8
0	8	6	22.1	-21.8
0	8	7	22.3	-22.5
0	8	8	17.0	-16.1
0	8	9	12.6	13.4
0	8	10	0.0	0.7
0	8	11	16.2	16.3
0	8	12	0.0	-1.0
0	8	13	-6.4	4.8
0	9	1	9.6	9.9
0	9	2	8.7	6.8
0	9	3	33.6	35.0
0	9	4	55.2	56.5
0	9	5	17.9	-18.3
0	9	6	14.0	-15.0
0	9	7	25.3	-25.0
0	9	8	21.4	-22.2
0	9	9	11.4	10.4
0	9	10	18.6	19.0
0	9	11	0.0	0.7
0	9	12	-2.1	-4.9
0	10	0	-5.9	-5.1
0	10	1	54.4	-55.2
0	10	2	-5.9	4.2
0	10	3	9.1	-8.6
0	10	4	-5.8	5.6
0	10	5	7.4	7.0
0	10	6	-3.9	-4.9
0	10	7	10.5	-10.6
0	10	8	-3.9	-3.5
0	10	9	17.3	17.8
0	10	10	18.2	-17.6
0	10	11	-6.4	5.4
0	11	1	-4.0	-3.6
0	11	2	11.4	11.1
0	11	3	0.0	2.3
0	11	4	18.1	-17.9
0	11	5	6.5	-7.4
0	11	6	29.9	-29.8
0	11	7	-6.3	-7.0
0	11	8	-2.1	2.8
0	11	9	6.7	-7.6
0	12	0	28.6	28.3
0	12	1	21.7	22.6
0	12	2	19.7	19.8
0	12	3	-4.1	2.6
0	12	4	7.2	-6.6
0	12	5	0.0	0.6
0	12	6	7.2	-7.2
0	12	7	20.8	20.4
0	12	8	10.6	-10.3
0	13	1	15.9	-15.4
0	13	2	-5.6	-1.7
0	13	3	0.0	3.0
0	13	4	25.4	-25.5
0	13	5	-4.7	4.9
1	0	-16	15.8	-15.8
1	0	-14	11.5	10.9
1	0	-12	39.1	39.4
1	0	-10	16.2	16.3
1	0	-8	51.6	50.2
1	0	-6	31.7	-32.9
1	0	-4	162.0	-171.8
1	0	-2	58.2	-57.8
1	0	0	8.9	-10.4
1	0	2	5.7	-7.2
1	0	4	133.5	136.7
1	0	6	68.6	67.3
1	0	8	5.7	-5.8
1	0	10	14.6	-15.1
1	0	12	46.6	-46.5
1	0	14	10.8	-11.2
1	1	-16	14.0	13.3
1	1	-15	-4.5	-1.4
1	1	-14	27.9	-28.6
1	1	-13	20.8	-21.0
1	1	-12	-5.8	3.5
1	1	-11	8.7	-8.6
1	1	-10	21.9	-22.2
1	1	-9	19.9	20.3
1	1	-8	24.6	-23.9
1	1	-7	43.4	42.9
1	1	-6	36.1	37.5
1	1	-5	14.4	15.3
1	1	-4	64.4	63.9
1	1	-3	36.2	-35.0
1	1	-2	58.8	-58.3
1	1	-1	39.5	-37.6
1	1	0	11.2	11.9
1	1	1	16.2	14.7
1	1	2	57.8	-56.2
1	1	3	42.8	42.4
1	1	4	-4.8	-4.5
1	1	5	15.9	15.0
1	1	6	30.9	-28.5
1	1	7	50.7	-49.2
1	1	8	11.8	12.3
1	1	9	21.3	-21.3
1	1	10	27.9	-28.2
1	1	11	-5.6	4.8
1	1	12	30.5	-30.2
1	1	13	12.8	11.7
1	1	14	-5.0	4.1
1	1	15	7.0	8.6
1	2	-16	-6.0	-3.9
1	2	-15	18.2	-18.3
1	2	-14	-3.6	3.0
1	2	-13	11.1	11.2
1	2	-12	-4.2	-1.5
1	2	-11	61.6	62.3
1	2	-10	18.1	17.9
1	2	-9	9.9	-9.8
1	2	-8	-4.6	-4.7
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H	K	L	FO	FC
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2	7	1	16.7	-16.9
2	7	2	-5.2	6.5
2	7	3	20.2	-20.9
2	7	4	31.1	-31.7
2	7	5	32.9	32.3
2	7	6	11.3	-11.2
2	7	7	30.2	31.0
2	7	8	10.9	11.7
2	7	9	10.8	-10.4
2	7	10	16.5	-15.7
2	7	11	6.6	8.4
2	7	12	-4.7	5.7
2	7	13	-4.7	4.1
2	8	-13	13.3	12.6
2	8	-12	15.0	-14.6
2	8	-11	9.7	-9.5
2	8	-10	8.4	9.1
2	8	-9	25.7	26.0
2	8	-8	6.4	-6.8
2	8	-7	30.8	32.8
2	8	-6	15.0	15.2
2	8	-5	52.2	-53.2
2	8	-4	12.5	12.2
2	8	-3	18.9	-18.9
2	8	-2	12.5	-12.9
2	8	-1	8.4	-8.0
2	8	0	12.6	-12.7
2	8	1	24.5	-24.5

H	K	L	FO	FC
2	8	2	16.9	-16.4
2	8	3	47.5	48.0
2	8	4	11.3	10.4
2	8	5	56.7	57.2
2	8	6	0.0	1.1
2	8	7	-4.6	-6.5
2	8	8	-5.6	5.9
2	8	9	-2.2	0.5
2	8	10	22.3	21.6
2	8	11	9.9	-8.8
2	8	12	7.3	-7.3
2	9	-12	6.7	4.3
2	9	-11	18.3	-17.7
2	9	-10	7.0	-4.1
2	9	-9	10.7	-10.5
2	9	-8	11.0	10.5
2	9	-7	23.2	23.6
2	9	-6	7.4	-8.0
2	9	-5	21.9	22.1
2	9	-4	28.2	-28.8
2	9	-3	17.6	17.3
2	9	-2	65.2	65.7
2	9	-1	6.3	5.5
2	9	0	-4.0	-0.3
2	9	1	41.5	-42.3
2	9	2	42.6	-43.0
2	9	3	8.7	-9.6
2	9	4	0.0	-3.4
2	9	5	15.2	14.1
2	9	6	18.6	-18.8
2	9	7	0.0	-1.1
2	9	8	-4.9	-4.0
2	9	9	10.5	9.9
2	9	10	23.9	24.0
2	9	11	9.7	-9.9
2	10	-11	0.0	0.4
2	10	-10	0.0	-2.0
2	10	-9	12.0	-11.5
2	10	-8	21.7	21.6
2	10	-7	20.0	20.1
2	10	-6	0.0	-3.4
2	10	-5	-3.5	3.4
2	10	-4	22.5	-22.2
2	10	-3	39.7	-40.6
2	10	-2	0.0	2.8
2	10	-1	-4.4	-2.6
2	10	0	17.3	-17.5
2	10	1	-3.5	-2.8
2	10	2	13.2	-13.1
2	10	3	26.5	26.4
2	10	4	16.4	16.6
2	10	5	24.8	25.0
2	10	6	-4.8	3.9
2	10	7	16.5	-15.5
2	10	8	10.0	10.6
2	10	9	9.7	-9.3
2	10	10	9.5	7.3
2	11	-9	-5.5	-3.6
2	11	-8	-6.3	-5.7
2	11	-7	10.0	10.6
2	11	-6	0.0	2.5
2	11	-5	-4.9	5.7
2	11	-4	6.5	-7.3
2	11	-3	19.7	19.0
2	11	-2	25.3	-25.5
2	11	-1	-2.7	-1.5
2	11	0	15.6	16.7
2	11	1	0.0	-2.6
2	11	2	-1.2	-2.3
2	11	3	-2.8	-3.5
2	11	4	0.0	0.7
2	11	5	-5.9	-6.4
2	11	6	17.4	17.4
2	11	7	10.0	10.2
2	11	8	18.4	18.4
2	11	9	-6.5	6.0
2	12	-7	-2.1	-3.8
2	12	-6	-5.1	5.1
2	12	-5	23.8	23.8
2	12	-4	20.9	20.4
2	12	-3	-1.6	-1.0
2	12	-2	11.5	-11.3
2	12	-1	16.5	-17.1
2	12	0	28.7	-28.2
2	12	1	18.9	19.0
2	12	2	-5.5	-6.7
2	12	3	-5.9	-5.2
2	12	4	15.0	-14.3
2	12	5	17.6	-17.7
2	12	6	15.1	15.5
2	12	7	-5.4	-5.9
2	13	-5	6.8	-3.0
2	13	-4	7.2	-7.0
2	13	-3	-3.0	-4.2
2	13	-2	12.7	-13.3

H	K	L	FO	FC
2	13	-1	-0.9	1.2
2	13	0	13.2	-14.2
2	13	1	14.2	15.0
2	13	2	20.8	21.4
2	13	3	8.2	7.0
2	13	4	9.5	8.6
3	0	-14	17.2	17.8
3	0	-12	-4.0	-5.9
3	0	-10	77.7	-78.4
3	0	-8	-3.2	-1.0
3	0	-6	58.1	57.5
3	0	-4	66.2	-61.7
3	0	-2	41.5	45.6
3	0	0	23.6	25.8
3	0	2	151.3	-152.9
3	0	4	31.4	29.9
3	0	6	53.6	-52.7
3	0	8	105.8	-108.8
3	0	10	65.1	65.8
3	0	12	42.9	43.6
3	0	14	11.5	10.3
3	1	-15	-3.3	3.5
3	1	-14	25.7	-24.9
3	1	-13	-1.5	2.4
3	1	-12	34.3	34.7
3	1	-11	10.8	10.1
3	1	-10	37.6	37.8
3	1	-9	28.6	-28.8
3	1	-8	-4.5	3.5
3	1	-7	19.9	-20.3
3	1	-6	16.1	17.0
3	1	-5	25.3	27.3
3	1	-4	26.4	-27.2
3	1	-3	21.5	19.8
3	1	-2	124.0	-129.1
3	1	-1	15.5	18.5
3	1	0	100.4	100.7
3	1	1	46.7	43.4
3	1	2	31.2	-27.4
3	1	3	39.5	35.3
3	1	4	10.2	-10.7
3	1	5	6.8	6.9
3	1	6	-4.7	-1.3
3	1	7	26.8	-25.2
3	1	8	0.0	0.2
3	1	9	30.6	29.9
3	1	10	9.1	-9.9
3	1	11	7.7	9.2
3	1	12	31.2	31.8
3	1	13	27.1	-22.4
3	1	14	-4.5	0.3
3	2	-15	7.4	-6.0
3	2	-14	-1.4	1.4
3	2	-13	20.7	-21.0
3	2	-12	21.6	-20.1
3	2	-11	-3.9	2.5
3	2	-10	-5.5	6.0
3	2	-9	69.3	-70.1
3	2	-8	9.3	-10.2
3	2	-7	37.1	-36.9
3	2	-6	42.4	41.7
3	2	-5	88.4	89.4
3	2	-4	69.2	69.0
3	2	-3	11.2	11.5
3	2	-2	32.3	-31.6
3	2	-1	38.0	37.6
3	2	0	-2.6	-2.4
3	2	1	50.9	48.8
3	2	2	44.4	43.3
3	2	3	56.2	-56.1
3	2	4	46.0	-44.5
3	2	5	5.9	7.3
3	2	6	15.1	-14.6
3	2	7	35.7	35.6
3	2	8	7.5	8.2
3	2	9	18.0	-18.5
3	2	10	14.6	-14.9
3	2	11	22.4	-23.2
3	2	12	23.7	23.6
3	2	13	-5.1	-2.9
3	2	14	13.8	14.5
3	3	-15	19.5	18.4
3	3	-14	10.5	-10.6
3	3	-13	-4.8	5.1
3	3	-12	15.7	-15.1
3	3	-11	24.3	-25.1
3	3	-10	47.7	49.1
3	3	-9	21.1	-21.3
3	3	-8	62.2	63.4
3	3	-7	73.0	-73.8
3	3	-6	9.0	-9.4
3	3	-5	10.8	10.1
3	3	-4	85.2	-84.1
3	3	-3	39.0	39.5
3	3	-2	24.1	20.8

H	K	L	FO	FC
3	3	-1	11.7	-11.1
3	3	0	75.7	-73.9
3	3	1	25.8	27.0
3	3	2	26.7	25.3
3	3	3	19.8	-20.1
3	3	4	11.7	11.7
3	3	5	112.9	-112.7
3	3	6	55.2	-56.0
3	3	7	9.7	9.5
3	3	8	0.0	-0.3
3	3	9	9.6	-9.8
3	3	10	68.6	70.8
3	3	11	13.5	13.4
3	3	12	0.0	2.6
3	3	13	38.1	37.7
3	3	14	-2.2	-1.9
3	4	-15	-4.8	4.6
3	4	-14	-2.9	4.4
3	4	-13	23.5	21.9
3	4	-12	-3.9	-2.4
3	4	-11	17.5	-17.8
3	4	-10	6.7	-8.1
3	4	-9	11.3	-10.8
3	4	-8	21.2	21.0
3	4	-7	-2.9	4.0
3	4	-6	32.6	-32.3
3	4	-5	45.0	-44.9
3	4	-4	-4.1	4.1
3	4	-3	29.6	29.9
3	4	-2	42.1	39.8
3	4	-1	48.5	47.5
3	4	0	14.0	12.9
3	4	1	9.2	-9.7
3	4	2	14.7	15.0
3	4	3	34.4	34.4
3	4	4	9.7	-8.6
3	4	5	5.5	5.7
3	4	6	26.7	25.9
3	4	7	14.4	-15.7
3	4	8	29.4	29.0
3	4	9	6.5	-5.5
3	4	10	12.7	-12.4
3	4	11	23.9	-24.2
3	4	12	-1.3	-1.5
3	4	13	12.2	-11.7
3	4	14	-5.9	-4.6
3	5	-14	-3.8	-3.1
3	5	-13	16.1	15.4
3	5	-12	32.0	-31.7
3	5	-11	24.6	-24.8
3	5	-10	26.1	-26.6
3	5	-9	28.3	-28.6
3	5	-8	65.2	66.5
3	5	-7	66.9	68.5
3	5	-6	9.8	9.4
3	5	-5	-1.8	2.5
3	5	-4	18.4	-18.0
3	5	-3	43.7	42.8
3	5	-2	6.9	7.6
3	5	-1	42.1	41.9
3	5	0	-1.6	1.7
3	5	1	30.9	-31.0
3	5	2	27.7	-26.6
3	5	3	43.1	-41.9
3	5	4	17.5	-17.2
3	5	5	7.0	8.1
3	5	6	38.0	-38.2
3	5	7	52.4	-53.7
3	5	8	31.0	31.9
3	5	9	-4.1	-5.2
3	5	10	37.8	37.9
3	5	11	27.4	26.5
3	5	12	-4.1	6.4
3	5	13	20.4	20.1
3	6	-14	-5.8	6.2
3	6	-13	8.5	9.4
3	6	-12	17.4	17.7
3	6	-11	14.5	14.3
3	6	-10	16.4	-15.9
3	6	-9	10.3	9.9
3	6	-8	52.0	-54.0
3	6	-7	11.4	-10.6
3	6	-6	60.3	-61.9
3	6	-5	-3.8	3.4
3	6	-4	35.4	-36.2
3	6	-3	31.0	-31.3
3	6	-2	75.1	75.0
3	6	-1	19.8	-19.8
3	6	0	32.6	31.4
3	6	1	40.6	40.3
3	6	2	29.9	-28.8
3	6	3	16.6	-17.1
3	6	4	16.7	-16.6
3	6	5	-2.1	-3.0
3	6	6	33.6	-34.9

H	K	L	FO	FC
3	6	7	23.1	23.4
3	6	8	15.3	15.8
3	6	9	13.2	-13.3
3	6	10	34.2	34.4
3	6	11	0.0	-0.4
3	6	12	15.2	-15.7
3	6	13	11.5	10.3
3	7	-13	-4.9	-5.9
3	7	-12	8.8	-7.8
3	7	-11	8.0	-8.2
3	7	-10	-6.1	5.7
3	7	-9	-3.9	2.7
3	7	-8	26.9	-27.3
3	7	-7	20.3	19.7
3	7	-6	23.2	23.2
3	7	-5	56.2	57.8
3	7	-4	28.2	28.2
3	7	-3	-4.3	-4.3
3	7	-2	33.3	-34.2
3	7	-1	-2.8	-2.1
3	7	0	45.4	46.3
3	7	1	36.1	-36.1
3	7	2	24.0	24.2
3	7	3	20.5	20.7
3	7	4	48.7	-49.8
3	7	5	8.5	8.8
3	7	6	25.0	25.2
3	7	7	13.1	-12.6
3	7	8	-3.6	-5.8
3	7	9	0.0	-1.4
3	7	10	18.0	-18.3
3	7	11	14.7	13.8
3	7	12	9.0	8.2
3	8	-12	-3.8	4.2
3	8	-11	6.8	6.3
3	8	-10	28.3	28.3
3	8	-9	17.5	17.7
3	8	-8	42.0	-42.4
3	8	-7	-5.0	3.5
3	8	-6	37.9	-39.5
3	8	-5	17.8	18.6
3	8	-4	46.4	47.5
3	8	-3	0.0	-2.2
3	8	-2	23.7	23.9
3	8	-1	34.8	-34.7
3	8	0	40.5	41.8
3	8	1	20.7	-21.3
3	8	2	0.0	2.9
3	8	3	26.4	-26.5
3	8	4	63.8	-65.9
3	8	5	9.0	-8.2
3	8	6	17.5	-17.3
3	8	7	17.0	16.5
3	8	8	24.9	25.3
3	8	9	20.7	20.2
3	8	10	-5.5	4.1
3	8	11	22.2	23.1
3	9	-11	0.0	-2.3
3	9	-10	-1.5	-2.8
3	9	-9	24.5	-24.0
3	9	-8	8.5	-9.2
3	9	-7	29.0	-28.2
3	9	-6	14.4	-14.7
3	9	-5	7.6	6.4
3	9	-4	10.2	10.0
3	9	-3	-0.9	0.1
3	9	-2	28.2	28.4
3	9	-1	20.7	-21.4
3	9	0	11.5	-11.5
3	9	1	31.0	31.6
3	9	2	10.4	11.0
3	9	3	24.6	-25.3
3	9	4	26.7	26.1
3	9	5	0.0	-2.4
3	9	6	10.1	-9.4
3	9	7	8.1	7.6
3	9	8	7.8	-6.9
3	9	9	-6.3	-4.7
3	9	10	10.4	-10.6
3	10	-10	-2.0	0.4
3	10	-9	15.0	14.7
3	10	-8	18.0	18.8
3	10	-7	27.1	26.9
3	10	-6	15.0	14.7
3	10	-5	17.1	-15.6
3	10	-4	-4.5	1.4
3	10	-3	7.9	7.0
3	10	-2	27.5	28.5
3	10	-1	0.0	4.7
3	10	0	17.5	17.1
3	10	1	41.6	-42.2
3	10	2	31.5	-31.6
3	10	3	15.0	15.0
3	10	4	22.2	-21.2
3	10	5	-1.9	-2.0

H	K	L	FO	FC
3	10	6	14.1	13.5
3	10	7	18.3	-18.3
3	10	8	-4.8	-5.4
3	10	9	31.3	30.0
3	11	-9	12.4	-12.6
3	11	-8	-4.6	-5.1
3	11	-7	12.3	-11.8
3	11	-6	18.1	18.2
3	11	-5	24.7	-24.1
3	11	-4	-5.1	2.4
3	11	-3	-6.1	5.2
3	11	-2	7.5	7.6
3	11	-1	36.0	36.2
3	11	0	9.6	-9.1
3	11	1	7.3	-8.1
3	11	2	34.9	-34.2
3	11	3	0.0	0.1
3	11	4	-3.7	5.8
3	11	5	-3.1	-3.2
3	11	6	10.4	11.3
3	11	7	-2.5	-1.3
3	11	8	7.8	7.6
3	12	-7	13.6	12.3
3	12	-6	-2.4	3.3
3	12	-5	6.7	4.6
3	12	-4	-1.3	2.8
3	12	-3	14.4	-13.7
3	12	-2	14.9	13.3
3	12	-1	10.2	9.5
3	12	0	10.2	-10.6
3	12	1	17.3	17.3
3	12	2	9.3	-8.9
3	12	3	-5.6	-5.5
3	12	4	-2.3	-0.7
3	12	5	0.0	1.5
3	12	6	17.9	-17.6
3	13	-4	12.5	12.8
3	13	-3	16.1	15.4
3	13	-2	12.0	-11.4
3	13	-1	-2.1	-3.6
3	13	0	15.1	-15.4
3	13	1	-2.1	2.9
3	13	2	9.0	-9.0
3	13	3	-5.6	7.0
4	0	-14	9.7	10.2
4	0	-12	15.3	-15.0
4	0	-10	8.4	7.6
4	0	-8	12.8	12.7
4	0	-6	6.4	6.1
4	0	-4	114.1	-114.0
4	0	-2	12.5	10.2
4	0	0	110.2	110.4
4	0	2	109.3	108.0
4	0	4	40.3	38.5
4	0	6	0.0	-1.2
4	0	8	92.6	-93.7
4	0	10	22.3	-22.3
4	0	12	0.0	0.7
4	0	14	7.1	-5.6
4	1	-15	-2.4	3.2
4	1	-14	27.0	-26.5
4	1	-13	28.7	28.6
4	1	-12	30.6	31.5
4	1	-11	36.9	37.6
4	1	-10	24.3	-24.3
4	1	-9	33.4	-32.9
4	1	-8	30.1	31.4
4	1	-7	37.4	-38.0
4	1	-6	73.6	72.8
4	1	-5	46.4	49.3
4	1	-4	26.9	-28.5
4	1	-3	0.0	-0.6
4	1	-2	28.1	27.4
4	1	-1	25.0	-24.4
4	1	0	14.0	14.2
4	1	1	30.5	-31.0
4	1	2	42.1	-44.0
4	1	3	76.9	-75.4
4	1	4	44.2	42.0
4	1	5	28.4	28.5
4	1	6	6.6	7.7
4	1	7	43.2	43.5
4	1	8	-3.5	4.1
4	1	9	11.1	-12.1
4	1	10	25.6	26.3
4	1	11	-4.4	0.8
4	1	12	11.9	-13.0
4	1	13	9.6	9.4
4	1	14	-2.5	-4.8
4	2	-15	0.0	4.9
4	2	-14	6.8	-6.2
4	2	-13	48.4	48.6
4	2	-12	-1.5	-1.7
4	2	-11	18.9	-18.4
4	2	-10	-3.4	1.0

H	K	L	FO	FC
4	2	-9	95.9	-98.2
4	2	-8	0.0	2.6
4	2	-7	52.2	53.1
4	2	-6	43.0	-42.2
4	2	-5	60.8	-60.3
4	2	-4	-3.6	-0.3
4	2	-3	72.6	-70.2
4	2	-2	33.5	-32.1
4	2	-1	86.4	86.9
4	2	0	34.6	33.9
4	2	1	53.5	-51.1
4	2	2	49.5	48.1
4	2	3	12.3	12.1
4	2	4	39.1	37.4
4	2	5	62.7	63.0
4	2	6	48.3	-48.4
4	2	7	80.5	-82.5
4	2	8	12.9	-12.6
4	2	9	16.1	-16.2
4	2	10	-5.4	-4.6
4	2	11	14.5	15.0
4	2	12	-2.3	-1.2
4	2	13	0.0	0.0
4	2	14	-4.7	2.6
4	3	-15	14.2	-13.4
4	3	-14	19.7	-19.4
4	3	-13	12.9	12.6
4	3	-12	-4.1	-4.6
4	3	-11	30.1	30.9
4	3	-10	27.0	28.1
4	3	-9	10.2	10.8
4	3	-8	22.7	23.4
4	3	-7	32.7	-32.9
4	3	-6	10.1	10.2
4	3	-5	23.4	-24.0
4	3	-4	13.9	13.6
4	3	-3	15.7	14.7
4	3	-2	34.3	34.7
4	3	-1	12.9	12.3
4	3	0	43.0	-41.0
4	3	1	12.4	12.9
4	3	2	26.1	-26.6
4	3	3	62.4	61.8
4	3	4	-1.7	0.7
4	3	5	13.8	13.8
4	3	6	44.5	-44.5
4	3	7	20.3	-20.5
4	3	8	16.6	16.1
4	3	9	27.4	-28.6
4	3	10	26.6	27.4
4	3	11	30.3	-30.3
4	3	12	9.0	-10.2
4	3	13	-5.2	7.3
4	4	-14	21.3	20.8
4	4	-13	11.6	-12.3
4	4	-12	9.9	7.8
4	4	-11	24.1	-23.9
4	4	-10	0.0	-4.1
4	4	-9	-5.0	6.0
4	4	-8	-5.0	5.7
4	4	-7	25.9	-26.2
4	4	-6	9.6	-8.8
4	4	-5	52.7	53.4
4	4	-4	27.7	-27.6
4	4	-3	-3.4	-3.3
4	4	-2	26.8	26.7
4	4	-1	50.2	-49.4
4	4	0	52.2	-51.9
4	4	1	37.7	37.0
4	4	2	-4.0	2.2
4	4	3	68.1	68.3
4	4	4	6.7	-4.2
4	4	5	16.0	15.7
4	4	6	9.1	-9.4
4	4	7	24.3	25.0
4	4	8	14.6	14.4
4	4	9	19.2	-20.1
4	4	10	13.8	13.0
4	4	11	9.4	-9.7
4	4	12	-7.0	1.9
4	4	13	-6.3	7.4
4	5	-14	-3.3	2.2
4	5	-13	-3.5	-0.6
4	5	-12	14.4	-14.1
4	5	-11	25.3	-25.3
4	5	-10	37.2	37.0
4	5	-9	18.8	19.4
4	5	-8	28.8	-28.6
4	5	-7	-4.9	3.9
4	5	-6	55.9	-56.7
4	5	-5	79.9	-81.7
4	5	-4	49.9	51.2
4	5	-3	34.4	34.0
4	5	-2	37.5	-37.3
4	5	-1	30.1	30.3

H	K	L	FO	FC
4	5	0	-5.1	6.3
4	5	1	10.6	10.6
4	5	2	46.9	46.3
4	5	3	72.3	73.0
4	5	4	95.0	-95.6
4	5	5	-3.0	-3.6
4	5	6	21.6	-21.9
4	5	7	51.0	-51.2
4	5	8	12.6	12.8
4	5	9	19.0	-19.0
4	5	10	12.4	-13.3
4	5	11	6.8	-6.3
4	5	12	13.9	15.4
4	5	13	0.0	1.2
4	6	-13	10.3	-9.4
4	6	-12	30.5	31.1
4	6	-11	14.9	-14.4
4	6	-10	14.7	15.2
4	6	-9	-4.1	0.9
4	6	-8	0.0	3.9
4	6	-7	24.2	24.4
4	6	-6	10.1	-10.0
4	6	-5	24.6	25.3
4	6	-4	13.6	-12.3
4	6	-3	7.6	7.3
4	6	-2	38.6	-38.9
4	6	-1	34.3	-35.1
4	6	0	11.3	10.4
4	6	1	30.3	29.9
4	6	2	12.8	13.0
4	6	3	24.7	-24.3
4	6	4	-4.9	-2.2
4	6	5	9.1	10.0
4	6	6	15.1	15.3
4	6	7	13.6	12.3
4	6	8	-4.6	4.7
4	6	9	24.7	-25.0
4	6	10	18.1	-17.7
4	6	11	0.0	0.1
4	6	12	-3.7	3.4
4	7	-13	9.3	-8.6
4	7	-12	6.8	7.0
4	7	-11	0.0	-3.4
4	7	-10	25.3	-25.0
4	7	-9	9.1	-8.2
4	7	-8	-1.7	4.6
4	7	-7	7.8	-7.7
4	7	-6	-4.4	4.9
4	7	-5	12.1	11.1
4	7	-4	29.0	-29.1
4	7	-3	37.5	-37.9
4	7	-2	8.2	7.1
4	7	-1	18.0	18.0
4	7	0	27.4	27.1
4	7	1	58.8	59.0
4	7	2	-2.8	-2.4
4	7	3	7.5	-7.7
4	7	4	26.6	27.3
4	7	5	17.2	-17.2
4	7	6	21.6	21.5
4	7	7	10.7	-11.0
4	7	8	-2.9	-5.6
4	7	9	10.9	-12.5
4	7	10	-2.2	1.7
4	7	11	10.4	8.9
4	8	-12	16.3	16.7
4	8	-11	0.0	-3.1
4	8	-10	18.8	19.1
4	8	-9	-4.2	-4.2
4	8	-8	31.1	-31.3
4	8	-7	0.0	0.4
4	8	-6	13.5	14.1
4	8	-5	10.2	-10.2
4	8	-4	6.2	-5.2
4	8	-3	11.4	11.6
4	8	-2	36.6	-37.0
4	8	-1	40.7	40.6
4	8	0	39.7	40.2
4	8	1	31.5	-31.3
4	8	2	7.4	7.6
4	8	3	6.2	-5.8
4	8	4	14.9	-14.8
4	8	5	40.2	-41.5
4	8	6	15.8	15.5
4	8	7	42.5	-42.1
4	8	8	12.2	-11.7
4	8	9	9.4	10.2
4	8	10	12.9	-12.9
4	8	11	11.8	12.5
4	9	-11	20.4	20.2
4	9	-10	20.1	-19.0
4	9	-9	10.1	9.9
4	9	-8	0.0	1.4
4	9	-7	-4.6	-2.9
4	9	-6	15.3	16.0

H	K	L	FO	FC
4	9	-5	20.6	-20.1
4	9	-4	13.5	-14.5
4	9	-3	34.0	-33.9
4	9	-2	6.4	6.3
4	9	-1	8.1	6.3
4	9	0	21.5	-21.9
4	9	1	16.9	17.2
4	9	2	-2.8	3.3
4	9	3	13.2	13.4
4	9	4	47.7	48.0
4	9	5	13.2	13.3
4	9	6	-3.6	0.4
4	9	7	18.8	-18.4
4	9	8	8.2	-8.4
4	9	9	0.0	-3.7
4	9	10	9.7	9.2
4	10	-10	9.5	-9.4
4	10	-9	-3.7	5.1
4	10	-8	-5.2	5.5
4	10	-7	11.8	-11.2
4	10	-6	9.7	-10.1
4	10	-5	7.0	-7.7
4	10	-4	-4.1	-2.3
4	10	-3	17.3	17.9
4	10	-2	37.3	38.3
4	10	-1	14.6	13.9
4	10	0	-5.1	5.9
4	10	1	14.8	14.8
4	10	2	7.1	-5.0
4	10	3	14.4	-14.1
4	10	4	10.1	9.2
4	10	5	20.2	-20.1
4	10	6	16.7	-17.0
4	10	7	0.0	-2.5
4	10	8	16.3	-15.4
4	11	-8	18.8	-18.2
4	11	-7	0.0	-2.6
4	11	-6	-3.2	5.4
4	11	-5	31.5	-31.0
4	11	-4	15.0	13.6
4	11	-3	0.0	-0.3
4	11	-2	11.1	-13.2
4	11	-1	11.9	-12.2
4	11	0	13.8	13.6
4	11	1	11.1	-8.2
4	11	2	-5.2	2.3
4	11	3	18.0	18.7
4	11	4	16.8	-16.1
4	11	5	0.0	-0.2
4	11	6	6.7	-6.2
4	11	7	-3.0	-0.3
4	12	-6	18.3	-18.9
4	12	-5	-3.9	-1.5
4	12	-4	0.0	-1.4
4	12	-3	8.3	-8.9
4	12	-2	7.0	5.5
4	12	-1	-5.3	6.2
4	12	0	-4.6	4.1
4	12	1	9.9	9.0
4	12	2	29.8	29.9
4	12	3	8.1	-8.9
4	12	4	-3.4	0.4
5	0	-14	14.6	-14.8
5	0	-12	21.8	-22.2
5	0	-10	33.8	34.7
5	0	-8	-4.0	4.6
5	0	-6	14.1	-14.1
5	0	-4	27.8	-29.4
5	0	-2	31.4	-30.7
5	0	0	7.9	8.8
5	0	2	-5.1	-5.4
5	0	4	56.7	55.5
5	0	6	57.4	58.8
5	0	8	17.2	17.6
5	0	10	26.6	25.4
5	0	12	23.2	-23.7
5	1	-15	0.0	2.0
5	1	-14	-4.4	5.4
5	1	-13	-4.1	-4.6
5	1	-12	-4.4	1.2
5	1	-11	-2.8	-0.6
5	1	-10	7.2	-6.7
5	1	-9	8.6	8.9
5	1	-8	34.6	-35.0
5	1	-7	36.8	36.9
5	1	-6	8.4	9.4
5	1	-5	32.9	33.3
5	1	-4	43.8	43.8
5	1	-3	28.1	-27.0
5	1	-2	14.9	15.4
5	1	-1	13.0	-12.2
5	1	0	13.1	11.8
5	1	1	34.8	-35.7
5	1	2	5.6	-4.6
5	1	3	25.5	-24.2

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	1	4	43.1	-43.4	5	5	-11	-5.6	-4.8	5	9	-8	10.9	10.1	6	2	-14	7.4	-8.2
5	1	5	24.2	26.4	5	5	-10	10.9	10.2	5	9	-7	13.8	13.8	6	2	-13	-6.5	-6.3
5	1	6	6.3	-6.2	5	5	-9	21.8	22.2	5	9	-6	6.5	4.8	6	2	-12	11.2	11.6
5	1	7	24.3	-24.5	5	5	-8	13.2	-12.7	5	9	-5	-3.9	-0.7	6	2	-11	-5.5	5.7
5	1	8	15.1	14.6	5	5	-7	-3.7	-0.7	5	9	-4	-2.5	-1.6	6	2	-10	0.0	2.9
5	1	9	20.2	-20.4	5	5	-6	21.6	-22.2	5	9	-3	6.6	-7.1	6	2	-9	12.0	-11.6
5	1	10	11.7	-12.6	5	5	-5	55.2	-56.4	5	9	-2	-5.3	-3.7	6	2	-8	23.2	-23.1
5	1	11	-2.2	4.8	5	5	-4	30.3	-30.6	5	9	-1	-6.1	4.0	6	2	-7	90.4	94.8
5	1	12	-4.4	1.5	5	5	-3	-3.6	-4.3	5	9	0	17.6	-17.9	6	2	-6	-5.9	-6.9
5	1	13	-3.9	0.7	5	5	-2	9.2	9.8	5	9	1	-1.5	-0.4	6	2	-5	11.5	11.9
5	2	-15	-4.8	-3.7	5	5	-1	15.9	15.8	5	9	2	8.2	7.6	6	2	-4	35.6	34.9
5	2	-14	9.6	-7.6	5	5	0	8.8	8.6	5	9	3	11.7	-11.6	6	2	-3	47.6	-48.6
5	2	-13	-3.4	-5.3	5	5	1	18.0	-18.2	5	9	4	-4.4	1.8	6	2	-2	8.3	-8.4
5	2	-12	6.7	7.5	5	5	2	6.7	-5.5	5	9	5	-3.3	3.4	6	2	-1	58.0	58.8
5	2	-11	8.1	8.7	5	5	3	20.9	21.5	5	9	6	21.6	-20.7	6	2	0	5.7	3.2
5	2	-10	13.0	12.8	5	5	4	42.2	43.7	5	9	7	11.1	11.4	6	2	1	55.3	-56.1
5	2	-9	24.5	24.5	5	5	5	27.9	27.1	5	9	8	10.5	11.1	6	2	2	51.4	-52.7
5	2	-8	-1.8	-1.0	5	5	6	27.2	26.8	5	10	-9	19.7	-19.4	6	2	3	71.4	-73.8
5	2	-7	32.2	32.1	5	5	7	-3.3	5.1	5	10	-8	7.1	-6.1	6	2	4	21.1	-20.6
5	2	-6	17.6	-17.4	5	5	8	18.6	-17.8	5	10	-7	-3.9	4.0	6	2	5	35.0	35.5
5	2	-5	22.3	-22.5	5	5	9	11.9	11.8	5	10	-6	9.4	-10.6	6	2	6	28.5	29.0
5	2	-4	6.8	-6.9	5	5	10	12.5	-13.5	5	10	-5	-5.3	-6.3	6	2	7	16.2	-15.7
5	2	-3	74.4	-74.4	5	5	11	7.2	-8.2	5	10	-4	17.7	-17.9	6	2	8	27.8	28.8
5	2	-2	19.4	-19.1	5	5	12	13.5	-12.9	5	10	-3	8.0	-8.9	6	2	9	18.5	18.9
5	2	-1	42.6	-43.5	5	6	-13	-5.3	-2.7	5	10	-2	0.0	0.6	6	2	10	8.0	-9.0
5	2	0	-3.8	-3.9	5	6	-12	9.0	-11.4	5	10	-1	23.4	22.6	6	2	11	29.4	28.7
5	2	1	36.3	35.1	5	6	-11	11.9	-12.9	5	10	0	6.7	-6.8	6	2	12	-6.0	4.1
5	2	2	28.1	27.8	5	6	-10	-2.3	-2.1	5	10	1	14.3	-13.8	6	3	-14	14.0	14.1
5	2	3	31.9	31.7	5	6	-9	12.0	-11.3	5	10	2	11.6	11.9	6	3	-13	-3.9	1.1
5	2	4	-3.3	-1.0	5	6	-8	25.9	25.7	5	10	3	-2.3	2.7	6	3	-12	8.2	8.5
5	2	5	-2.9	0.3	5	6	-7	8.0	8.9	5	10	4	14.2	15.2	6	3	-11	16.0	-15.1
5	2	6	6.9	6.2	5	6	-6	55.3	56.5	5	10	5	15.9	16.4	6	3	-10	18.1	-18.9
5	2	7	-5.8	6.5	5	6	-5	15.4	14.3	5	10	6	-5.3	5.0	6	3	-9	-6.2	-5.7
5	2	8	8.8	8.5	5	6	-4	16.0	16.2	5	10	7	-6.0	-6.9	6	3	-8	34.6	-35.6
5	2	9	-4.4	3.4	5	6	-3	-3.1	2.7	5	11	-7	23.0	23.3	6	3	-7	-2.6	-0.4
5	2	10	16.1	-15.7	5	6	-2	17.6	-17.1	5	11	-6	15.8	15.4	6	3	-6	-5.2	0.3
5	2	11	-2.1	-0.7	5	6	-1	14.3	14.8	5	11	-5	12.3	11.6	6	3	-5	39.3	40.7
5	2	12	8.2	-8.3	5	6	0	51.8	-52.4	5	11	-4	32.0	-32.1	6	3	-4	-4.9	-4.6
5	2	13	11.6	11.3	5	6	1	25.8	26.0	5	11	-3	0.0	1.4	6	3	-3	45.3	45.4
5	3	-14	-4.7	-2.4	5	6	2	35.9	-36.1	5	11	-2	-2.7	-2.4	6	3	-2	10.0	-10.3
5	3	-13	8.7	-6.7	5	6	3	24.5	-24.6	5	11	-1	12.6	-12.2	6	3	-1	13.8	-14.0
5	3	-12	14.8	15.4	5	6	4	32.0	32.2	5	11	0	17.5	16.8	6	3	0	19.9	-20.7
5	3	-11	-1.7	-1.0	5	6	5	-3.8	-2.4	5	11	1	18.3	-17.3	6	3	1	6.8	6.8
5	3	-10	14.9	-15.3	5	6	6	31.3	31.5	5	11	2	-5.0	-4.9	6	3	2	30.1	30.5
5	3	-9	10.2	10.8	5	6	7	0.0	-1.9	5	11	3	-3.5	-2.0	6	3	3	15.1	-14.4
5	3	-8	42.2	-42.0	5	6	8	7.9	-7.1	5	11	4	21.2	21.5	6	3	4	53.5	54.8
5	3	-7	27.3	28.4	5	6	9	16.5	-16.5	5	11	5	-4.1	2.9	6	3	5	44.9	-45.6
5	3	-6	9.9	-9.0	5	6	10	10.3	8.8	5	12	-4	-3.3	-4.0	6	3	6	-2.4	0.5
5	3	-5	19.9	19.8	5	6	11	14.7	13.8	5	12	-3	-2.9	0.6	6	3	7	6.5	7.4
5	3	-4	28.7	28.9	5	7	-12	0.0	1.0	5	12	-2	7.0	-7.4	6	3	8	8.2	-9.4
5	3	-3	10.2	-9.5	5	7	-11	24.7	24.8	5	12	-1	-3.5	6.0	6	3	9	19.9	19.3
5	3	-2	41.6	41.9	5	7	-10	17.9	16.6	5	12	0	-4.1	2.5	6	3	10	11.4	-11.5
5	3	-1	70.2	-70.8	5	7	-9	10.8	11.7	5	12	1	8.1	-8.2	6	3	11	-6.3	6.6
5	3	0	25.5	25.6	5	7	-8	9.5	10.2	5	12	2	9.9	10.0	6	4	-13	16.3	-15.8
5	3	1	9.5	-9.1	5	7	-7	34.4	-35.8	6	0	-14	8.8	10.1	6	4	-12	21.3	-21.0
5	3	2	7.5	-6.5	5	7	-6	15.0	-15.0	6	0	-12	16.5	15.8	6	4	-11	0.0	1.9
5	3	3	28.8	28.1	5	7	-5	24.1	-24.6	6	0	-10	8.3	8.8	6	4	-10	8.5	-8.8
5	3	4	6.5	-4.0	5	7	-4	6.5	6.9	6	0	-8	29.6	-29.2	6	4	-9	45.4	45.8
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5	3	8	-5.6	3.9	5	7	0	14.2	-13.6	6	0	0	26.1	-26.5	6	4	-5	-4.8	2.2
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5	3	10	10.7	-11.9	5	7	2	10.3	10.9	6	0	4	29.8	-29.3	6	4	-3	23.7	23.1
5	3	11	22.9	-21.8	5	7	3	10.7	-10.4	6	0	6	26.7	27.6	6	4	-2	20.8	20.5
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5	4	-13	-1.9	-2.3	5	7	6	14.6	14.5	6	0	12	-4.2	0.8	6	4	1	17.9	16.9
5	4	-12	14.6	15.3	5	7	7	-6.3	5.9	6	1	-14	-5.3	7.9	6	4	2	27.2	26.9
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5	4	-10	10.2	-10.7	5	7	9	0.0	-1.0	6	1	-12	32.8	31.5	6	4	4	8.9	8.6
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5	4	-3	13.9	-14.5	5	8	-6	31.7	31.5	6	1	-5	21.4	22.3	6	4	11	-4.5	-4.2
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5	4	1	30.2	-30.1	5	8	-2	43.0	-44.1	6	1	-1	7.7	-8.8	6	5	-10	0.0	2.0
5	4	2	9.8	6.7	5	8	-1	21.7	-22.1	6	1	0	58.9	59.5	6	5	-9	-3.9	2.5
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5	4	4	0.0	2.3	5	8	1	31.2	32.6	6	1	2	44.7	-44.0	6	5	-7	12.1	12.7
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5	4	9	26.8	27.0	5	8	6	22.7	23.6	6	1	7	12.0	-11.9	6	5	-2	33.7	-34.6
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5	5	-13	0.0	-2.6	5	9	-10	-4.2	1.3	6	1	11	-3.7	4.0	6	5	2	31.1	32.0
5	5	-12	17.5	16.5	5	9	-9	19.9	18.7	6	1	12	-5.8	-2.7	6	5	3	-2.5	-4.9

H	K	L	FO	FC
6	5	4	0.0	1.5
6	5	5	-3.4	-2.1
6	5	6	12.7	13.1
6	5	7	-6.2	6.8
6	5	8	25.5	24.8
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6	5	10	16.9	-16.1
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6	6	-12	12.6	-12.7
6	6	-11	-6.2	7.1
6	6	-10	26.8	-26.8
6	6	-9	0.0	2.0
6	6	-8	8.9	8.8
6	6	-7	12.2	-11.6
6	6	-6	25.8	25.3
6	6	-5	11.9	-12.1
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6	6	7	-3.5	4.4
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6	7	-6	20.1	27.9
6	7	-5	14.8	15.4
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6	7	-2	-2.8	2.9
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6	7	6	8.6	9.6
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6	7	8	21.4	-21.4
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6	8	-1	7.4	8.2
6	8	0	27.2	28.3
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6	11	-2	-3.8	1.8
6	11	-1	10.8	10.0
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6	11	1	-4.3	-5.8
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6	11	3	13.4	13.7
7	0	-12	12.9	-13.8
7	0	-10	29.2	30.3
7	0	-8	-1.1	-7.4
7	0	-6	44.9	-46.9
7	0	-4	26.7	27.1
7	0	-2	26.6	26.8
7	0	0	32.1	-33.0
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7	1	-5	15.4	-14.8
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7	1	-2	13.3	-11.9
7	1	-1	26.3	28.0
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7	3	-5	33.5	-33.5
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7	3	2	6.8	6.5
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7	4	-11	18.1	18.2
7	4	-10	19.1	-18.8
7	4	-9	10.2	-10.0
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7	4	-7	24.0	-24.1
7	4	-6	-4.5	1.9
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7	4	10	-2.9	2.0
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7	5	-4	19.9	21.0
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7	5	-1	10.9	-11.4
7	5	0	27.8	28.5
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7	5	5	23.0	-23.4
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7	5	7	13.6	-14.0
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7	6	-6	50.0	-50.6
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7	8	-7	-2.7	-4.7
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8	0	-12	8.9	-7.5
8	0	-10	-4.3	5.0
8	0	-8	0.0	-3.8
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8	0	-4	-4.5	5.0
8	0	-2	74.2	-74.4
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8	0	2	9.9	9.6
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8	1	-12	-5.0	-4.0
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8	1	-1	28.8	29.8
8	1	0	20.4	21.2
8	1	1	10.4	9.9
8	1	2	40.5	-40.9
8	1	3	23.7	-23.2
8	1	4	0.0	-4.3
8	1	5	10.8	10.8
8	1	6	-0.8	1.3
8	1	7	10.5	9.7
8	1	8	13.2	-12.5
8	1	9	-4.6	4.8
8	2	-12	-6.0	-7.9
8	2	-11	12.8	12.1
8	2	-10	-1.3	-2.0
8	2	-9	17.9	-17.7
8	2	-8	0.0	1.5
8	2	-7	10.6	-11.0
8	2	-6	-5.2	6.4
8	2	-5	27.3	-27.8
8	2	-4	-5.3	-1.9
8	2	-3	27.0	-26.6
8	2	-2	12.3	-12.1
8	2	-1	21.9	22.0
8	2	0	-3.1	-2.0
8	2	1	15.7	-14.8
8	2	2	30.8	31.6
8	2	3	20.7	20.4
8	2	4	12.0	11.7
8	2	5	49.0	48.4
8	2	6	0.0	-1.4
8	2	7	17.3	-17.2
8	2	8	8.8	-10.1
8	2	9	16.7	-16.7
8	3	-11	8.7	-9.9
8	3	-10	-3.2	2.8
8	3	-9	25.6	26.0
8	3	-8	13.9	14.1
8	3	-7	16.2	15.5
8	3	-6	23.5	23.8
8	3	-5	29.6	-29.7

H	K	L	FO	FC
8	3	-4	7.6	-7.2
8	3	-3	8.2	7.2
8	3	-2	0.0	1.3
8	3	-1	19.5	-18.7
8	3	0	11.5	11.5
8	3	1	20.0	-20.1
8	3	2	15.6	-16.0
8	3	3	10.5	9.8
8	3	4	19.6	-19.8
8	3	5	-2.0	0.2
8	3	6	17.6	-17.6
8	3	7	8.2	7.9
8	3	8	-4.5	-1.1
8	4	-11	7.9	-6.2
8	4	-10	-4.9	-5.3
8	4	-9	13.8	-13.8
8	4	-8	20.7	20.2
8	4	-7	21.3	-21.1
8	4	-6	34.9	-36.0
8	4	-5	6.6	8.8
8	4	-4	13.7	-12.9
8	4	-3	31.9	32.6
8	4	-2	24.4	24.7
8	4	-1	19.6	-19.4
8	4	0	14.1	-13.7
8	4	1	0.0	1.6
8	4	2	11.2	12.4
8	4	3	20.3	21.1
8	4	4	13.2	13.9
8	4	5	0.0	-3.5
8	4	6	14.1	-15.0
8	4	7	15.9	15.1
8	4	8	10.5	10.2
8	5	-10	18.8	18.4
8	5	-9	8.2	8.0
8	5	-8	14.3	13.4
8	5	-7	-4.0	2.2
8	5	-6	20.3	-19.7
8	5	-5	-3.9	-2.4
8	5	-4	11.5	-10.7
8	5	-3	9.0	9.6
8	5	-2	17.1	-17.7
8	5	-1	0.0	-4.0
8	5	0	-5.9	4.0
8	5	1	-5.5	3.0
8	5	2	29.6	30.4
8	5	3	34.8	34.5
8	5	4	13.4	-13.1
8	5	5	-4.0	-1.9
8	5	6	16.4	-16.3
8	5	7	12.1	-12.1
8	6	-9	-2.7	1.7
8	6	-8	-1.1	-1.9
8	6	-7	-4.0	-4.2
8	6	-6	9.3	8.5
8	6	-5	7.1	7.8
8	6	-4	22.9	-23.6
8	6	-3	15.9	15.3
8	6	-2	19.0	-18.7
8	6	-1	0.0	-2.0
8	6	0	-3.2	-3.4
8	6	1	8.4	-7.8
8	6	2	19.6	-19.8
8	6	3	10.7	-10.3
8	6	4	-2.2	-1.5
8	6	5	-3.1	-2.4
8	6	6	13.2	13.1
8	6	7	8.4	7.8

H	K	L	FO	FC
8	7	-8	-6.7	-6.3
8	7	-7	0.0	-2.1
8	7	-6	-6.0	-7.1
8	7	-5	22.3	21.7
8	7	-4	-2.9	-0.1
8	7	-3	27.6	-26.6
8	7	-2	-6.1	5.7
8	7	-1	8.8	8.6
8	7	0	10.4	9.9
8	7	1	36.8	36.9
8	7	2	-1.8	3.0
8	7	3	9.0	-7.1
8	7	4	-1.7	2.9
8	7	5	7.3	7.6
8	8	-7	-3.6	4.1
8	8	-6	-6.4	4.5
8	8	-5	0.0	-1.6
8	8	-4	0.0	-1.5
8	8	-3	15.7	-15.6
8	8	-2	12.0	-10.8
8	8	-1	-1.2	1.4
8	8	0	16.5	17.1
8	8	1	11.1	11.1
8	8	2	-0.9	-4.4
8	8	3	9.5	-9.4
8	8	4	-5.4	-5.6
8	9	-5	8.9	-7.5
8	9	-4	10.0	10.0
8	9	-3	8.3	-6.7
8	9	-2	7.9	8.7
8	9	-1	21.7	-21.5
8	9	0	-3.1	-5.4
8	9	1	9.3	-8.8
8	9	2	9.7	-8.2
9	0	-10	-3.8	-3.9
9	0	-8	-2.5	-0.7
9	0	-6	22.4	-21.9
9	0	-4	0.0	2.1
9	0	-2	8.0	8.2
9	0	0	6.6	-5.6
9	0	2	19.5	18.9
9	0	4	-2.6	5.7
9	0	6	13.1	-12.7
9	1	-10	-5.6	-6.7
9	1	-9	16.4	16.8
9	1	-8	-6.4	-3.6
9	1	-7	11.1	9.8
9	1	-6	12.6	-12.4
9	1	-5	9.9	9.0
9	1	-4	16.1	-16.3
9	1	-3	13.1	12.2
9	1	-2	41.2	41.4
9	1	-1	10.3	-11.2
9	1	0	7.4	4.0
9	1	1	22.7	-23.0
9	1	2	0.0	0.5
9	1	3	7.4	-6.6
9	1	4	10.7	10.1
9	1	5	-3.9	-2.1
9	1	6	19.9	-18.5
9	1	7	0.0	3.9
9	2	-10	-5.7	4.8
9	2	-9	0.0	-2.5
9	2	-8	-1.5	2.0
9	2	-7	28.2	27.9
9	2	-6	11.4	9.4
9	2	-5	-3.2	3.7
9	2	-4	19.1	-18.7

H	K	L	FO	FC
9	2	-3	13.0	-12.4
9	2	-2	15.8	-16.3
9	2	-1	19.9	-19.9
9	2	0	18.2	18.2
9	2	1	37.3	-37.0
9	2	2	-2.7	-4.6
9	2	3	17.1	17.0
9	2	4	-3.1	1.1
9	2	5	17.4	16.8
9	2	6	11.8	12.3
9	2	7	-3.8	-4.8
9	3	-10	-5.2	3.9
9	3	-9	26.3	-25.7
9	3	-8	14.3	-13.9
9	3	-7	-4.3	5.8
9	3	-6	-4.6	-6.8
9	3	-5	21.9	20.9
9	3	-4	-2.2	1.2
9	3	-3	-5.7	-5.5
9	3	-2	16.2	16.9
9	3	-1	8.4	7.4
9	3	0	26.7	26.2
9	3	1	-1.0	4.2
9	3	2	6.4	-6.0
9	3	3	29.0	-28.9
9	3	4	13.2	-12.1
9	3	5	7.0	6.8
9	3	6	9.0	-7.5
9	4	-9	-5.5	-4.9
9	4	-8	9.1	9.0
9	4	-7	9.3	-10.8
9	4	-6	9.5	8.7
9	4	-5	16.5	16.5
9	4	-4	-5.3	4.1
9	4	-3	10.6	-11.3
9	4	-2	-5.4	-6.2
9	4	-1	19.2	-19.7
9	4	0	17.5	-16.8
9	4	1	16.3	16.6
9	4	2	0.0	-1.2
9	4	3	0.0	0.3
9	4	4	-1.8	0.2
9	4	5	-5.2	6.0
9	4	6	-2.1	3.9
9	5	-8	-5.3	5.1
9	5	-7	0.0	-2.2
9	5	-6	-3.6	-4.1
9	5	-5	17.9	-17.4
9	5	-4	-3.5	5.3
9	5	-3	6.9	4.1
9	5	-2	-3.8	-5.2
9	5	-1	9.3	-8.2
9	5	0	-2.6	-2.9
9	5	1	0.0	-3.1
9	5	2	11.7	-11.3
9	5	3	27.2	27.3
9	5	4	13.3	-13.9
9	5	5	10.2	-8.6
9	6	-7	-4.1	-2.1
9	6	-6	-2.7	-0.3
9	6	-5	8.9	-8.3
9	6	-4	29.3	29.2
9	6	-3	10.9	10.0
9	6	-2	20.9	20.6
9	6	-1	9.4	10.4
9	6	0	32.3	-32.8
9	6	1	-5.5	2.0
9	6	2	19.7	-18.9

H	K	L	FO	FC
9	6	3	0.0	2.7
9	6	4	0.0	0.9
9	7	-5	13.9	-14.1
9	7	-4	9.9	-8.7
9	7	-3	25.3	-25.0
9	7	-2	0.0	3.5
9	7	-1	-3.3	-2.1
9	7	0	13.4	-13.2
9	7	1	16.6	16.7
9	7	2	-2.3	-0.9
10	0	-8	25.1	-24.2
10	0	-6	23.0	-22.0
10	0	-4	9.0	9.7
10	0	-2	21.8	-21.8
10	0	0	38.4	37.2
10	0	2	7.1	6.4
10	0	4	28.2	-26.5
10	1	-8	9.5	8.3
10	1	-7	-2.6	4.8
10	1	-6	-3.0	-1.5
10	1	-5	35.6	35.7
10	1	-4	15.0	-15.3
10	1	-3	-4.7	-5.7
10	1	-2	10.8	11.0
10	1	-1	11.2	-11.9
10	1	0	-3.5	-0.3
10	1	1	7.8	5.9
10	1	2	-3.3	-1.0
10	1	3	-5.5	-8.2
10	1	4	20.3	20.4
10	2	-7	14.1	13.2
10	2	-6	0.0	-2.4
10	2	-5	-5.9	-3.7
10	2	-4	16.7	-15.9
10	2	-3	-3.7	-1.3
10	2	-2	18.8	18.2
10	2	-1	15.4	15.2
10	2	0	-2.6	0.8
10	2	1	17.5	-16.7
10	2	2	-4.3	-6.3
10	2	3	10.3	-11.3
10	2	4	-6.8	-7.6
10	3	-7	12.2	11.7
10	3	-6	0.0	-0.5
10	3	-5	25.1	-24.2
10	3	-4	-5.1	-6.7
10	3	-3	14.2	13.6
10	3	-2	-2.2	-2.7
10	3	-1	12.5	11.9
10	3	0	9.2	9.9
10	3	1	12.4	-12.9
10	3	2	0.0	-1.8
10	3	3	17.5	17.4
10	4	-6	-1.8	-2.3
10	4	-5	-4.3	4.0
10	4	-4	10.2	8.4
10	4	-3	9.2	-9.4
10	4	-2	17.5	17.1
10	4	-1	-6.3	-3.3
10	4	0	16.8	-17.7
10	4	1	12.2	11.9
10	4	2	-5.6	-4.5
10	5	-4	14.2	13.2
10	5	-3	-4.3	2.8
10	5	-2	0.0	4.3
10	5	-1	6.8	-5.9
10	5	0	-3.3	-4.7
10	5	1	0.0	3.0

CHAPTER 6

The Crystal Structure of $S_5N_5^+[SnCl_5POCl_3]^-$

6.1 Introduction.

The discovery that sulphur-nitrogen cations such as $S_4N_3^+$ are pseudo-aromatic species has introduced theoretical justifications for the possible existence of further sulphur-nitrogen Hückel aromatic compounds. The type of compounds possible have been outlined earlier (section 2.5). One of the species predicted was $S_4N_4^{2+}$ which ideally would be a planar eight-membered ring compound containing a 10π system. A series of experiments were designed in an attempt to prepare this ion (Banister, 1975). These were unsuccessful in their initial aims, but were highly successful in preparing another derivative of $S_5N_5^+$, $S_5N_5^+[SnCl_5POCl_3]^-$. The structure of this compound has been studied in an attempt to understand the difference in the shape of the cation observed in $S_5N_5^+AlCl_4^-$ and $S_5N_5^+S_3N_3O_4^-$.

The compound was prepared by reacting a mixture of $SnCl_4$ and SO_2Cl_2 with a slurry of S_4N_4 in $POCl_3$ as a solvent. Initially the Lewis adduct $(S_4N_4)_2SnCl_4$ formed and was precipitated as a red brown solid. On heating, the reaction mixture became lighter in colouration and on cooling yellow crystals were deposited. These were removed by filtration and separated in a glove box by hand from the other reaction residues. The stoichiometry of the reaction was,

$$2\tfrac{1}{2}\ S_4N_4 + SO_2Cl_2 + 2\ SnCl_4 \xrightarrow{2\ POCl_3} 2\ S_5N_5^+[SnCl_5POCl_3]^-$$

Originally it was hoped that the SO_2Cl_2 would oxidise the S_4N_4 to give SO_2 and $S_4N_4^{2+}$, together with producing the $SnCl_6^{2-}$ anion. From the reaction product, it would appear that the $(S_4N_4)_2SnCl_4$ adduct is oxidised by the $SOCl_2$ to give NSCl, which is thought to react with the S_4N_4 adduct to give $S_5N_5^+$ and $SnCl_5POCl_3^-$ (Banister and Durrant 1975).

6.2 Crystal Data.

The compound crystallised as well formed thin yellow plates showing prominent {001} faces bounded by {110} faces. It was extremely sensitive to moisture and consequently the crystals were sealed in quartz tubes. The crystal used for data collection had dimensions 0.3 x 0.25 x 0.15mm.

Preliminary studies using precession and Weissenberg methods showed the unit cell to be monoclinic. The conditions limiting reflections were,

$$h\ 0\ l \quad l = 2n, \qquad 0\ k\ 0 \quad k = 2n$$

and these uniquely define the space group as $P2_1/c$. Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections, as measured on a four-circle diffractometer.

$S_5N_5^+[SnCl_5POCl_3]^-$

M = 679.62
a = 8.272(1)Å $\alpha = 90^\circ$
b = 12.834(2)Å $\beta = 97.083^\circ$
c = 18.515(3)Å $\gamma = 90^\circ$
U = 1950.6$Å^3$
Z = 4
Dm = 2.39g cm^{-3} (by floatation in CH_3I/CH_2Br_2)
Dc = 2.31g cm^{-3}

Absorption coefficient for MoKα radiation (λ = 0.7107Å) = 29.9cm^{-1}

6.3 Data Collection and Correction.

Data was collected on a four-circle diffractometer as before, using a $2\theta - \omega$ scan technique. Each reflection was scanned in 80 steps of 0.01° with a counting time of 2.5 seconds per step and a stationary background count of 50 seconds at the beginning and end of each scan. Standard reflections were measured every 50 reflections and these showed no systematic variations during data measurement, indicating that the crystal was stable throughout the experiment. These standard reflections were used to place the intensities on a common scale.

One octant of the sphere of reflection was recorded for $0 < \theta \leq 25^{\circ}$ giving 3440 independent reflections, of which 2054 were considered to be observed having net counts > 2.5 e.s.d's. The data was corrected for Lorentz and polarisation effects, but not for absorption.

6.4 Solution and Refinement.

The structure was solved from its Patterson function which for the space group $P2_1/c$ takes the form

$$P(u,v,w) = \frac{4}{V} \sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty} \{ |F(hkl)|^2 \cos 2\pi (hu + lw) + |F(hk\bar{l})|^2 \cos 2\pi (hu - lw) \} \cos 2\pi kv$$

this was computed for a quarter of the unit cell from

$u = 0 \rightarrow 1.0$ in intervals of 0.27573Å

$v = 0 \rightarrow 0.5$ in intervals of 0.26737Å

$w = 0 \rightarrow 0.5$ in intervals of 0.30858Å

The coefficients used were $|F_{obs}|^2$ weighted by $(Lp)^{-1}$ for each reflection. This increased the importance of the higher order planes and thus enhanced the magnitude of the tin-tin vectors in the map.

The position of the tin atom in the assymmetric unit was located from its Harker peaks. For an atom in a general position the following Harker peaks are expected

$$\begin{array}{ccc} 0 & \frac{1}{2} + 2y & \frac{1}{2} \\ 2x & \frac{1}{2} & \frac{1}{2} + 2z \end{array}$$

There were two large peaks in the map at (0, 0.052, 0.5) and (0.333, 0.5, 0.233) with peak heights of 168 and 155 with respect to the peak height of 500 at the origin. These are consistent with a tin atom at (0.333, 0.224, 0.133) and the corresponding single weight Sn-Sn vector was found at (0.666, 0.448, 0.267) with a height of 90. This position of the tin atom was refined using least squares methods with the block-diagonal approximation. Initially the tin atom was given an isotropic temperature factor of 3.0Å^2 and after two cycles of refinement the R value was 0.48. The structure factors thus calculated were used to compute a difference synthesis which revealed the positions of all of the atoms except N(5). The heights of the heavier atoms varied from 5.5 - 8.3e. Å^{-3} and the lighter atoms from 2.3 - 4.0e.Å^{-3}, with the background showing spurious peaks of up to 6e.Å^{-3}. All of the atoms except N(3) were included in the subsequent refinement with isotropic temperature factors of 3.0Å^2 after which R fell to 0.20. A difference synthesis revealed the position of N(5). This was included in the further refinement during which all atoms were refined with anisotropic thermal parameters giving an R value of 0.069. The refinement was completed using full matrix least squares methods which saw R converge on its final value of 0.0630. During the last cycle all the parameter shifts were < 0.1 of their e.s.d's.

A difference synthesis was computed from the final structure factors and showed no significant features above 0.6e.Å^{-3} except for a spherical ripple around the position of the tin atom. At the tin position there was a negative hole of -0.5e.Å^{-3} around which the ripple reached a maximum height of 1.9e.Å^{-3}. This indicates that the form factors for the tin atom are not wholly satisfactory. The scattering factors for tin had been taken from International Tables Vol. III, however replacement of these by more recent values (Doyle and Turner, 1968) produced only small changes in the ripple.

The weighting scheme used in the initial stages of refinement was the same as described previously with $P_1 = 10.0$ and $P_2 = 0.01$. This was replaced by one based on counting statistics as used in previous refinements. The most even distribution of $w\Delta^2$ as a function of $|F_o|$ was obtained with $P = 0.09$. The unobserved reflections were not included in the refinement. The final least squares totals are given in table 6.1. The final calculated and observed structure factors are given in table 6.8. The tin, chlorine, sulphur and phosphorus atoms were corrected for anomolous dispersion. For all atoms except tin these correction factors and their scattering factors were taken from International Tables Vol. III.

Table 6.1 $S_5N_5^+[SnCl_5POCl_3]^-$

Least Squares Totals.

$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	R
109114.87	107925.06	6879.14	0.0630

Final Weighting Analysis

$\lvert F_o\rvert$ Ranges	No.	$\Sigma w\Delta^2$	R
10 - 20	41	4.44	0.188
20 - 30	482	4.53	0.142
30 - 40	429	2.81	0.069
40 - 50	314	3.34	0.053
50 - 60	217	3.04	0.044
60 - 70	129	3.63	0.044
70 - 80	120	4.61	0.050
80 -100	137	3.47	0.040
100 - Upwards	185	5.11	0.054

Table 6.2 $S_5N_5^+[SnCl_5POCl_3]^-$

Final Atomic Coordinates with their Estimated Standard Deviations (x 10^5) and Isotropic Temperature Factors Å^2 †

Atom	$^x/a$	$^y/b$	$^z/c$	B
SN	0.33097(10)	0.22205(7)	0.13340(5)	2.28
Cl(1)	0.09452(44)	0.19587(34)	0.19157(23)	4.29
Cl(2)	0.22047(48)	0.15261(33)	0.01878(21)	4.34
Cl(3)	0.26431(50)	0.39324(29)	0.08880(22)	4.29
Cl(4)	0.48114(43)	0.29333(32)	0.24158(19)	3.94
Cl(5)	0.45101(44)	0.05477(30)	0.16466(23)	3.92
Cl(6)	0.53858(62)	0.29913(74)	-0.06664(31)	8.11
Cl(7)	0.71314(104)	0.10319(45)	-0.00111(40)	9.04
Cl(8)	0.85984(52)	0.31937(49)	0.03671(28)	6.01
S(1)	-0.07873(54)	0.62069(38)	0.10641(24)	4.90
S(2)	-0.29955(47)	0.48029(35)	0.17862(22)	4.15
S(3)	-0.15348(46)	0.37364(37)	0.30663(24)	4.37
S(4)	0.18577(45)	0.43249(38)	0.33147(24)	4.32
S(5)	0.22387(47)	0.58015(34)	0.21466(23)	4.20
P	0.65328(46)	0.24408(32)	0.02109(21)	3.49
O	0.56701(118)	0.24931(79)	0.08532(56)	3.78
N(1)	-0.22826(162)	0.55657(119)	0.12564(72)	5.31
N(2)	-0.16093(127)	0.44022(101)	0.23746(61)	3.09
N(3)	0.02633(147)	0.37385(120)	0.34800(72)	4.82
N(4)	0.15221(138)	0.50054(98)	0.26564(69)	3.90
N(5)	0.09546(152)	0.61699(100)	0.15047(71)	4.40

† The temperature factors from the last cycle of isotropic refinement.

Table 6.3 $S_5N_5^+[SnCl_5POCl_3]^-$

Anisotropic Thermal Parameters and their Estimated Standard Deviations (Both $\mathring{A}^2$ x 10^5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
SN	3282(44)	3978(50)	3965(49)	- 201(46)	596(32)	- 203(44)
Cl(1)	3806(189)	7384(294)	7475(267)	998(217)	2137(178)	- 326(185)
Cl(2)	5881(230)	6421(268)	5282(226)	-1692(204)	-1104(182)	643(207)
Cl(3)	6679(245)	3756(204)	6587(259)	534(184)	502(204)	581(184)
Cl(4)	4822(201)	6301(261)	4467(201)	- 801(182)	- 93(155)	-898(182)
Cl(5)	4579(198)	4485(220)	7144(257)	656(190)	426(179)	662(173)
Cl(6)	5842(299)	27715(1007)	8509(373)	8965(514)	344(255)	1077(429)
Cl(7)	20330(754)	6870(378)	14419(600)	-2074(379)	9235(561)	1226(425)
Cl(8)	4578(233)	13138(466)	8720(338)	409(317)	2000(222)	-1622(271)
S(1)	6475(265)	7669(312)	5994(267)	2039(239)	314(210)	- 919(242)
S(2)	4428(211)	7004(284)	5594(247)	1126(211)	-438(177)	- 258(196)
S(3)	4154(211)	7374(294)	6574(266)	1840(230)	243(189)	- 570(206)
S(4)	3623(199)	7754(292)	6688(268)	691(236)	-342(179)	- 100(200)
S(5)	4259(206)	6356(264)	6510(261)	750(215)	1025(183)	- 640(192)
P	4342(204)	5803(263)	4488(213)	496(176)	1530(165)	62(175)
O	4567(573)	6078(717)	6557(655)	- 840(518)	2870(492)	- 74(479)
N(1)	5904(801)	8510(1051)	6026(874)	1804(795)	-207(666)	-1521(791)
N(2)	3113(581)	6889(857)	4490(695)	- 346(630)	1022(510)	257(585)
N(3)	4435(722)	8442(1062)	6494(878)	1504(768)	134(620)	-1313(714)
N(4)	4042(669)	6058(860)	6404(842)	- 95(683)	2172(619)	- 427(603)
N(5)	5645(776)	4971(790)	6830(886)	846(669)	404(667)	700(652)

The anomolous dispersion correction and scattering factors used for tin were those values calculated by Cromer, 1965 and Doyle and Turner, 1968. The final atomic coordinates and anisotropic thermal parameters are given in tables 6.2 and 6.3 respectively.

6.5 Results and Discussion.

The structure consists of discrete $S_5N_5^+$ cations and $[SnCl_5POCl_3]^-$ anions and it is convenient to discuss these separately. The bond distances and angles are given in tables 6.4 and 6.5 respectively.

6.5.a The Structure of the $S_5N_5^+$ Cation.

The cation consists of a ten-membered ring of alternating sulphur and nitrogen atoms as shown in figure 6.1. It is immediately apparent that this ion has essentially the same shape as that found in $S_5N_5^+S_3N_3O_4^-$ described in chapter 5. The ring is roughly planar (table 6.6) and the deviations of the atoms from their mean plane are of the same order as those seen previously. However the deviations do not show the systematic variation around the ring as clearly as before and any buckling appears to be masked by the larger errors. The bond distances on either side of the ring are the same within experimental error, eg. S(1)-N(1) and S(1)-N(5) of length 1.563(15)Å and 1.567(14)Å. The corresponding bond angles at sulphur on either side of the ring are also the same within experimental error, whereas those at the nitrogen atoms show greater differences than can be ascribed to experimental error.

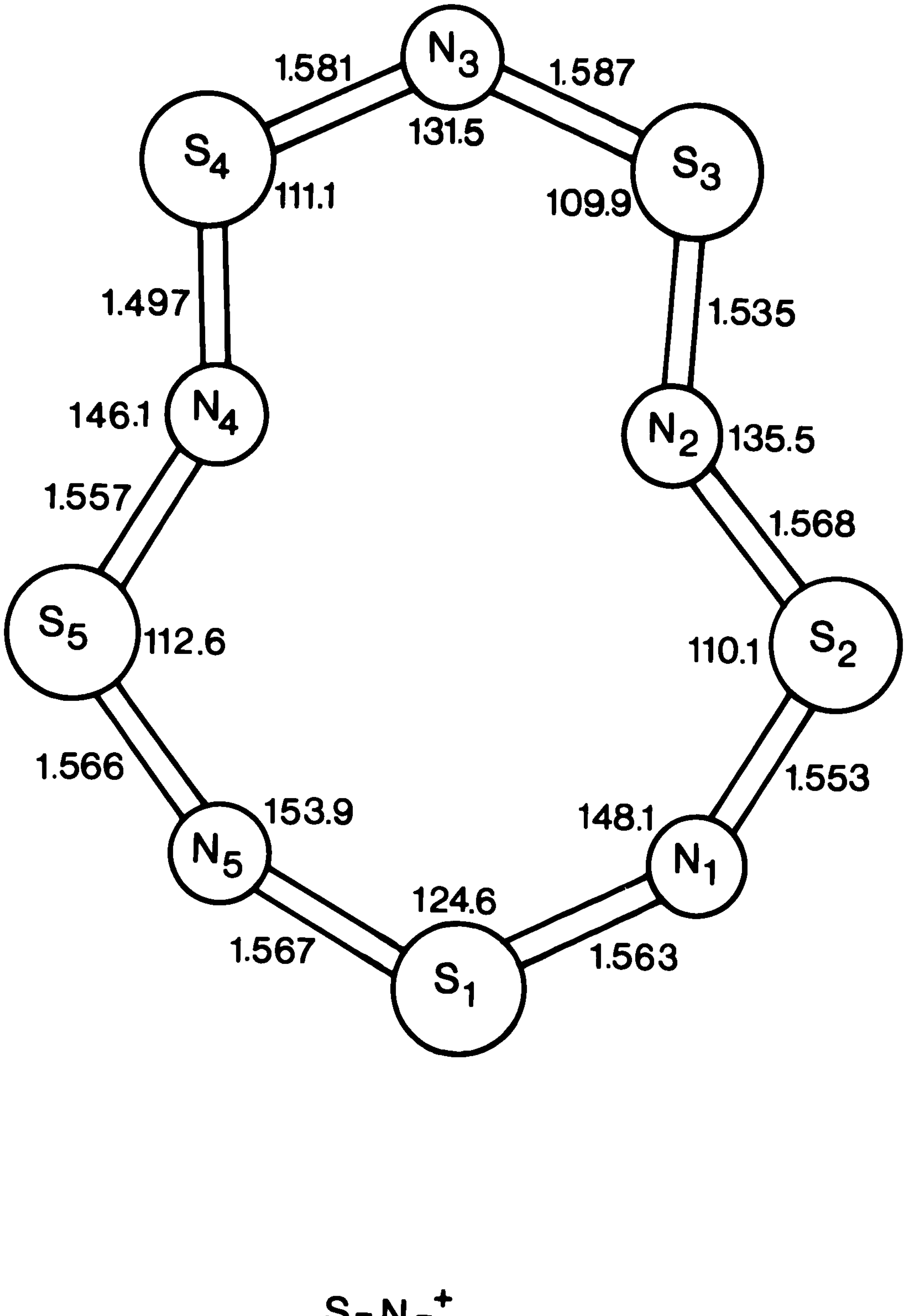


Figure 6.1

The $S_5N_5^+$ Cation found in $S_5N_5^+[SnCl_5POCl_3]^-$

The mean bond lengths and average bond angles found in the $S_5N_5^+$ cations in $S_5N_5^+[SnCl_5POCl_3]^-$ and $S_5N_5^+S_3N_3O_4^-$ are shown in figure 6.2. Except for the mean values of S(3)-N(2) and S(4)-N(4) the mean S-N distances in the $S_5N_5^+$ rings in these two compounds are the same within experimental error. Likewise the average bond angles are similar in the $S_5N_5^+$ rings in both derivatives. It is significant that the greatest differences between corresponding bond distances and bond angles on either side of the ring are associated with those two parts of the ion most involved in secondary bonding, namely S(2)-N(2)-S(3) and S(4)-N(4)-S(5). As described in section 6.6, S(2) and S(3) participate in bridging interactions with two chlorine atoms, whereas S(4) and S(5) interact with only one. The smaller re-entrant angle at nitrogen is associated with the stronger secondary interactions involving S(2) and S(3). This is directly analogous to the interaction observed in $S_5N_5^+S_3N_3O_4^-$ which is also associated with the smaller re-entrant angle at nitrogen. There may be a correlation between the angles at N(2) and N(4) because the N(2)-N(4) cross-ring distance of 2.69Å is substantially less than the nitrogen-nitrogen van der Waals distance of 3.1Å (Bondi, 1964). Both N(2) and N(4) carry lone pairs so that there must be a repulsive interaction between them. Thus any distortion that shifts the position of one nitrogen atom should result in a similar shift in the other, which may account for the small angle at N(2) and the large angle at N(4). The difference between the angle of 148.1 at N(1) and 154.0 at N(5) may be the result of a short contact of 3.246Å between N(1) and Cl(6) at (-x, 1-y, -z).

It is not meaningful to discuss the variations in bond distances around the ring in these $S_5N_5^+$ cations because they cannot be

Table 6.4 $S_5N_5^+[SnCl_5POCl_3]^-$

Final Bond Distances (Å) and their Estimated Standard Deviations (Å x 10^3)

Sn	-	Cl(1)	2.370(4)
Sn	-	Cl(2)	2.378(4)
Sn	-	Cl(3)	2.388(4)
Sn	-	Cl(4)	2.404(4)
Sn	-	Cl(5)	2.406(4)
Sn	-	O	2.271(10)
P	-	Cl(6)	1.913(7)
P	-	Cl(7)	1.932(7)
P	-	Cl(8)	1.953(6)
P	-	O	1.462(11)
S(1)	-	N(1)	1.563(15)
S(1)	-	N(5)	1.567(14)
S(2)	-	N(1)	1.553(15)
S(2)	-	N(2)	1.568(12)
S(3)	-	N(2)	1.535(13)
S(3)	-	N(3)	1.587(13)
S(4)	-	N(3)	1.581(14)
S(4)	-	N(4)	1.497(14)
S(5)	-	N(4)	1.557(13)
S(5)	-	N(5)	1.566(14)

Table 6.5 $S_5N_5^+[SnCl_5POCl_3]^-$

Bond Angles (degrees) with their Estimated Standard Deviations

(deg x 10^2)

Cl(1) - Sn - Cl(2)	96.00(14)
Cl(1) - Sn - Cl(3)	96.85(14)
Cl(1) - Sn - Cl(4)	92.63(14)
Cl(1) - Sn - Cl(5)	95.94(14)
Cl(1) - Sn - O	176.06(28)
Cl(2) - Sn - Cl(3)	89.39(14)
Cl(2) - Sn - Cl(4)	171.30(14)
Cl(2) - Sn - Cl(5)	88.97(14)
Cl(2) - Sn - O	87.85(27)
Cl(3) - Sn - Cl(4)	90.66(13)
Cl(3) - Sn - Cl(5)	167.21(14)
Cl(3) - Sn - O	84.02(27)
Cl(4) - Sn - Cl(5)	89.06(13)
Cl(4) - Sn - O	83.51(27)
Cl(5) - Sn - O	83.25(27)
Cl(6) - P - Cl(7)	106.16(36)
Cl(6) - P - Cl(8)	106.04(32)
Cl(6) - P - O	115.67(50)
Cl(7) - P - Cl(8)	104.59(33)
Cl(7) - P - O	112.31(50)
Cl(8) - P - O	111.27(48)
N(1) - S(1) - N(5)	124.64(76)
N(1) - S(2) - N(2)	110.09(72)
N(2) - S(3) - N(3)	109.92(71)
N(3) - S(4) - N(4)	111.09(74)
N(4) - S(5) - N(5)	112.63(70)
SN - O - P	147.29(64)
S(1) - N(1) - S(2)	148.08(102)
S(2) - N(2) - S(3)	135.50(83)
S(3) - N(3) - S(4)	131.46(93)
S(4) - N(4) - S(5)	146.10(91)
S(1) - N(5) - S(5)	153.96(94)

Table 6.6 $S_5N_5^+[SnCl_5POCl_3]^-$

The mean plane of the $S_5N_5^+$ cation.

$$0.3151X \; -0.7597Y \; -0.5689Z + 7.4534 = 0$$

Atom	S(1)	S(2)	S(3)	S(4)	S(5)
P	0.0081	-0.0054	-0.0151	0.0179	-0.0173
σ(P)	0.0047	0.0043	0.0045	0.0047	0.0043

Atom	N(1)	N(2)	N(3)	N(4)	N(5)
P	0.0286	0.0891	-0.0105	0.0026	0.0060
σ(P)	0.0145	0.0122	0.0144	0.0126	0.0129

Where P and σ(P) are the distance and its e.s.d. of an atom from the mean plane.

X, Y and Z are orthogonal coordinates in Å oriented in the direction of a, b, and c* respectively.

adequately described in classical terms.

6.5.b Discussion on the variations in shape observed for the $S_5N_5^+$ cation.

The $S_5N_5^+$ cation found originally in $S_5N_5^+AlCl_4^-$ (shape I) differs markedly from that found in $S_5N_5^+S_3N_3O_4^-$ and $S_5N_5^+[SnCl_5POCl_3]^-$ (shape II), as shown in figure 6.2. In both cases the sulphur atoms have approximately the same distribution and the main differences are in the positions of two nitrogen atoms. There is also a far wider variation in the S-N bond distances and angles at nitrogen in shape I than in II i.e. 1.465 - 1.590Å and 129 - 177° as compared to the variation in the mean bond lengths of 1.543 - 1.580Å and average bond angles of 133-151° in $S_5N_5^+S_3N_3O_4^-$.

There are two possible explanations for this difference; firstly that the $S_5N_5^+$ cation can exist in more than one conformation or secondly that the shape observed in $S_5N_5^+AlCl_4^-$ represents the mean positions of two disordered $S_5N_5^+$ cations of the type seen in $S_5N_5^+S_3N_3O_4^-$ or $S_5N_5^+[SnCl_5POCl_3]^-$.

The difference between I and II cannot be explained by intermolecular forces, because the only significant interactions in all three of these structures occur between the sulphur atoms and atoms in the anion carrying some negative charge whereas the distribution of sulphur atoms is approximately the same in shapes I and II. Conversely there are no short contacts involving the nitrogen atoms which could account for the differences observed. So that there do not appear to be any reasons why the forces in the crystal should compel the ion to take up different conformations.

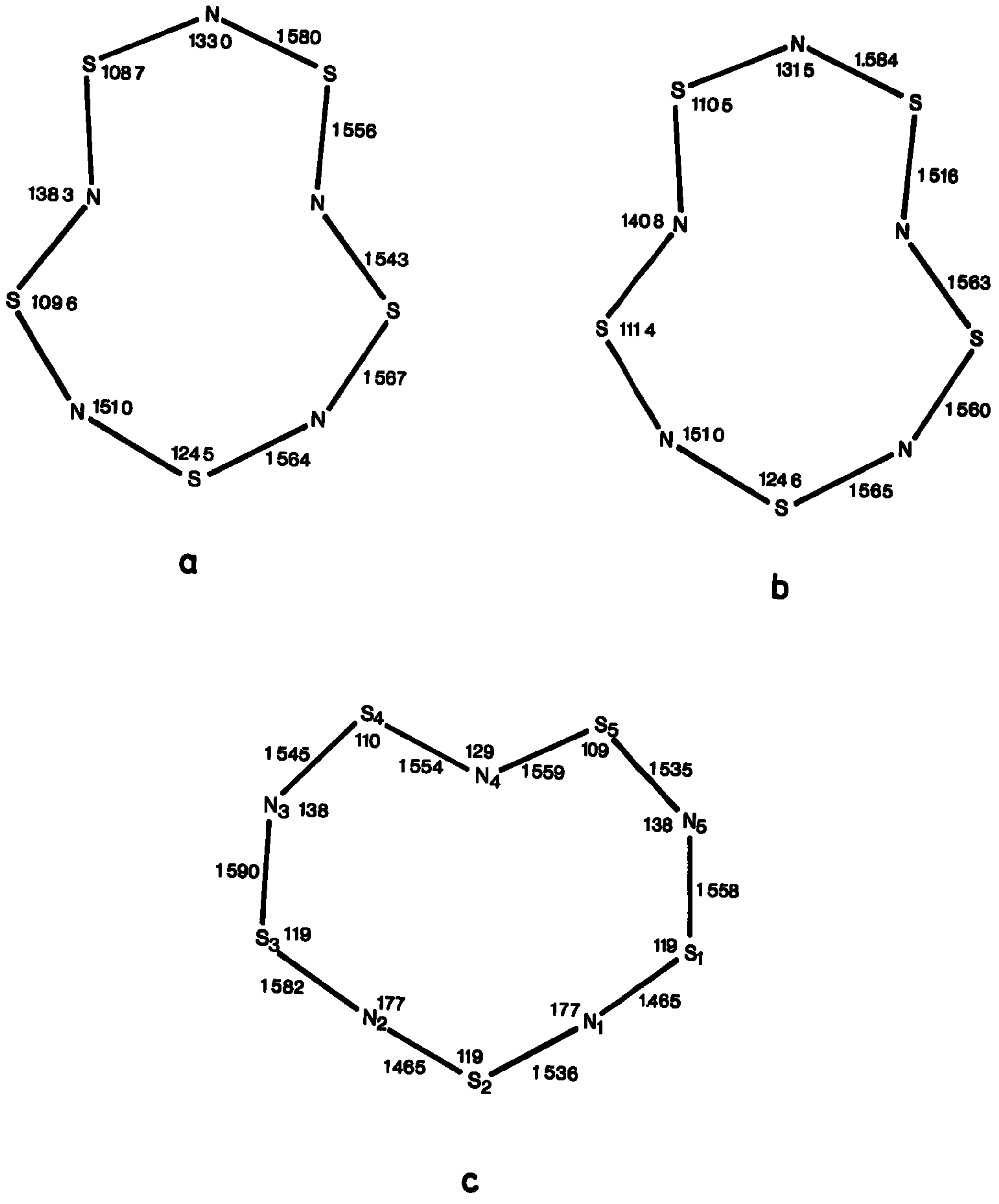


Figure 6.2

The $S_5N_5^+$ Cations in (a) $S_5N_5^+S_3N_3O_4^-$

(b) $S_5N_5^+[SnCl_5POCl_3]^-$ (c) $S_5N_5^+AlCl_4^-$

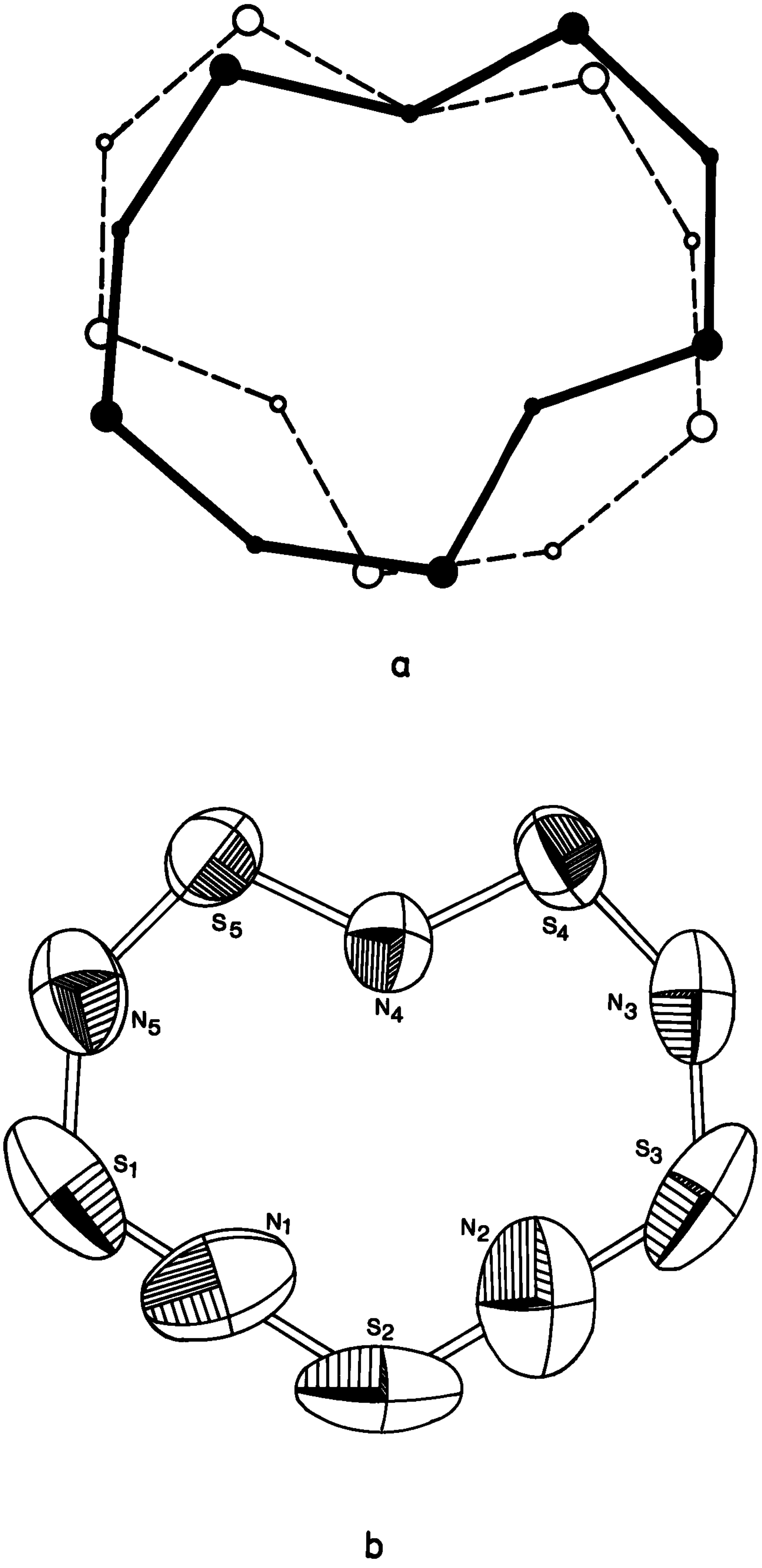


Figure 6.3

(a) Superposition of two $S_5N_5^+$ cations as found in $S_5N_5^+S_3N_3O_4^-$

(b) Thermal epipsoids for $S_5N_5^+$ in $S_5N_5^+AlCl_4^-$

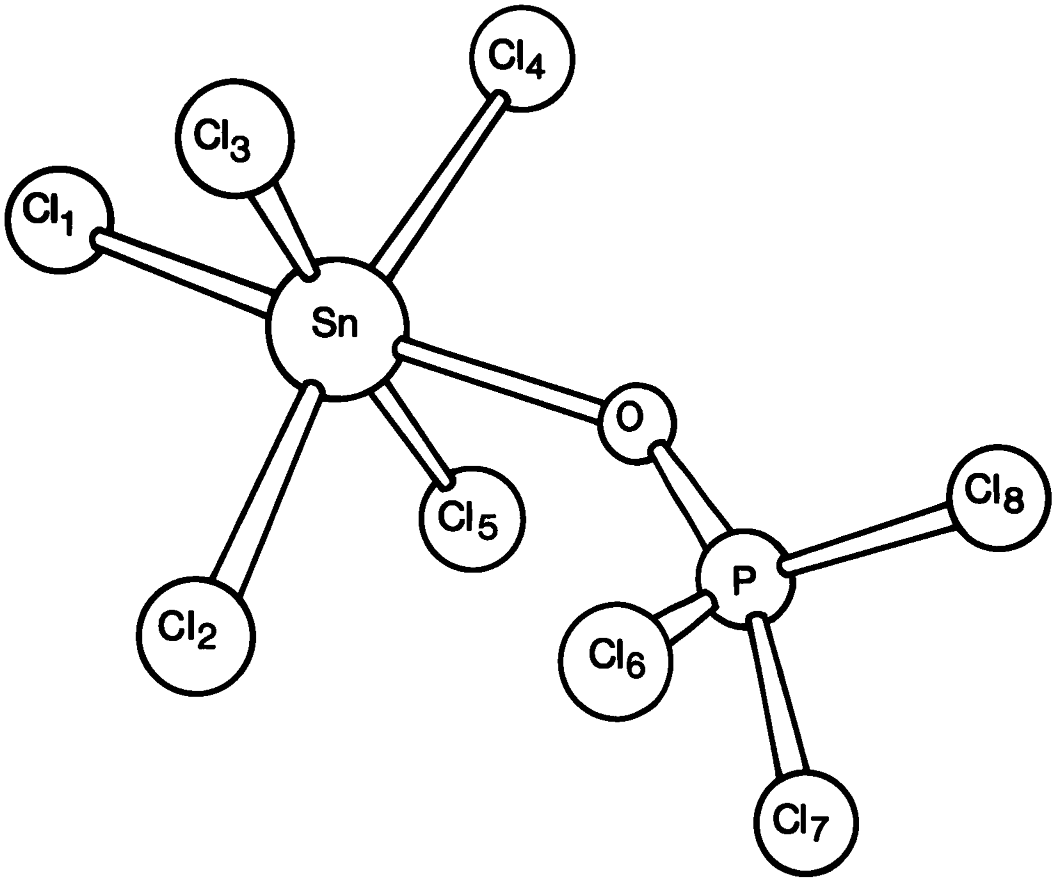
The second explanation in terms of disordering is illustrated graphically in figure 6.3. This would account for the greater range of bond lengths observed in shape I and also the larger angles at N(1) and N(2). Support for this explanation is given by the large anisotropic thermal parameters and the orientation of the thermal elipsoids for N(1) and N(2) in $S_5N_5^+AlCl_4^-$, as shown in figure 6.3.

It would appear that the cation reported in $S_5N_5^+AlCl_4^-$ could arise from the superposition of two cations of the shape observed in $S_5N_5^+S_3N_3O_4^-$ or $S_5N_5^+[SnCl_5POCl_3]^-$. The best way of establishing the existance of shape I would be by further study on $S_5N_5^+AlCl_4$ preferably at low temperature.

6.5.c Description and Discussion of the $[SnCl_5POCl_3]^-$ anion.

The anion consists of a central tin atom coordinated to five chlorine atoms and a $POCl_3$ molecule as shown in figure 6.4. The structures of several related compounds have been studied i.e. $SnCl_4(POCl_3)_2$ (Brandon, 1963), $SbCl_5POCl_3$ and $NbCl_5POCl_3$ (Brandon and Lindqvist, 1963). The second compound is isoelectronic with $[SnCl_5POCl_3]^-$ whilst the first and third provide examples of coordinated $POCl_3$.

The most interesting features in this ion concern the coordination of the $POCl_3$ ligand and its effect on the rest of the ion. As expected the Sn-O distance of 2.271Å is longer than the normal single bond distance of 2.11Å calculated from Pauling's covalent radii or of 2.07Å seen in $[SnCl_3OHH_2O]_2$ (Bokii and Struchov, 1971) which contains two $SnCl_3H_2O$ units linked by bridging OH groups.



$[SnCl_5POCl_3]^-$

Figure 6.4

The distance is the same within experimental error as the mean value of 2.28(3)Å found in $SnCl_4(POCl_3)_2$ but because of the large e.s.d's in this last example it is not possible to consider fine differences in structure between these two species. The Sn-O-P angle of 147.3° is similar to the mean value of 148° found in $SnCl_4(POCl_3)_2$ and to the value of 145° in $SbCl_5POCl_3$. Since there are no contacts between the phosphorus atom and the chlorine atoms bonded to tin less than their van der Waals distance of 3.55Å, the magnitude of this angle must be governed by the distribution of electrons at the oxygen atom. The size of the angle suggests that the hybridisation of the oxygen atom lies between sp and sp^2 hybrid states.

The P-O distance of 1.462Å does not differ significantly from that of 1.447Å observed in free $POCl_3$ (Moritani et al., 1971) and is the same within experimental error as the mean value of 1.45(5)Å found in $SnCl_4(POCl_3)_2$ and that of 1.47(2)Å found in $SbCl_5POCl_3$.

The P-Cl distances vary from 1.913 to 1.953Å and this range is greater than can be accounted for by statistical variation. All of the chlorine atoms bonded to phosphorus have large thermal parameters, e.g. in the last cycle of isotropic refinement the temperature factors of the chlorine atoms bonded to the tin atom varied from 3.92 - 4.34Å^2 whereas the temperature factors for Cl(6), Cl(7) and Cl(8) were 8.11, 9.04 and 6.01Å^2. It is noticeable that the shortest bond lengths, namely P-Cl(6) and P-Cl(7) of length 1.913(7)Å and 1.932(7)Å, are associated with the chlorine atoms with the largest temperature factors so that the variation in the P-Cl distances may be a result of contraction of the observed values of the bond distances due to thermal motion.

The P-Cl distances are all significantly shorter than that of 1.991(1)Å observed in free $POCl_3$ but are close to the mean values of 1.94(3)Å in $SnCl_4(POCl_3)_2$ and 1.95(1)Å in $SbCl_5POCl_3$. This may be the result of reduced π bonding between the oxygen and phosphorus atoms allowing the chlorine atoms to bond more strongly.

The coordination about phosphorus is roughly tetrahedral. The Cl-P-O angles vary from 111.3-115.7° and this range is greater than can be accounted for by statistical variation. Cl(7) and Cl(8) which are involved in the smallest Cl-P-O angles, have Cl---Cl contacts less than or close to the normal van der Waals distance of 3.50Å, namely 3.351Å between Cl(7) and Cl(2) at 1-x,-y, -z and 3.497Å between Cl(8) and Cl(3) at 1+x, y, z, whereas there are no short contacts to Cl(6). Movement of Cl(7) and Cl(8) towards the other atom in the contact increases the Cl-P-O angle, suggesting that the variation may be caused by packing. The Cl-P-Cl angles range from 104.6°-106.2° with a mean value of 105.6°. The Cl-P-O angles and Cl-P-Cl angles observed here are close to the values of 115.1° and 103.3° in free $POCl_3$.

The environment of the tin is that of a distorted octahedron. The Sn-Cl bond distances range from 2.370-2.406Å, and their average of 2.389Å is shorter than the Sn-Cl distance of 2.43Å in $SnCl_6^{2-}$ (Schaffer, 1954). The shortening can be attributed to the orbital contraction caused by the presence of only one negative charge.

The two longest Sn-Cl bonds, namely Sn-Cl(4) and Sn-Cl(5) of length 2.404Å and 2.406Å, are involved in S---Cl contacts less than the van der Waals distance of 3.55Å, as given in table 6.7. These interactions may account for the large variation found in the Sn-Cl bond distances.

The coordination at the tin atom appears to be governed by steric effects since the four chlorine atoms adjacent to the oxygen atom have Cl-Sn-O angles less than 90° ranging from 83.3-87.9°, and the Cl-Sn-Cl angles involving the chlorine atom trans to the oxygen atom are all greater than 90°, ranging from 92.6-96.9°. This overall distortion can be explained by the larger size of the chlorine atom as compared to oxygen, so that it is sterically favourable for the chlorine atoms to spread towards the oxygen.

6.6 Intermolecular Interactions.

The packing of the $S_5N_5^+$ cations and $[SnCl_5POCl_3]^-$ anions is characterised by a large number of intermolecular contacts less than the appropriate van der Waals distance. This is to be expected on account of the ionic nature of the structure. As mentioned before contacts between sulphur and chlorine atoms are likely to lower the potential energy of the structure, so that it is not surprising that all the sulphur atoms have S---Cl contacts less than the van der Waals distance of 3.55Å (Bondi, 1964); these are shown in table 6.7. The shortest intermolecular contacts involve the interaction of one chlorine with two sulphur atoms. Both S(2) and S(3) interact with $Cl(4^{I})$ at (x-1, y, z) and $Cl(5^{II})$ at ($\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$), and their interactions are fairly symmetrical as shown by their distances, namely 3.306Å and 3.279Å for S(2)---Cl(4^{I}) and S(3)---Cl(4^{I}), and 3.435Å and 3.474Å for S(2)---Cl(5^{II}) and S(3)---Cl(5^{II}). In these two interactions Cl(4^{I}) and Cl(5^{II}) lie 0.54Å and 2.88Å away from the mean plane of the S_5N_5 ring. There is a similar interaction involving S(4) and S(5) with Cl(5^{III}) at (1-x, $\frac{1}{2}$+y, $\frac{1}{2}$- z) with distances of 3.383Å and 3.294Å respectively, where Cl(5^{III}) lies 0.27Å away from the mean plane of the S_5N_5 ring. This type of interaction is possible because the intervening nitrogen is inset into the ring and a short N---Cl contact does not occur. It is of interest that the shortest S---Cl contacts occur with the two chlorine atoms which are closest to the mean plane of the S_5N_5 ring, and this suggests that these interactions may involve the overlap of a lone pair on a chlorine atom with a vacant orbital on the S_5N_5 ring. These interactions are analogous to that seen in $S_5N_5^+S_3N_3O_4^-$ between two sulphur atoms and an oxygen atom described in section 5.6 and are related to the interaction between an oxygen atom and two sulphurs in $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$ described in section 3.6.

There are very few Cl---Cl contacts less than their van der Waals distance of 3.5Å. Those present are between the chlorine atoms on the $POCl_3$ group and those bonded to tin, and have been used in section 6.5.c to account for the variations in the angles seen in the $POCl_3$ group. Likewise there is only one N---Cl distance less than the van der Waals distance of 3.330Å, namely N(1)---Cl(6) at ($\bar{x}$, 1-y, $\bar{z}$) of distance 3.246Å.

A projection along $\underline{a}$ of the contents of a unit cell is shown in figure 6.5.

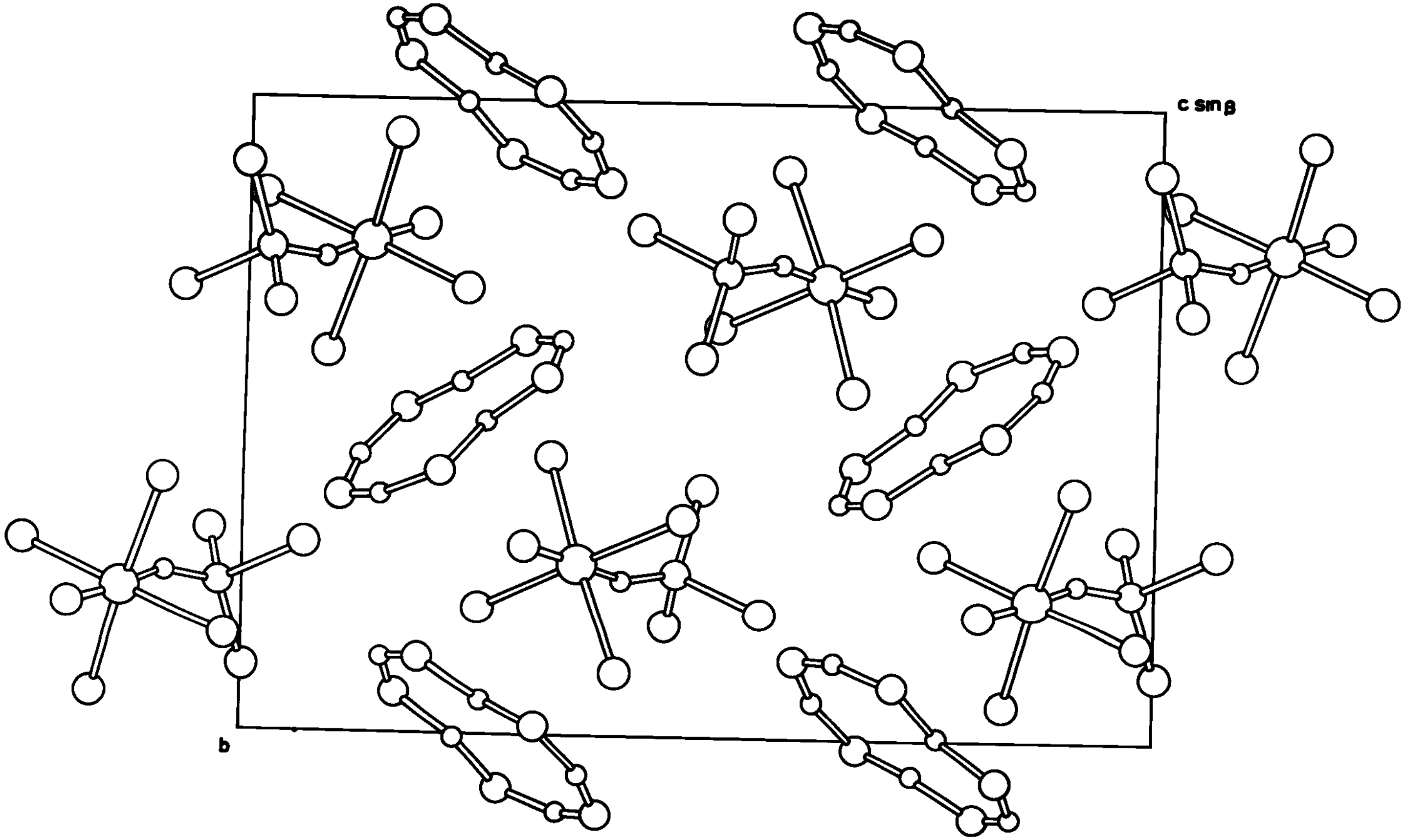
Table 6.7 $S_5N_5^+[SnCl_5POCl_3]^-$

Some Intermolecular Contacts (Å) < 3.8Å.

Atom A	Atom B	Equivalent	Cell	A-B
S(1)	Cl(3)	2	(0, 1, 0)	3.753
S(1)	Cl(8)	2	(1, 1, 0)	3.475
S(2)	Cl(4)	1	(-1,0, 0)	3.306
S(2)	Cl(5)	3	(0, 0, 0)	3.435
S(2)	Cl(8)	1	(-1,0, 0)	3.710
S(3)	Cl(4)	1	(-1,0, 0)	3.279
S(3)	Cl(5)	3	(0, 0, 0)	3.474
S(4)	Cl(2)	4	(0, 0, 0)	3.613
S(4)	Cl(5)	3	(1, 0, 0)	3.383
S(5)	Cl(1)	3	(0, 0, 0)	3.645
S(5)	Cl(4)	3	(1, 0, 0)	3.689
S(5)	Cl(5)	3	(1, 0, 0)	3.294
Cl(1)	Cl(8)	1	(-1,0, 0)	3.623
Cl(2)	Cl(7)	2	(1, 0, 0)	3.351
Cl(3)	Cl(8)	1	(1, 0, 0)	3.497
N(1)	Cl(6)	2	(0, 1, 0)	3.244
N(3)	Cl(2)	4	(0, 0, 0)	3.382
N(4)	Cl(1)	3	(0, 0, 0)	3.388

The intermolecular contacts refer to the position of atom A as in the original coordinates list and B as obtained from this using the symmetry operations given

Equivalent				
	1	x	y	z
	2	$\bar{x}$	$\bar{y}$	$\bar{z}$
	3	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
	4	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$



$S_5N_5^+[SnCl_5POCl_3]^-$

projection on the [100] plane

Figure 6.5

Table 6.8 $S_5N_5^+[SnCl_5POCl_3]^-$

Final Calculated and Observed Structure Factors (Both x 10)

H	K	L	FO	FC
0	0	2	559	-642
0	0	4	604	-707
0	0	6	1354	1500
0	0	8	841	881
0	0	10	151	-143
0	0	12	0	-33
0	0	14	0	-17
0	0	16	359	328
0	0	18	627	-576
0	0	20	372	-324
0	1	1	0	154
0	1	2	1833	-1814
0	1	3	0	-74
0	1	4	321	-377
0	1	5	1280	1456
0	1	6	328	346
0	1	7	1271	1395
0	1	8	945	-1052
0	1	9	513	-501
0	1	10	1487	-1496
0	1	11	156	180
0	1	12	0	-21
0	1	13	159	148
0	1	14	0	-58
0	1	15	219	197
0	1	16	597	-581
0	1	17	0	-28
0	1	18	532	-521
0	1	19	0	-63
0	1	20	604	556
0	1	21	0	-56
0	2	0	2091	-1909
0	2	1	402	-351
0	2	2	1647	-1596
0	2	3	792	-801
0	2	4	342	346
0	2	5	752	740
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8	6	-10	0	-15
8	6	-9	301	-324
8	6	-8	-144	-36
8	6	-7	329	363
8	6	-6	240	-202
8	6	-5	-61	-123
8	6	-4	370	-377
8	6	-3	398	-444
8	6	-2	-83	169
8	6	-1	-86	50
8	6	0	-87	241
8	6	1	326	314
8	6	2	-201	-110
8	6	3	258	-242
8	6	4	0	7
8	6	5	280	-355
8	6	6	342	345
8	6	7	-132	148
8	7	-10	-90	164
8	7	-9	-89	108
8	7	-8	0	-18
8	7	-7	250	319
8	7	-6	0	45
8	7	-5	497	-525
8	7	-4	256	276
8	7	-3	-187	-197
8	7	-2	0	35
8	7	-1	532	534
8	7	0	-195	221
8	7	1	0	46
8	7	2	-85	10
8	7	3	598	-614
8	7	4	-163	153
8	7	5	492	502
8	8	-7	265	-333
8	8	-6	391	366
8	8	-5	0	-7
8	8	-4	-193	-121
8	8	-3	531	571
8	8	-2	-95	99
8	8	-1	0	-16
8	8	0	0	-26
8	8	1	461	-469
8	8	2	-114	-179
8	8	3	-216	255
9	0	-10	465	-462
9	0	-8	-173	147
9	0	-6	-159	246
9	0	-4	520	-549
9	0	-2	298	237
9	0	0	642	648
9	0	2	-54	-58
9	0	4	-193	-224
9	0	6	254	235
9	1	-11	-24	-12
9	1	-10	417	425
9	1	-9	0	5
9	1	-8	257	191
9	1	-7	274	311
9	1	-6	-92	-147
9	1	-5	-156	-157
9	1	-4	-192	-165
9	1	-3	0	-28
9	1	-2	683	695
9	1	-1	-134	73
9	1	0	260	321
9	1	1	-115	158
9	1	2	343	-406
9	1	3	-161	12
9	1	4	-201	127
9	1	5	0	-16
9	1	6	413	437
9	2	-10	-134	120
9	2	-9	-114	55
9	2	-8	-184	-74
9	2	-7	0	65
9	2	-6	-61	-64
9	2	-5	-32	40
9	2	-4	230	200
9	2	-3	229	-275
9	2	-2	-85	163
9	2	-1	472	479
9	2	0	564	-581
9	2	1	447	-475
9	2	2	325	-301
9	2	3	-115	-228
9	2	4	456	521
9	2	5	-206	234
9	3	-10	418	-470
9	3	-9	-148	-193
9	3	-8	0	-24
9	3	-7	306	-348
9	3	-6	-172	139
9	3	-5	0	27
9	3	-4	0	46
9	3	-3	-94	124
9	3	-2	502	-598
9	3	-1	0	-133
9	3	0	-78	-86
9	3	1	263	-271
9	3	2	241	232
9	3	3	-128	49
9	3	4	0	64
9	3	5	-113	67
9	4	-9	374	-398
9	4	-8	220	256
9	4	-7	-140	153
9	4	-6	0	137
9	4	-5	-127	94
9	4	-4	419	-424
9	4	-3	0	-125
9	4	-2	0	-29
9	4	-1	-61	21
9	4	0	402	415
9	4	1	0	159
9	4	2	0	115
9	4	3	310	254
9	4	4	347	-344
9	5	-7	-140	146
9	5	-6	-213	-274
9	5	-5	-193	173
9	5	-4	-152	-7
9	5	-3	-216	-214
9	5	-2	308	337
9	5	-1	0	-30
9	5	0	-24	4
9	5	1	504	486
9	5	2	281	-272
9	6	-4	0	137
9	6	-3	-161	-17
9	6	-2	0	16
9	6	-1	395	418

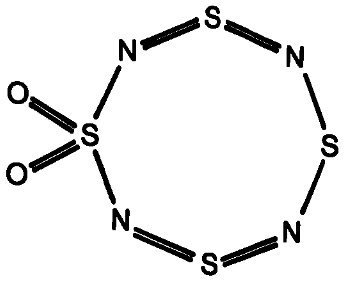
CHAPTER 7

The Crystal Structure of $S_4N_4O_2$

7.1 Introduction.

This section describes the work performed on the second compound isolated from the reaction between $(CH_3)_3Si-N=S=N-Si(CH_3)_3$ and $FSO_2-N=S=O$ as described in section 5.1. This compound gave an analysis and mass spectrum corresponding to the formulation $S_4N_4O_2$. The compound was found to be monomeric in the gas phase and also its molecular weight as determined cryoscopically corresponded to $S_4N_4O_2$.

The infrared spectrum could be interpreted in terms of the structure



This compound was of interest because it represented the second known oxide of S_4N_4.

7.2 Crystal Data.

The crystals were obtained as orange needles elongated along <u>c</u> and bounded by prominent {120} faces. Individual crystals were cut to appropriate lengths and sealed in quartz tubes to prevent hydrolysis. The crystal used for data collection had dimensions 0.5 x 0.25 x 0.25mm. Preliminary work using precession and Weissenberg methods showed the unit cell to be orthorhombic with systematic absences

h k l	k + l = 2n
0 k l	k = 2n
h 0 l	(l = 2n)
h k 0	(k = 2n)
h 0 0	no conditions
0 k 0	(k = 2n)
0 0 l	(l = 2n)

These are consistent with the noncentrosymmetric space group Abm2 (No.39) and also with the centrosymmetric space group Abmm (a non-standard representation of Cmma No.67) the reflections observed on the precession and Weissenberg photographs could be interpreted in terms of two superimposed reciprocal lattices each showing the absences of the space group and the same relative intensity to each other but differing slightly in orientation. This suggested that there were two pieces of crystal present which were slightly misaligned with respect to each other. The apparent splitting of the reflections on the films was most evident on the 0kl net, although it was evident on all other nets except for the hk0 net. The separation of the two parts of the reflections became more noticeable with increasing values of l and for the 00ℓ reflections was about 2°.

Several attempts were made to recrystallise the material. It was originally crystallised from methylene chloride, in which it is highly soluble. This was replaced by chloroform in which it is only slightly soluble, in order to recrystallise from a less concentrated solution. In this way several batches of very well formed crystals were obtained, a large number of which were examined, but all showed the apparent splitting of the reflections when photographed. The imperfections were not a consequence of the cutting since they were also shown by tiny uncut crystals. Data was finally collected from a split crystal.

Cell dimensions were obtained from the positions of twelve reflections measured on a diffractometer. Because for many reflections both parts overlapped, it was impossible to obtain accurate dimensions from the reflections from one part of the crystal. Consequently for the reflections which were split the positions of both parts were found and averaged, and where broadening was observed the mean position was taken. This work showed that each part of the reflection had the same θ value and differed only in orientation. It also showed that the ratio of the intensities of the two parts was constant for all reflections. The unit cell dimensions were obtained from a least squares treatment of these positions. The dimensions shown correspond to α, β and γ being constrained to 90^{o}, however refinement without this constraint gave values for the angles very close to 90^{o} (within $0.07(7)^{o}$).

$S_4N_4O_2$ M = 216.28

a = 8.088(5)Å

b = 18.920(10)Å

c = 8.683(7)Å

U = 1328.7$Å^3$

Z = 8

Dm = 2.15g cm^{-3} (by floatation in $C_2H_5I/C_2H_4Br_2$)

Dc = 2.16g cm^{-3}

Absorption coefficient for MoKα radiation (λ = 0.7107Å) = 13.7cm^{-1}.

7.3 Data Collection and Correction.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer using Zr-filtered MoKα radiation. To record both parts of the reflection an ω scan of 160 steps of 0.01° together with an open counter was used. Counting times of 2 seconds per step were allowed with a stationary background count of 80 seconds at the beginning and end of each scan. Reflections which showed a splitting of greater than 0.8° were recorded in steps of 0.01° over 2.0° and the middle 40 steps were removed so that the background:count ratio was retained. Three reflections were measured as standards every 30 reflections, and showed no systematic variations indicating that the crystal was stable throughout the experiment. Two sets of equivalent reflections were recorded for $0 < \theta \leq 25^\circ$. These gave a total of 657 independent reflections, of these 505 were taken as observed having net counts > 2 e.s.d's. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

7.4 Solution and Refinement.

An attempt was made initially to solve the structure in the centrosymmetric space group Cmma using symbolic addition procedures since the statistical distribution of the normalised structure factors, as shown in table 7.1 seemed to match better with the centrosymmetric case than the noncentrosymmetric. A multisolution program was used as described earlier and this gave several sets of highly self-consistent phases; however the E-maps calculated from these could not be interpreted in terms of a meaningful structure. This was later shown to be due to the wrong choice of space group. Finally the structure was solved from it's Patterson function.

The Patterson function for the space groups Abm2 and Abmm takes the form

$$P(uvw) = \frac{8}{V}\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty} |F(hkl)|^2 \cos 2\pi hu \cos 2\pi kv \cos 2\pi lw$$

this was calculated from

$u = 0 \rightarrow \frac{1}{4}$ intervals of 0.29526Å

$v = 0 \rightarrow \frac{1}{2}$ intervals of 0.27134Å

$w = 0 \rightarrow \frac{1}{2}$ intervals of 0.25275Å

The coefficients used were $|F_{obs}|^2$ weighted by $(Lp)^{-1}$ for each reflection. The vector map could only be interpreted in terms of the noncentrosymmetric space group.

The positions of all sulphur atoms were determined from their

Harker peaks. For an atom in a general position x, y, z in the space group Abm2 the following Harker peaks should be observed in the Patterson function

$2x$	$2y$	0
$2x$	$\frac{1}{2}$	0
0	$\frac{1}{2} - 2y$	0

and for atoms on the mirror planes at $x = {}^1/_4$ and ${}^3/_4$

$\frac{1}{2}$	0	$2\bar{z}$

The density measurements showed that there was one molecule per assymmetric unit corresponding to four sulphur atoms in general positions. The vector map was characterised by having very few large peaks in general positions, indicating that some of the sulphur atoms may be in special positions, and that the distribution of the sulphur atoms might have a higher symmetry than required by the space group. The two most significant peaks were at 0.219, 0.109, 0.125 and 0.281, 0.141, 0.25; the first of these corresponds to the vector between adjacent sulphur atoms in the same $S_4N_4O_2$ molecule, and the second to a vector between sulphur atoms in adjacent molecules. Although there are two crystallographically independent types of molecules per cell, they have approximately the same orientation so that only one intramolecular S-S vector is seen in a general position in the vector map.

The first sulphur atom was found at 0.218, 0,0 from its Harker peaks at

0.436	0	0	(62)
0.436	$\frac{1}{2}$	0	(73)
0	$\frac{1}{2}$	0	(114)

The position of the origin on the z axis for this space group is not specified by symmetry requirements, and was fixed by setting z = 0 for this atom. Harker peaks were found for four further sulphur atoms (two of these were in special positions on a mirror plane). The value of the z-coordinates relative to S(1) was found by generating the vectors between these atoms and S(1) and searching for a peak with the appropriate coordinates in a u and v. The positions found were

	x	y	z
S(1)	0.218	0.0	0.0
S(2)	-0.01	0.108	0.125
S(3)	0.05	0.141	0.250
S(4)	0.281	0.25	0.375
S(5)	0.719	0.25	0.375

These positions were refined by least squares methods using the block-diagonal approximation. The sulphur atoms were given isotropic temperature factors of 3.0Å^2, and at the end of two cycles the R value was 0.40. An Fo map was calculated, which revealed the positions of the four nitrogen atoms. Further refinement and calculation of difference syntheses gave the positions of the four oxygen atoms. The molecules of $S_4N_4O_2$ occupy two different crystallographic positions in the cell; half the molecules lie on mirror planes and the other half are disordered about two-fold axes to produce the observed symmetry. Two of the oxygen atoms lie on a mirror plane at $y = \frac{1}{4}$ whereas the other two lie in general positions with an occupation factor of 0.5 due to disordering. With the inclusion of these R fell to 0.20. A difference map at this stage showed that the sulphur atoms were vibrating anisotropically; this was allowed for during the subsequent refinement after which R fell to 0.148.

The atomic coordinates for the ring atoms in the disordered molecule correspond to the mean positions of two superimposed S_4N_4 rings. Calculation of a difference synthesis showed that this approximation was satisfactory for all the ring atoms except S(1), for which a more accurate description was that of two sulphur atoms each with an occupation factor of 0.5 separated by about 0.7Å. These were included with isotropic temperature factors in the subsequent refinement, which resulted in an R value of 0.125. Further refinement using full matrix least squares methods saw R stand at 0.117. The parameter shifts in the last cycle were all $< 0.2\sigma$. A difference synthesis calculated from the final structure factors showed no prominent features associated with the atomic positions; however the map did contain ripples of $\pm$ 1.2 e.Å^{-3}.

The initial weighting scheme used was the same as in previous refinements, with values of $P_1 = 35.0$ and $P_2 = 0.01$. This was replaced in the final stages of refinement by a weighting scheme of the form

$$\sqrt{w} = [1-\exp(-P_2.\sin^2\theta/\lambda^2]/[P_1 + |F_o|]^{\frac{1}{2}}$$

This was found to give a more uniform distribution of $w\Delta^2$ than the previous scheme and the scheme based on counting statistics mentioned earlier. The optimum values of the parameters were $P_1 = 30.0$ $P_2 = 60.0$. $w\Delta^2$ was analysed as a function of the magnitude of $|F_o|$ and also as a function of ℓ. The latter was performed in order to investigate whether the imperfections of the crystals produced any systematic errors dependent on the magnitude of ℓ, but none were observed. The final least squares totals and weighting analysis are given in table 7.1. The final calculated and observed structure factors are given in table 7.7 the sulphur atoms were not corrected for anomolous dispersion. The scattering factors used were taken from International tables Vol. III. The final atomic coordinates, isotropic thermal parameters and anisotropic thermal parameters are given in table 7.2. This structure determination is less accurate than others described in this thesis, due to the poor quality of the data, to the disorder and to the large number of parameters relative to the number of observed reflections.

Table 7.1 $S_4N_4O_2$

Least squares totals

Number of observed reflections 505

$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	$\Sigma w\Delta^2$	R
19282.46	18855.80	2253.84	237.76	.117

Weighting Analysis

$\|F_o\|$ ranges	N	$\Sigma w\,\Delta^2/N$	R
0 - 20	145	0.46	0.230
20 - 30	140	0.47	0.159
30 - 40	68	0.43	0.129
40 - 50	45	0.49	0.126
50 -100	82	0.54	0.082
100 -200	22	0.33	0.046
200-upwards	3	0.47	0.060

The Statistical Distribution of the Normalised Structure Factors

	Centrosymmetric	Noncentrosymmetric	Observed
$<\|E\|>$	0.798	0.886	0.824
$<\|E\|^2>$	1.00	1.00	1.060
$<\|E^2-1\|>$	0.968	0.736	0.982
$\|E\| > 3$	0.3%	0.01%	0.43%
$\|E\| > 2$	5.0%	1.8%	4.41%
$\|E\| > 1$	32.0%	37.0%	32.86%

Table 7.2 $S_4N_4O_2$

Final Atomic Coordinates with their Estimated Standard Deviations (x 10^4) and Isotropic Thermal Parameters (Å^2)

Atom	x/a	y/b	z/c	B	Occupation Factor
S(11)	0.2497(21)	0.0202(7)	0.0035(27)	3.34(30)	0.5
S(12)	0.1894(20)	0.0050(9)	-0.0229(25)	3.27(30)	0.5
S(2)	-0.0338(8)	0.1077(3)	0.0996(13)	2.6 †	1.0
S(3)	0.4996(14)	0.1433(3)	0.2658 *	3.7 †	1.0
S(4)	0.2506(11)	0.25	0.3621(19)	4.3 †	1.0
S(5)	0.7034(9)	0.25	0.3763(17)	2.6 †	1.0
O(1)	0.1004(40)	-0.0074(20)	-0.1481(49)	3.08(68)	0.5
O(2)	0.3757(56)	0.0191(23)	-0.0453(69)	4.89(94)	0.5
O(3)	0.5889(28)	0.25	0.5129(37)	2.53(41)	1.0
O(4)	0.8718(32)	0.25	0.4016(40)	3.58(54)	1.0
N(1)	0.1447(29)	0.0791(13)	0.0636(32)	3.82(48)	1.0
N(2)	-0.1871(28)	0.0566(12)	0.0665(30)	3.27(43)	1.0
N(3)	0.3398(28)	0.1732(13)	0.3255(36)	3.83(51)	1.0
N(4)	0.6619(27)	0.1863(13)	0.2541(32)	3.40(46)	

* This parameter was used to fix the origin on c.

† The isotropic temperature factor before anisotropic refinement.

Anisotropic Thermal Parameters and their Estimated Standard Deviations (Both Å^2 x 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(2)	377(43)	296(28)	746(73)	- 18(42)	168(40)	41(24)
S(3)	865(51)	264(26)	663(74)	16(44)	-197(51)	-127(41)
S(4)	37(33)	1059(88)	655(87)		- 45(49)	
S(5)	197(35)	212(32)	334(47)		- 14(42)	

Table 7.3 $S_4N_4O_2$

Final Bond Distances (Å) and their Estimated Standard Deviations

(Å x 10^2)

$S(11^{II})$	-	$N(1^{II})$	1.49(3)
$S(11^{II})$	-	N(2)	1.63(3)
S(12)	-	O(1)	1.33(4)
S(12)	-	O(2)	1.54(5)
S(12)	-	N(1)	1.63(3)
S(12)	-	$N(2^{II})$	1.40(3)
S(2)	-	N(1)	1.57(2)
S(2)	-	N(2)	1.60(2)
S(3)	-	N(3)	1.50(3)
S(3)	-	N(4)	1.55(2)
S(4)	-	N(3)	1.65(3)
S(5)	-	O(3)	1.51(3)
S(5)	-	O(4)	1.38(3)
S(5)	-	N(4)	1.64(3)

Table 7.3 continued...

Table 7.3 continued

Some Non-bonding Intramolecular Distances (Å) and their Estimated Standard Deviations (Å x 10^2)

S(11)	---S(12)	0.61(2)
S(11^{II})	---S(12)	3.59(2)
S(11)	---S(2)	2.95(2)
S(12)	---S(2)	2.86(2)
S(2)	---S(2^{II})	4.11(2)
N(1)	---N(1^{II})	3.80(3)
N(1)	---N(2)	2.72(3)
N(1)	---N(2^{II})	2.59(3)
N(2)	---N(2^{II})	3.71(3)
S(3)	---S(3^{I})	4.04(1)
S(3)	---S(4)	2.97(1)
S(3)	---S(5)	2.78(1)
S(4)	---S(5)	3.62(1)
N(3)	---N(3^{I})	2.91(4)
N(4)	---N(4^{I})	2.41(3)
N(3)	---N(4^{I})	3.77(3)

Where I and II refer to atoms in the equivalent positions respectively x, $\frac{1}{2}$-y, z and -x, -y, z with respect to the original coordinates.

Table 7.4 $S_4N_4O_2$

Final Bond Angles (degrees) and their Estimated Standard Deviations

(deg. x 10)

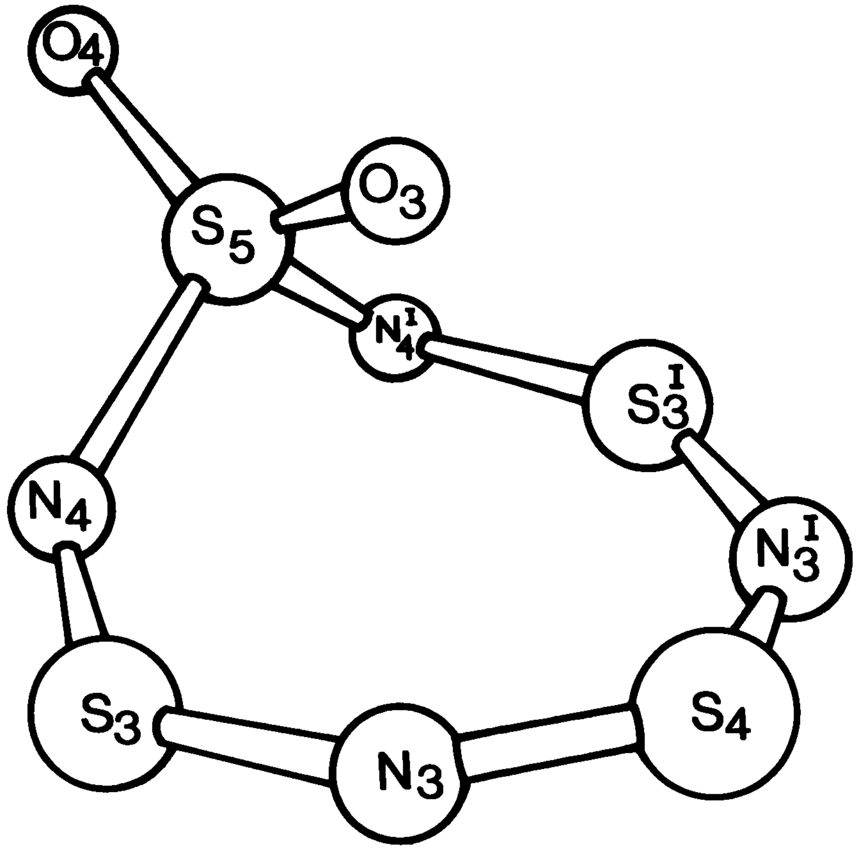
N(1^{II}) - S(11^{II}) - N(2)	111.7(17)
O(1) - S(12) - O(2)	117.3(28)
O(1) - S(12) - N(1)	114.2(22)
O(1) - S(12) - N(2^{II})	107.5(23)
O(2) - S(12) - N(1)	97.2(23)
O(2) - S(12) - N(2^{II})	103.1(24)
N(1) - S(2) - N(2^{II})	117.9(13)
S(11^{II}) - N(1^{II}) - S(2^{II})	147.9(20)
S(12) - N(1) - S(2)	126.2(18)
S(11^{II}) - N(2) - S(2)	147.0(18)
S(12) - N(2^{II}) - S(2^{II})	127.8(18)
N(1) - S(12) - N(2^{II})	117.2(18)
N(3) - S(3) - N(4)	123.6(15)
N(3) - S(4) - N(3^{I})	123.1(15)
O(3) - S(5) - O(4)	118.8(15)
O(3) - S(5) - N(4)	112.6(14)
O(4) - S(5) - N(4)	107.8(15)
N(4) - S(5) - N(4^{I})	94.6(15)
S(3) - N(3) - S(4)	140.6(19)
S(3) - N(4) - S(5)	121.2(16)

7.5 The Structure and Bonding in $S_4N_4O_2$

The unit cell contains two crystallographically independent sets of $S_4N_4O_2$ molecules. One set is situated on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$ and the other half are situated about the two-fold axes at $(0,0,z)$ and $(0,\frac{1}{2},z)$ and are disordered to produce the observed symmetry. The bond lengths and angles are given in tables 7.3 and 7.4 respectively.

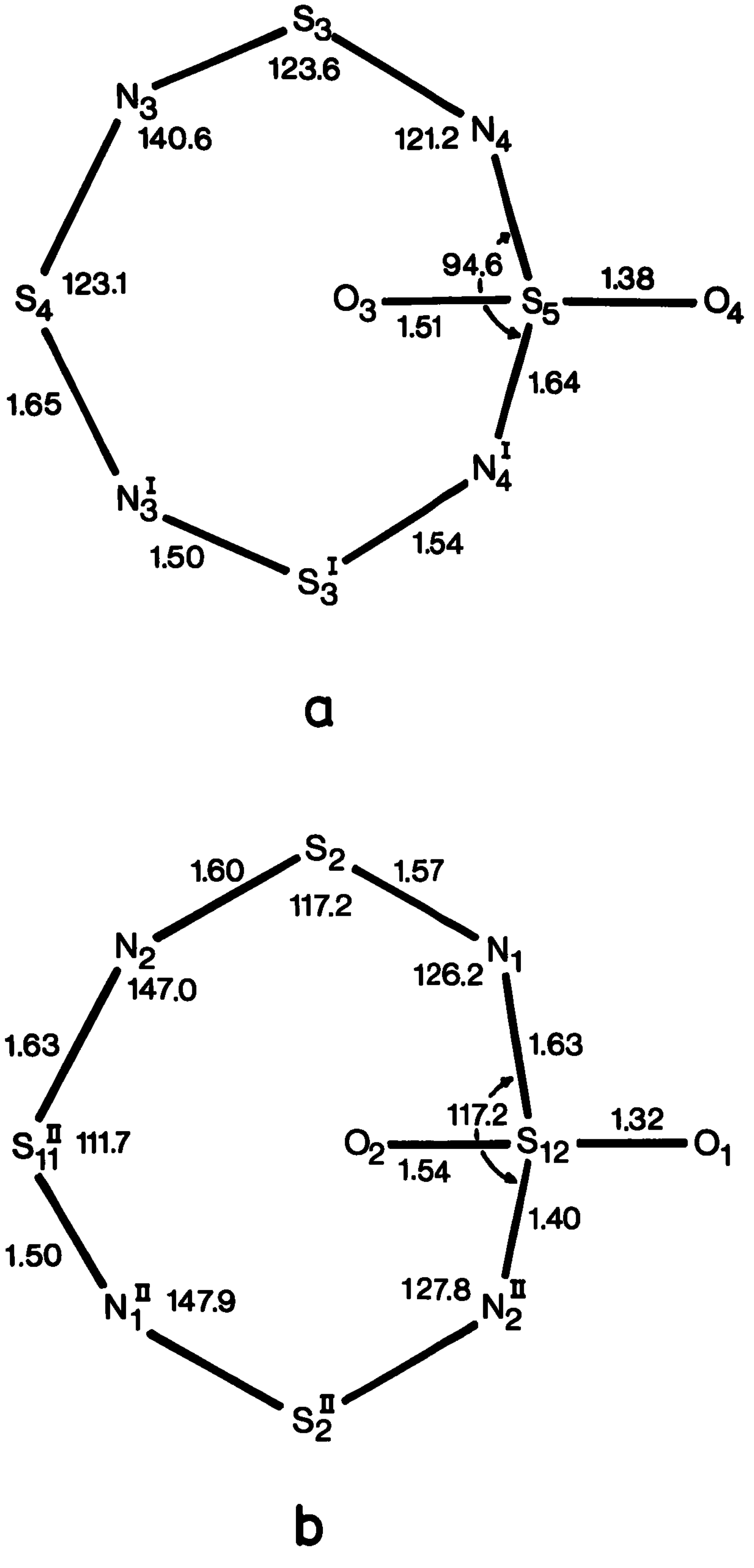
Both types of molecule consist of an eight-membered S_4N_4 ring with both oxygen atoms attached to the same sulphur atom. The ordered molecule which sits on the mirror plane is shown in figure 7.1. The dimensions of both the ordered and disordered molecules are shown on figure 7.2.

The atomic arrangement about the two-fold axis corresponds to the mean positions of two superimposed $S_4N_4O_2$ molecules of the dimensions seen in the molecule on the mirror plane. This can be shown by a comparison of the S---S and N---N intramolecular distances. The cross-ring distances S(4)---S(5) and $S(3)---S(3^{I})$ of length 3.62(1)Å and 4.04(1)Å should not be affected by disordering. This is observed in the disordered molecule where the corresponding distances $S(11^{II})---S(12)$ and $S(2)---S(2^{II})$ are 3.59 Å and 4.11(2)Å. Similarly the $N(3)---N(4^{I})$ cross ring distance of 3.77(3)Å in the ordered molecule is the same within experimental error as the length of 3.80(3)Å for $N(1)---N(1^{II})$ and 3.71(3)Å for $N(2)---N(2^{II})$. The $N(3)---N(3^{I})$ and $N(4)---N(4^{I})$ distances of length 2.91(4)Å and 2.41(3)Å are averaged on disordering and their average of 2.66Å is not



$S_4N_4O_2$

Figure 7.1



$S_4N_4O_2$

Figure 7.2

Some bond distances and angles for (a) the ordered
(b) the disordered molecules

significantly different from the N(1)---N(2^{II}) distance of 2.59(3)Å in the disordered molecule. The averaging of the S---S distances around the ring on disordering is not observed because of the separate treatment of S(11) and S(12).

The averaging of the nitrogen positions is reflected in the differences in angle between the S_4N_4 rings in the ordered and disordered molecule. In the ordered molecule the angles N(4)-S(5)-N(4^I) and N(3)-S(4)-N(3^I) have magnitudes of 95° and 123° respectively, whereas the corresponding angles in the disordered molecule, N(1)-S(12)-N(2^{II}) and N(1^{II})-S(11^{II})-N(2) are 117° and 112° the averaging increases the separation of the nitrogen atoms bonded to the sulphur which carries the oxygen atoms and hence accounts for the increase in the angle at S(12), and conversely the decrease at S(11).

The following discussion of the molecular shape and dimensions is confined to the ordered molecule. The S_4N_4 ring is not planar. The sulphur atom S(5) which is attached to the two oxygen atoms, and its adjacent nitrogen atoms N(4) and N(4^I) lie 1.52Å and 0.41Å above the mean plane of the remaining ring atoms. The maximum deviation from the mean plane of S(3), S(3^I), S(4), N(3) and N(3^I) is 0.014Å as shown in table 7.5. The estimated standard deviations for all bond lengths are large (about 0.03Å) so that a detailed discussion of the differences in bond distances is not warranted.

S(3)-N(3) and S(3)-N(4) of lengths 1.55Å and 1.50Å are significantly shorter than the normal single bond distance of 1.73Å and indicate considerable multiple bonding across this part of the molecule. Conversely S(5)-N(4) of length 1.64Å does not differ

Table 7.5 $S_4N_4O_2$

The Equation of the Mean Plane of S(3), S(3^I), S(4), N(3) and N(3^I)

$$-0.3822X \quad + 0.0Y \quad - 0.9241Z \quad + 3.6765 \; = \; 0$$

Atom	S(3)	S(3^I)	S(4)	S(5)†	N(3)	N(3^I)	N(4)†
P	-0.0004	-0.0004	-0.0030	-1.517	0.0140	0.0140	-0.409
σ(P)	0.0044	0.0044	0.0159	0.014	0.0305	0.0305	0.027

Where P and σ(P) are the distance and its standard deviation from the mean plane.

X, Y and Z refer to orthogonal coordinates in Å which lie in the direction of a, b and c respectively.

† This atom was not included in the calculation of the mean plane.

significantly from the normal single bond distance, although some shortening of this bond might be expected on account of the sp^2 hybridisation at N(4) and the contraction of the orbitals on S(5) caused by the oxygen atoms bonded to it. Similarly S(4)-N(3) of length 1.65Å is not significantly different from the normal single bond distance and likewise some shortening might be expected on account of the hybridisation at N(3).

The S-O distances are the same within experimental error and the mean value of 1.45Å is similar to that of 1.449Å found in $[(CH_3)_2N]_2SO_2$ (Jordan, et al., 1963) and 1.391Å in $(H_2N)_2SO_2$ (Trueblood and Mayer, 1956) and is normal for an S-O double bond.

The coordination about S(5) is roughly tetrahedral. The angle between the terminal oxygen atoms of 118.8° is larger than the tetrahedral angle; this is a consequence of the multiple bonding in the S-O bonds. Conversely the angle in the ring at S(5), i.e. N(4)-S(5)-N(4^I) has a magnitude of 94.6° which suggests that the S(5)-N(4) bond has a large proportion of p character and is essentially a single bond. Further support for this is given from the N-S-N angle of 113° in $[(CH_3)_2N]_2SO_2$ in which there is π-bonding to the central sulphur atom. The N-S-O bond angles are intermediate between the O-S-O and N-S-N angles with values of 112.6° and 107.8° for N(4)-S(5)-O(3) and N(4)-S(5)-O(4).

The bonding in the S_4N_4 ring could be described in terms of two sulphur diimide fragments i.e., N(3)-S(3)-N(4), and N(3^I)-S(3^I)-N(4^I), which are similar to that seen in $S_3N_3O_4^-$ (section 5.5.b), linked together by single bonds to a sulphur atom and an $-SO_2-$ group. This description fits the short S-N distances in the N(3)-S(3)-N(4) part and also the angles at N(4) of 121.2° and S(3) of 123.6°. The angle in the ring at N(3) of 140.6° is larger than necessitated by π-bonding to S(3) alone, and suggests that the π-bonding may extend to S(4) giving delocalisation over the whole of the S_3N_4 fragment. S_3N_4 represents, using the electron counting rule a 10π system, and in view of the rough planarity of this part of the molecule, the bonding could be described as a delocalised 10π-system bridged by an SO_2 unit. The SO_2 unit would then be analogous to the $\overset{+}{S}$-Cl or S=N- units in $S_3N_2Cl^+$ and $-N-S_3N_2$ described earlier in section 4.5.b in that they stabalise the formation of a ring system.

7.6 Molecular Packing.

The most significant feature in the packing of the $S_4N_4O_2$ molecules is a very short oxygen-oxygen contact between the molecules around the two-fold axis at the origin and those disordered about the two-fold axis at (1,0,0). Specifically this is the distance of 2.14Å between O(2) and $O(2^V)$ at 1-x, -y, z and may be viewed as the contact between the oxygen atom O(2) on one molecule of $S_4N_4O_2$ and that on another rotated through 180° and translated through (1,0,0). It is unreasonable to expect this interaction to actually occur implying that the $S_4N_4O_2$ molecules around the two-fold axes are ordered in rows parallel to a, although the rows are disordered with respect to one another.

If an individual $S_4N_4O_2$ molecule is considered to be sitting at the origin then the equivalent positions x, -y, $\frac{1}{2}$+z and -x, y, $\frac{1}{2}$+z would give two orientations for the molecule situated above the first along c. In the first of these orientations the $S_4N_4O_2$ molecule is approximately superimposed, in projection along c, on the molecule beneath because the plane of the molecule, which contains S(11), S(12), O(1) and O(2), lies roughly in the a b plane. In the second orientation the molecule is rotated approximately 180° with respect to that at the origin. As shown in table 7.6 there are two short N---O intermolecular contacts between the molecule at the origin and that directly above it along c, namely N(1)---$O(1^{III})$ and N(2)---$O(1^{IV})$ of length 2.87Å and 2.85Å. Because of the disordering the nitrogen positions represent the mean positions of the nitrogen atoms in two superimposed $S_4N_4O_2$ molecules. Consequently the same contacts are observed for both orientations and from these it is not possible to predict which orientation is more favourable. In the ordered molecule N(3) and N(4) lie 0.34Å and 1.06Å respectively below the plane which passes through S(4) and S(5) and lies perpendicular to the mirror plane. Since the observed contact corresponds to the mean of these two positions a longer contact will arise between the molecule at the origin and one above it, if the latter is rotated 180° with respect to the first. The alternative orientation will result in much shorter intermolecular contacts than are observed. This implies that there should be alternation in the orientation of the $S_4N_4O_2$ molecules along the two-fold axes. Together with the ordering mentioned initially, this suggests that the packing of the molecules in the $\underline{a}$ $\underline{c}$ planes at $y = 0, \frac{1}{2}, \ldots\ldots$ tends to be ordered although the planes are randomly oriented with respect to each other. The imperfections in the crystals may be related to this ordering. If one row of $S_4N_4O_2$ molecules parallel to $\underline{a}$ was superimposed directly on the row beneath, then because of the increased repulsions between the oxygen and nitrogen atoms, the separation of the rows along $\underline{c}$ would increase. This would produce a misalignment in the lattice which would be greatest in the $\underline{b}$ $\underline{c}$ plane and would account for the separation of the two parts of each reflection being most noticeable on the 0kl reciprocal lattice net.

Apart from the contacts just mentioned all others which are less than the appropriate van der Waals distance involve sulphur atoms with either oxygen or nitrogen atoms. This is expected on account of the small positive charge on the sulphur atoms and the small negative charge on the oxygen and nitrogen atoms. It is significant that there are few interactions between the molecules on the mirror planes and those about the two-fold axes which may account for the disordering being energetically possible.

A projection on the [001] plane of half of the contents of the unit cell is shown in figure 7.3. The equivalent positions shown correspond to the projection of the contents of the unit cell without the centering, (0, ½, ½).

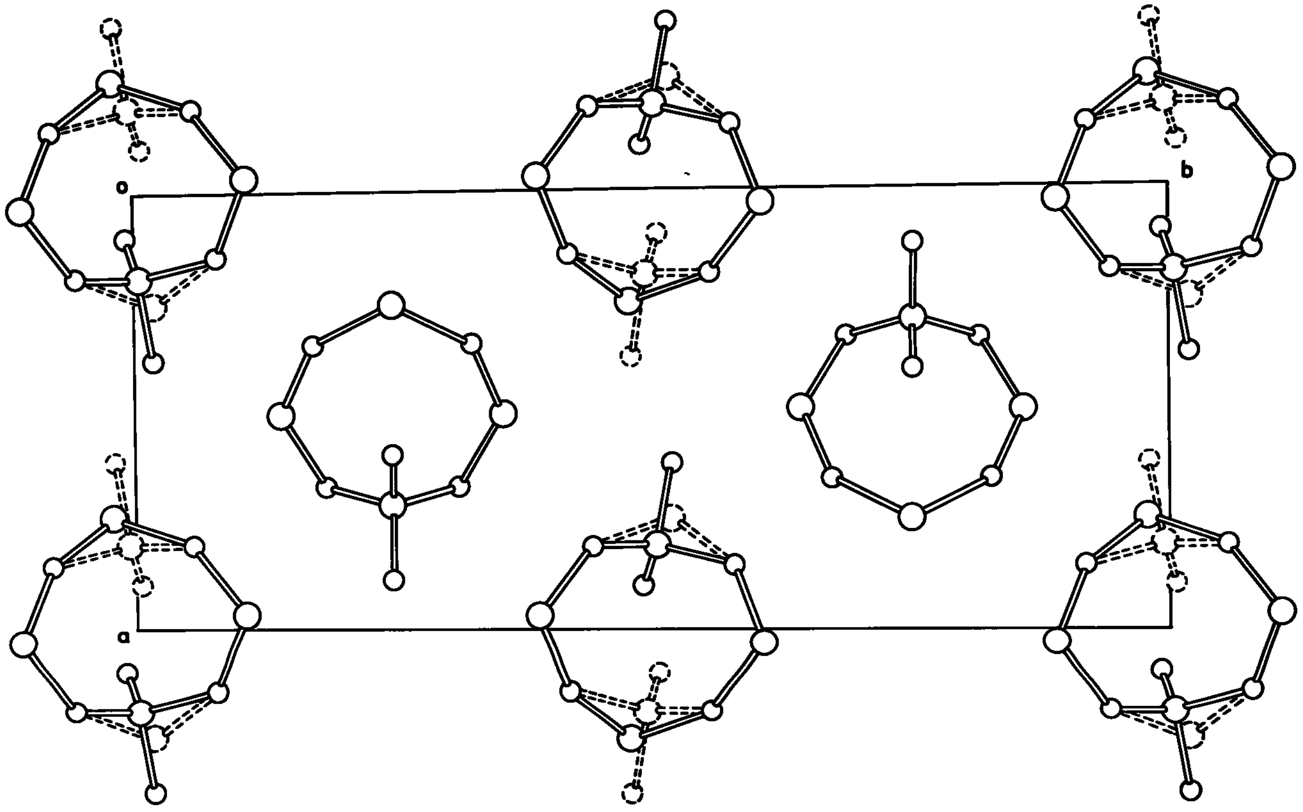
Table 7.6 $S_4N_4O_2$

Some Intermolecular Contacts < 3.35Å

S(11) - O(1^{III})	3.27
S(11) - O(2^{V})	3.15
S(12) - O(1^{III})	3.33
S(2) - O(1^{IV})	3.14
S(2) - O(1^{III})	3.10
S(2) - N(4^{VI})	3.17
S(3) - O(2^{VII})	3.04
S(3) - O(3^{VIII})	3.07
S(4) - O(3^{VIII})	3.30
S(4) - O(4^{VI})	3.08
N(1) - O(1^{III})	2.87
N(2) - O(1^{IV})	2.85
O(2) - O(2^{V})	2.14

The equivalent positions with respect to an atom at x,y,z

III	x, -y, ½+z	VI	-1+x, y, z
IV	-x, y, ½+z	VII	1-x, y, ½ + z
V	1-x, -y, z	VIII	1-x, y, -½ + z



$S_4N_4O_2$

projection of half of the contents of the unit cell

on the [001] plane

Figure 7.3

Table 7.7 $S_4N_4O_2$

Final Calculated and Observed Structure Factors

H	K	L	FO	FC
0	2	0	11.5	2.3
0	4	0	92.1	86.8
0	6	0	24.2	7.7
0	8	0	177.6	191.5
0	10	0	53.4	35.2
0	12	0	103.3	102.3
0	14	0	28.2	39.2
0	16	0	53.3	54.6
0	18	0	18.0	28.2
0	20	0	51.2	59.1
0	22	0	21.7	19.8
0	0	2	99.7	100.6
0	2	2	240.3	254.6
0	4	2	261.7	275.5
0	6	2	113.4	109.8
0	8	2	99.6	98.2
0	10	2	111.8	113.0
0	12	2	84.4	87.9
0	14	2	28.2	33.7
0	16	2	38.3	42.6
0	18	2	59.9	62.3
0	20	2	-0.8	14.0
0	22	2	25.2	29.5
0	0	4	128.4	128.8
0	2	4	69.8	76.0
0	4	4	79.8	80.8
0	6	4	161.5	159.7
0	8	4	26.9	32.5
0	10	4	20.4	14.4
0	12	4	11.6	21.7
0	14	4	85.9	84.8
0	16	4	18.5	17.9
0	18	4	28.8	28.9
0	20	4	16.8	14.7
0	0	6	23.4	29.2
0	2	6	50.8	54.7
0	4	6	121.8	114.9
0	6	6	76.8	83.9
0	8	6	13.5	18.0
0	10	6	45.5	49.0
0	12	6	35.7	40.3
0	14	6	34.9	26.0
0	16	6	21.2	23.1
0	18	6	17.2	22.0
0	0	8	74.6	60.8
0	2	8	33.0	37.9
0	4	8	35.2	35.9
0	6	8	-9.6	5.1
0	8	8	53.9	54.6
0	10	8	44.6	37.8
0	12	8	21.9	18.9
0	14	8	-8.0	15.7
0	0	10	26.9	31.4
0	2	10	-9.7	5.6
0	4	10	-9.5	13.5
1	0	0	-4.0	0.9
1	2	0	162.1	163.9
1	4	0	-0.4	4.5
1	6	0	142.6	133.9
1	8	0	10.9	11.5
1	10	0	128.9	134.7
1	12	0	-4.5	1.2
1	14	0	53.8	53.1
1	16	0	-0.7	3.5
1	18	0	70.0	76.8
1	20	0	-0.8	2.6
1	22	0	23.5	23.0
1	1	1	41.5	26.6
1	3	1	41.3	21.0
1	5	1	80.8	76.0
1	7	1	14.6	9.3
1	9	1	65.7	59.0
1	11	1	12.3	14.8
1	13	1	65.7	58.0
1	15	1	45.9	39.5
1	17	1	55.5	52.7
1	19	1	-5.3	16.0
1	21	1	24.7	18.7
1	0	2	180.6	223.1
1	2	2	15.0	13.8
1	4	2	172.0	172.5
1	6	2	67.0	70.4
1	8	2	11.4	17.4
1	10	2	31.9	30.7
1	12	2	-10.3	13.9
1	14	2	47.5	53.7
1	16	2	15.6	9.8
1	18	2	20.1	21.1
1	20	2	78.2	24.6
1	1	3	47.0	49.4
1	3	3	-1.6	15.3
1	5	3	48.1	44.9
1	7	3	38.0	47.7
1	9	3	52.9	54.7
1	11	3	36.8	32.6
1	13	3	29.6	41.4
1	15	3	37.8	38.8
1	17	3	-10.9	12.0
1	19	3	23.5	24.4
1	21	3	29.6	25.5
1	0	4	121.6	133.2
1	2	4	55.8	59.5
1	4	4	74.8	71.5
1	6	4	48.2	42.8
1	8	4	52.0	50.6
1	10	4	47.4	41.6
1	12	4	-8.2	16.2
1	14	4	73.8	19.7
1	16	4	-9.6	7.7
1	18	4	23.3	21.4
1	20	4	19.4	21.1
1	1	5	36.4	31.7
1	3	5	31.9	35.9
1	5	5	11.8	15.9
1	7	5	43.4	45.9
1	9	5	13.2	11.3
1	11	5	40.9	46.3
1	13	5	-5.3	4.0
1	15	5	15.8	20.2
1	17	5	-2.8	3.6
1	19	5	26.8	24.0
1	0	6	12.8	12.6
1	2	6	10.9	7.5
1	4	6	-0.6	7.4
1	6	6	66.1	63.4
1	8	6	14.6	14.2
1	10	6	35.1	78.5
1	12	6	-10.2	5.4
1	14	6	50.0	50.8
1	16	6	-8.9	6.5
1	18	6	25.7	24.1
1	1	7	46.3	37.5
1	3	7	20.9	20.4
1	5	7	12.5	16.7
1	7	7	-0.7	15.4
1	9	7	23.5	24.1
1	11	7	-10.7	17.2
1	13	7	18.9	21.2
1	15	7	20.6	19.8
1	0	8	42.8	40.5
1	2	8	20.0	16.0
1	4	8	16.5	18.6
1	6	8	-9.7	7.1
1	8	8	21.1	22.2
1	10	8	24.4	22.5
1	12	8	-8.9	2.3
1	14	8	-8.4	7.6
1	1	9	16.5	17.7
1	3	9	23.3	11.4
1	5	9	18.3	19.3
1	7	9	-0.8	7.3
1	9	9	-7.2	19.6
1	0	10	-12.0	10.8
1	2	10	-5.1	7.8
1	4	10	16.6	13.6
2	0	0	59.0	56.9
2	2	0	12.7	1.1
2	4	0	271.6	290.2
2	6	0	26.1	13.4
2	8	0	38.6	35.0
2	10	0	10.2	20.2
2	12	0	73.2	75.5
2	14	0	26.7	27.7
2	16	0	51.7	49.2
2	18	0	-4.1	14.9
2	20	0	19.9	20.5
2	22	0	-3.5	12.5
2	1	1	34.6	21.9
2	3	1	33.4	21.0
2	5	1	47.9	41.9
2	7	1	27.4	27.0
2	9	1	47.1	37.6
2	11	1	-5.6	17.4
2	13	1	11.9	10.5
2	15	1	30.7	30.1
2	17	1	26.1	29.9
2	19	1	-8.1	11.5
2	21	1	25.2	21.5
2	0	2	167.7	176.5
2	2	2	124.5	132.3
2	4	2	31.6	24.0
2	6	2	123.4	123.8
2	8	2	109.2	104.9
2	10	2	50.6	40.3
2	12	2	38.3	33.7
2	14	2	99.8	105.1
2	16	2	19.4	22.3
2	18	2	29.4	30.3
2	20	2	21.7	25.9
2	1	3	33.2	46.4
2	3	3	14.0	17.2
2	5	3	-8.2	17.9
2	7	3	20.6	20.6
2	9	3	12.2	8.4
2	11	3	29.2	26.3
2	13	3	-0.7	3.9
2	15	3	26.0	29.2
2	17	3	-8.3	14.7
2	19	3	-5.9	4.7
2	21	3	-0.9	10.1
2	0	4	23.3	25.6
2	2	4	122.6	126.0
2	4	4	27.6	33.0
2	6	4	48.6	46.9
2	8	4	57.3	54.5
2	10	4	124.5	123.4
2	12	4	21.7	20.8
2	14	4	22.4	20.9
2	16	4	-11.1	14.8
2	18	4	46.4	49.9
2	20	4	19.4	25.3
2	1	5	14.9	16.7
2	3	5	34.6	26.8
2	5	5	38.3	32.9
2	7	5	22.0	25.8
2	9	5	38.7	30.2
2	11	5	13.7	12.0
2	13	5	12.0	7.5
2	15	5	-7.3	9.3
2	17	5	-0.8	8.7
2	19	5	-8.0	4.8
2	0	6	85.7	94.9
2	2	6	39.6	40.9
2	4	6	16.3	18.9
2	6	6	52.0	51.5
2	8	6	59.3	60.8
2	10	6	43.0	35.7
2	12	6	-0.8	5.7
2	14	6	24.3	20.8
2	16	6	-3.7	11.7
2	1	7	-0.7	20.9
2	3	7	21.3	24.7
2	5	7	12.7	12.2
2	7	7	28.4	21.2
2	9	7	19.2	10.3
2	11	7	23.4	20.7
2	13	7	-9.4	10.4
2	15	7	-8.4	8.9
2	0	8	13.6	18.3
2	2	8	-0.8	9.2
2	4	8	55.6	50.3
2	6	8	24.3	16.7
2	8	8	19.7	19.9
2	10	8	17.3	18.4
2	12	8	24.5	19.3
2	1	9	22.5	18.6
2	3	9	-0.8	5.1
2	5	9	-5.6	4.7
2	7	9	-10.3	9.1
2	9	9	-0.9	4.0
2	0	10	-0.9	13.0
2	2	10	-0.9	11.0
3	0	0	11.9	11.3
3	2	0	97.6	102.7
3	4	0	11.3	9.5
3	6	0	42.2	39.4
3	8	0	-5.5	13.1
3	10	0	73.2	62.7
3	12	0	-6.0	0.7
3	14	0	125.1	127.3
3	16	0	-7.3	7.5
3	18	0	22.6	23.6
3	20	0	19.7	7.9
3	1	1	60.8	35.8
3	3	1	86.6	64.8
3	5	1	48.7	39.1
3	7	1	37.0	41.1
3	9	1	-9.8	7.0
3	11	1	76.0	66.0
3	13	1	28.2	29.1
3	15	1	13.4	15.5
3	17	1	14.6	11.5
3	19	1	16.7	12.2
3	21	1	25.5	19.0
3	0	2	23.4	27.7
3	2	2	26.3	33.4
3	4	2	95.3	94.6
3	6	2	-0.5	7.8
3	8	2	88.0	85.8
3	10	2	63.8	73.0
3	12	2	47.2	47.3
3	14	2	15.8	19.0
3	16	2	39.1	35.6
3	18	2	33.3	36.1
3	20	2	-10.4	15.5
3	1	3	23.4	22.6
3	3	3	17.4	11.0
3	5	3	15.2	18.0
3	7	3	43.2	35.6
3	9	3	14.8	11.9
3	11	3	35.6	36.2
3	13	3	13.8	17.8
3	15	3	26.7	18.6
3	17	3	29.3	24.8
3	19	3	24.5	15.6
3	0	4	84.7	87.6
3	2	4	23.5	27.4
3	4	4	37.9	36.7
3	6	4	18.0	17.0
3	8	4	76.4	79.6
3	10	4	35.9	38.0
3	12	4	-9.7	16.5
3	14	4	36.3	32.2
3	16	4	-5.8	6.2
3	18	4	22.6	20.7
3	1	5	23.9	14.2
3	3	5	20.6	11.4
3	5	5	-9.6	18.4
3	7	5	38.8	46.6
3	9	5	19.1	15.9
3	11	5	-4.1	16.8
3	13	5	-7.8	7.6
3	15	5	30.9	30.2
3	17	5	16.5	12.9
3	0	6	-4.3	11.8
3	2	6	23.2	23.7
3	4	6	30.7	30.4
3	6	6	14.5	17.3
3	8	6	28.8	33.8
3	10	6	56.5	56.1
3	12	6	12.9	15.8
3	14	6	29.4	25.5
3	16	6	-10.1	13.6
3	1	7	16.2	16.1
3	3	7	-0.7	17.1
3	5	7	-0.7	14.9
3	7	7	27.3	27.4
3	9	7	-5.7	7.2
3	11	7	12.2	11.8
3	13	7	-11.3	8.4
3	0	8	13.0	19.6
3	2	8	-0.8	17.0

H	K	L	FO	FC
3	4	8	31.8	30.3
3	6	8	30.1	34.1
3	8	8	-0.8	9.2
3	10	8	-7.8	9.6
3	12	8	14.0	9.8
3	1	9	-4.1	7.8
3	3	9	-0.8	9.5
3	5	9	-2.8	7.7
3	7	9	-0.9	9.5
4	0	0	79.5	79.8
4	2	0	15.8	16.5
4	4	0	39.5	39.7
4	6	0	27.7	15.0
4	8	0	102.5	94.1
4	10	0	40.1	31.4
4	12	0	25.0	23.1
4	14	0	12.1	5.3
4	16	0	-9.1	13.3
4	18	0	16.9	12.2
4	20	0	24.9	22.9
4	1	1	51.6	45.9
4	3	1	41.6	39.6
4	5	1	35.0	30.0
4	7	1	51.0	50.2
4	9	1	22.7	16.5
4	11	1	45.1	45.0
4	13	1	44.7	38.6
4	15	1	22.3	22.3
4	17	1	17.3	14.6
4	19	1	21.9	23.5
4	0	2	24.1	26.1
4	2	2	55.7	59.1
4	4	2	62.6	53.8
4	6	2	40.9	43.8
4	8	2	23.8	26.1
4	10	2	71.6	78.4
4	12	2	24.1	19.7
4	14	2	52.2	41.4
4	16	2	13.6	8.4
4	18	2	38.0	39.5
4	1	3	32.2	35.3
4	3	3	34.6	32.8
4	5	3	34.8	29.6
4	7	3	96.5	81.1
4	9	3	42.6	34.5
4	11	3	19.1	19.9
4	13	3	28.6	32.2
4	15	3	24.0	18.6
4	17	3	23.1	23.3
4	19	3	-11.6	17.2
4	0	4	19.5	20.1
4	2	4	52.9	52.6
4	4	4	-0.6	13.7
4	6	4	73.1	75.0
4	8	4	32.0	34.5
4	10	4	14.4	17.9
4	12	4	27.5	16.3
4	14	4	51.5	51.6
4	16	4	13.4	19.2
4	18	4	12.8	17.8
4	1	5	-9.8	8.9
4	3	5	50.9	42.2
4	5	5	45.5	43.1
4	7	5	16.2	17.6
4	9	5	44.1	34.1
4	11	5	30.1	33.1
4	13	5	15.1	10.5
4	15	5	-0.8	9.3
4	17	5	25.6	26.1
4	0	6	-3.4	9.0
4	2	6	16.5	20.9
4	4	6	62.6	61.5
4	6	6	-6.9	11.5
4	8	6	11.8	10.5
4	10	6	23.6	14.3
4	12	6	11.8	12.9
4	14	6	14.1	14.3
4	1	7	30.2	26.8
4	3	7	-4.9	9.2
4	5	7	-0.8	7.1
4	7	7	22.2	24.2
4	9	7	-0.8	2.0
4	11	7	-0.8	3.2
4	13	7	25.5	24.7
4	0	8	35.5	40.0
4	2	8	-6.7	12.6
4	4	8	-7.0	6.8
4	6	8	-0.8	23.9
4	8	8	25.5	19.2
4	10	8	-11.2	8.8
4	1	9	13.7	11.3
4	3	9	24.0	20.2
4	5	9	-0.9	10.5
5	0	0	20.1	15.7
5	2	0	85.0	78.4
5	4	0	10.8	17.0
5	6	0	-0.6	7.1
5	8	0	20.5	15.3
5	10	0	65.2	63.5
5	12	0	15.4	19.0
5	14	0	14.5	8.6
5	16	0	19.0	2.3
5	18	0	56.0	51.2
5	1	1	60.8	46.4
5	3	1	53.3	60.0
5	5	1	41.9	37.6
5	7	1	87.9	71.9
5	9	1	23.5	22.7
5	11	1	18.5	23.2
5	13	1	-9.7	11.3
5	15	1	16.8	16.2
5	17	1	15.3	21.0
5	19	1	-0.9	9.5
5	0	2	123.6	123.7
5	2	2	35.3	31.9
5	4	2	20.3	11.2
5	6	2	53.8	55.8
5	8	2	55.0	52.6
5	10	2	-8.1	26.8
5	12	2	19.0	20.1
5	14	2	36.3	40.6
5	16	2	28.7	25.6
5	18	2	-0.9	7.6
5	1	3	25.6	30.6
5	3	3	40.8	51.3
5	5	3	56.2	43.5
5	7	3	23.4	26.3
5	9	3	59.5	51.9
5	11	3	26.4	28.1
5	13	3	19.7	19.7
5	15	3	13.7	8.0
5	17	3	25.3	18.6
5	0	4	17.2	18.3
5	2	4	15.1	12.8
5	4	4	89.3	92.2
5	6	4	31.4	38.4
5	8	4	25.7	32.1
5	10	4	-10.8	12.7
5	12	4	44.4	46.4
5	14	4	13.4	23.1
5	16	4	24.0	29.4
5	1	5	33.0	32.7
5	3	5	15.0	16.2
5	5	5	22.2	21.9
5	7	5	40.8	41.3
5	9	5	13.4	11.3
5	11	5	16.2	22.5
5	13	5	32.5	30.8
5	15	5	14.3	8.9
5	0	6	38.8	34.2
5	2	6	-0.7	11.6
5	4	6	29.9	30.3
5	6	6	16.9	17.8
5	8	6	28.1	36.1
5	10	6	15.6	16.7
5	12	6	20.6	24.2
5	14	6	27.8	22.0
5	1	7	-0.8	5.9
5	3	7	32.4	29.4
5	5	7	-0.8	9.9
5	7	7	-2.7	17.2
5	9	7	-2.2	8.2
5	11	7	19.2	19.3
5	0	8	23.1	23.7
5	2	8	14.5	14.3
5	4	8	-0.8	9.2
5	6	8	-0.9	8.6
5	8	8	-1.5	12.0
6	0	0	40.9	32.1
6	2	0	-0.6	13.2
6	4	0	79.1	81.1
6	6	0	28.4	35.7
6	8	0	28.8	30.3
6	10	0	21.7	7.9
6	12	0	19.9	8.9
6	14	0	18.3	20.0
6	16	0	15.8	6.9
6	1	1	58.7	48.6
6	3	1	59.7	50.7
6	5	1	29.9	27.1
6	7	1	53.7	54.2
6	9	1	24.8	23.5
6	11	1	35.6	30.2
6	13	1	18.4	19.1
6	15	1	30.7	34.7
6	17	1	25.4	23.9
6	0	2	48.7	51.1
6	2	2	18.8	22.0
6	4	2	-8.4	21.8
6	6	2	47.1	48.5
6	8	2	34.9	18.3
6	10	2	21.8	17.4
6	12	2	-3.0	5.5
6	14	2	-9.0	9.3
6	16	2	14.1	9.6
6	1	3	26.3	20.8
6	3	3	81.9	70.3
6	5	3	25.9	24.0
6	7	3	18.6	21.2
6	9	3	27.7	27.7
6	11	3	46.6	39.6
6	13	3	26.7	24.4
6	15	3	-8.6	15.0
6	0	4	14.7	21.1
6	2	4	20.6	24.1
6	4	4	27.4	29.0
6	6	4	13.3	13.8
6	8	4	20.2	23.2
6	10	4	15.1	15.9
6	12	4	14.3	10.8
6	14	4	20.5	24.6
6	1	5	40.7	44.3
6	3	5	-2.8	8.3
6	5	5	26.8	24.8
6	7	5	35.5	36.8
6	9	5	19.0	17.6
6	11	5	-6.2	10.7
6	13	5	31.0	25.4
6	0	6	52.1	53.2
6	2	6	-5.1	7.4
6	4	6	-7.7	11.0
6	6	6	-7.3	5.1
6	8	6	20.8	28.3
6	10	6	-9.5	13.4
6	1	7	-9.4	7.7
6	3	7	14.6	27.1
6	5	7	-2.5	17.7
6	7	7	-0.9	2.0
6	0	8	-0.9	7.4
6	2	8	-0.9	10.3
7	0	0	-7.9	3.7
7	2	0	34.1	28.8
7	4	0	-7.2	28.1
7	6	0	70.9	63.3
7	8	0	-9.1	17.6
7	10	0	15.2	15.5
7	12	0	23.3	17.7
7	14	0	30.0	28.9
7	1	1	47.1	42.7
7	3	1	62.7	53.8
7	5	1	30.4	27.3
7	7	1	30.2	36.9
7	9	1	15.9	14.9
7	11	1	37.8	32.3
7	13	1	13.4	17.4
7	15	1	18.0	20.7
7	0	2	19.5	21.3
7	2	2	39.0	34.4
7	4	2	42.1	33.4
7	6	2	27.0	26.2
7	8	2	11.4	15.6
7	10	2	29.9	29.4
7	12	2	-10.1	12.1
7	14	2	-6.2	16.7
7	1	3	47.3	38.3
7	3	3	38.7	32.8
7	5	3	50.7	47.7
7	7	3	31.8	37.2
7	9	3	33.0	32.5
7	11	3	-9.6	10.5
7	13	3	27.9	23.1
7	0	4	42.1	41.4
7	2	4	19.1	17.0
7	4	4	15.3	11.4
7	6	4	14.5	6.3
7	8	4	33.3	25.0
7	10	4	12.6	14.2
7	12	4	12.2	11.3
7	1	5	16.0	11.2
7	3	5	34.9	36.7
7	5	5	20.5	23.5
7	7	5	25.1	26.3
7	9	5	29.6	26.2
7	0	6	22.1	22.5
7	2	6	-8.2	15.2
7	4	6	16.4	19.4
7	6	6	-10.8	6.3
7	8	6	14.3	14.0
7	1	7	17.9	24.9
8	0	0	20.1	20.4
8	2	0	-10.8	16.7
8	4	0	-6.2	7.0
8	6	0	-0.8	3.3
8	8	0	19.6	16.1
8	10	0	16.6	16.3
8	12	0	-7.5	4.7
8	1	1	12.1	18.4
8	3	1	22.2	29.5
8	5	1	17.0	19.7
8	7	1	20.1	21.4
8	9	1	14.0	16.5
8	11	1	27.0	30.0
8	0	2	-11.1	25.3
8	2	2	-5.5	12.6
8	4	2	21.2	12.5
8	6	2	12.8	13.9
8	8	2	-0.8	14.6
8	10	2	-9.4	10.1
8	1	3	15.4	26.2
8	3	3	-10.9	12.1
8	5	3	-0.8	0.4
8	7	3	25.9	25.4
8	9	3	15.7	10.1
8	0	4	-0.8	4.5
8	2	4	12.2	11.1
8	4	4	17.5	17.1
8	6	4	-9.0	11.3
8	8	4	13.3	11.1
8	1	5	20.6	18.6
8	3	5	19.4	20.4
8	5	5	-10.4	15.6
9	0	0	-3.2	18.1
9	2	0	-0.8	1.2
9	4	0	-0.8	1.0
9	6	0	16.3	16.8
9	1	1	35.5	39.9
9	3	1	26.0	40.6
9	5	1	29.7	29.7
9	7	1	45.2	43.3
9	0	2	13.8	12.4
9	2	2	-6.9	9.9
9	4	2	-4.3	10.6
9	6	2	-0.9	4.3
9	1	3	29.0	33.2
9	3	3	14.9	28.9

CHAPTER 8

The Crystal Structure of $(BCH_3)_6(CH)_4$

8.1 Introduction

Studies of boron hydrides and carboranes have been responsible for a considerable improvement in the understanding of chemical bonding. When diborane was first prepared in 1912 by Stock it was realised that there were insufficient valence electrons in the molecule for its bonding to be explained in terms of two-centre two electron bonds. The subsequent discovery of further boron hydrides and carboranes, which showed the same feature, caused this class of compounds to be called electron deficient compounds. The bonding in these molecules is based on multicentre bonds so that there are sufficient electrons in the molecule to completely fill all the bonding orbitals and this accounts for their stability (Rudolph and Pretzer, 1972). The chemistry of carboranes has been reviewed recently by Snaith and Wade (1972), which gives references to the earlier reviews.

The structures of both boron hydrides and carboranes are based on triangular faced, n-cornered polyhedra, and are classified as closo, nido or arachno according to the number of corners on the polyhedra occupied by a cage atom.

In closo structures all n corners are occupied; this form is taken up by cage species of the general formula $C_aB_mH_{m+2}$, where $m = 5-12$, $a = 0,1,2$ and $a + m = n$. For example compounds such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$ have cage structures based on a regular icosohedron.

In nido structures all n corners except one in the polyhedra are occupied by cage atoms, and this form is taken up by compounds of the general formula $C_aB_mH_{m+4}$, where $n = a + m + 1$. Examples of this type include a series of carboranes, for which $a + m = 6$ and $a = 0 \rightarrow 4$, based on the pentagonal bipyramid in which one apical position is vacant giving a pentagonal prism. Similarly in arachno structures all but two corners of the n-cornered polyhedra are occupied; this form is taken up by compounds of the general formula $C_aB_mH_{m+6}$ where $n = a + m + 2$.

These structures may be rationalised according to the number of skeletal bonding electrons they contain. Molecular orbital treatments of closo $B_nH_n^{2-}$ anions have shown that n atoms at the corners of an n-cornered polyhedron give rise to n+1 bonding molecular orbitals (Klanberg et al., 1967) and therefore require n+1 electron pairs for stability. In these boron hydride anions n pairs of skeletal electrons are provided by the boron atoms, and one pair by the charge. This requirement also applies to carboranes except that each carbon contributes three electrons to the skeletal bonding.

In nido species, which are formally derived from the hypothetical $B_nH_n^{4-}$ species, there are n+2 pairs of electrons available for skeletal bonding, which give rise to a structure based on an (n+1)-cornered polyhedron. Likewise the arachno compounds contain n+3 electron pairs available for cage bonding and possess structures based on (n+2)-cornered polyhedra. This theory has been seen to apply to all delocalised boron-carbon cage systems and has been extended to clusters involving transition metals (Wade 1972a, 1972b). It was therefore of considerable interest that a boron-carbon compound, $(C_4B_6)H_4Me_6$, was prepared which did not appear to fit these rules.

This compound was prepared by the thermal decomposition of trimethyl borane (Brown et al., 1975). A sample of $(CH_3)_3B$ sealed in a pyrex tube was heated in a furnace at 450°C for about 40 minutes.

The products were separated by vacuum distillation and sublimation, giving as the major product the boron-carbon compound just mentioned in approximately 18% yield. The product was characterised by its mass spectrum and n.m.r. spectrum. The latter was particularly simple; the ^{1}H spectrum showed only two singlet resonances with the correct relative intensities and positions corresponding to BCH_3 and CH. The ^{11}B spectrum showed only one resonance. This indicated that all the boron atoms were magnetically equivalent as were the methyl groups and also the cage carbon atoms. This information is consistent with an adamantane type structure whereas the electron counting rules would have suggested a nido structure based on the 11 cornered octadecahedron. The n.m.r. spectra of the latter would not be expected to be as simple as that observed. A structure determination was undertaken in order to provide further information about a molecule which appeared to be an exception to the electron counting rule.

8.2 Crystal Data.

The crystals were grown by vacuum sublimation at room temperature and were obtained as prisms elongated along c with well formed {110} faces. The crystals were extremely sensitive to oxygen and so were sealed in quartz capillary tubes. The crystal used for data collection had dimensions 0.4 x 0.3 x 0.2mm.

Preliminary work using precession methods showed the unit cell to be orthorhombic, and that the conditions limiting reflections were: $0kl$ $k+l = 2n$, $hk0$ $h = 2n$. These are consistent with the space groups Pnma and $Pn2_1a$. Solution of the structure showed that the space group was Pnma. Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections as measured on a four-circle diffractometer.

$C_{10}H_{22}B_6$ M = 207.02

a = 16.184(1)Å

b = 13.251(1)Å

c = 6.999(1)Å

U = 1501.0Å^3

Dm = 0.87g cm^{-3}(by floatation in isooctane and chlorobenzene)

Z = 4

Dc = 0.905g cm^{-3}

Absorption coefficient for CuKα radiation (λ = 1.5418Å) = 3.2cm^{-1}.

8.3 Data Collection and Correction.

The data were collected as before using a 2θ-ω scan technique. Each peak was scanned in 70 steps of 0.01° at 2 seconds per step. A background count of 35 seconds was allowed at the beginning and end of each scan.

Three reflections were measured as standards every 40 ordinary reflections; these showed a general decrease throughout the data collection. Part of this was due to slight movements of the crystal within the capillary tube and part due to the compound's volatility at room temperature. As a result the orientation of the crystal was redetermined whenever the intensity of the standards had fallen by 15%.

The standard reflections were not used to scale the data.

A quarter of the sphere of reflection was recorded for $0 < \theta \leq 50^{o}$ and one octant was measured for $50 < \theta \leq 55^{o}$. After averaging, 993 independent reflections were obtained, of which 639 were considered observed having net counts > 3 esd's. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

8.4 Solution and Refinement.

The structure was solved using the symbolic addition procedure as described earlier. A set of normalised structure factors was calculated and 126 of these with $E \geq 1.5$ were phased through iterative application of Sayre's relationship. The program used (Ahmed and Hall, 1968) chose three reflections which were arbitrarily given positive signs and hence determined the origin; then during the next stage, in which signs or symbols were given to the 69 reflections with $E > 1.9$, it was necessary to assign symbols to three further reflections, as shown below.

Origin Determining reflections				Reflections to which symbols were assigned					
			$\|E\|$				$\|E\|$	Symbol	Sign
12	5	0	5.183	10	6	0	3.925	A	-
2	3	1	3.337	4	5	5	3.439	B	+
3	5	4	2.487	7	0	5	3.087	C	+

There was only one set of signs consistent with the three symbols. From these 69 planes the phases of the remaining 57 planes with $1.5 \leq E \leq 1.9$ were estimated. An E-map computed from these reflections which revealed the positions of all the non-hydrogen atoms. The peak heights of the boron and carbon atoms in the map ranged from 2.3 - 3.3e.$\text{\AA}^{-3}$ and 2.3 - 4.1e.$\text{\AA}^{-3}$ respectively, with a background fluctuation of ± 0.5e.$\text{\AA}^{-3}$.

These positions were refined by least squares methods using the block-diagonal approximation. Initially all atoms were given isotropic temperature factors of 6.8$\text{\AA}^2$, which was the overall temperature factor calculated using the Wilson plot method. The R value after two cycles was 0.21, and with further refinement, including anisotropic thermal parameters for all atoms, this fell to 0.13.

A difference synthesis revealed peaks of electron density of 0.4e.$\text{\AA}^{-3}$ which could be assigned to the hydrogen atoms attached to the cage carbon atoms. Likewise it showed annuli of electron density of height 0.2 - 0.3e.$\text{\AA}^{-3}$ associated with the methyl carbon atoms, indicating that the methyl groups were rotating about the B-C bonds. Hydrogen atoms were placed at the positions observed for those attached to the cage carbon atoms. An allowance for the rotation of the methyl groups was made by placing six hydrogen atoms, each with an occupation factor of one half, at equal intervals on a circle whose position was calculated assuming normal bond lengths and angles for the C-H bonds. All hydrogen atoms were included in the refinement with isotropic temperature factors of 8.0$\text{\AA}^2$ but their parameters were not refined. Refinement using full matrix least squares methods saw R converge to its final value of 0.0598. The parameter shifts during the last cycle were all less than 0.15σ.

Inclusion of the hydrogen atoms lead to significant changes in the B-C bond lengths. Before their inclusion, the terminal and cage

Table 8.1 $(BCH_3)_6(CH)_4$

Final Least Squares Totals

$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	R
5065.37	5051.14	302.97	0.0598

Weighting Analysis

$\lvert F_o\rvert$ Ranges	N	$\Sigma\, w\Delta^2/N$	R
0 - 3	172	0.03	1.62
3 - 7	256	0.01	0.66
7 -15	132	0.02	0.43
15 -20	30	0.03	0.47
20 -45	40	0.02	0.34
45 upwards	7	0.05	0.86

Table 8.2 $(BCH_3)_6(CH)_4$

Final Atomic Coordinates with their Estimated Standard Deviations (x 10^5) and Isotropic Thermal Parameters ($Å^2$)

Atom	$^x/a$	$^y/b$	$^z/c$	B†
B(1)	0.01292(32)	0.25	-0.17082(91)	6.00
B(2)	0.19157(31)	0.25	0.11520(76)	5.65
B(3)	0.14750(20)	0.15757(27)	-0.17346(60)	5.67
B(4)	0.05794(24)	0.15579(30)	0.11709(52)	6.28
C(1)	0.00709(26)	0.25	0.05125(69)	6.16
C(2)	0.10112(26)	0.25	-0.26176(63)	5.35
C(3)	0.14928(18)	0.14937(22)	0.05047(45)	6.27
C(4)	-0.06714(33)	0.25	-0.29598(90)	8.79
C(5)	0.27347(30)	0.25	0.23445(76)	7.54
C(6)	0.01870(27)	0.07159(32)	0.24610(58)	9.14
C(7)	0.19418(23)	0.07912(25)	-0.30129(59)	7.88

† Where B refers to the Isotropic Temperature Factor from the last cycle of isotropic refinement.

continued.

Table 8.2 continued

Atom	$^{x}/a$	$^{y}/b$	$^{z}/c$	B	Occupation Factor
H(1)	-0.050	0.25	0.125	8.0	1.0
H(2)	0.092	0.25	-0.417	8.0	1.0
H(3)	0.183	0.083	0.083	8.0	1.0
H(41)	-0.054	0.25	-0.450	8.0	0.5
H(42)	-0.123	0.25	-0.198	8.0	0.5
H(43)	-0.106	0.182	-0.261	8.0	0.5
H(44)	-0.071	0.182	-0.387	8.0	0.5
H(51)	0.326	0.25	0.135	8.0	0.5
H(52)	0.309	0.182	0.199	8.0	0.5
H(53)	0.275	0.182	0.325	8.0	0.5
H(54)	0.258	0.25	0.388	8.0	0.5
H(61)	0.068	0.014	0.274	8.0	0.5
H(62)	0.054	0.067	0.381	8.0	0.5
H(63)	-0.003	0.104	0.381	8.0	0.5
H(64)	-0.046	0.088	0.274	8.0	0.5
H(65)	-0.033	0.035	0.168	8.0	0.5
H(66)	0.025	-0.002	0.168	8.0	0.5
H(71)	0.257	0.108	-0.331	8.0	0.5
H(72)	0.212	0.116	-0.438	8.0	0.5
H(73)	0.160	0.070	-0.438	8.0	0.5
H(74)	0.153	0.015	-0.331	8.0	0.5
H(75)	0.197	0.007	-0.225	8.0	0.5
H(76)	0.250	0.054	-0.225	8.0	0.5

Table 8.3 $(BCH_3)_6(CH)_4$

Anisotropic Thermal Parameters and their Estimated Standard Deviations (both $Å^2 \times 10^5$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B(1)	7002(317)	7171(335)	10349(405)		- 632(320)	
B(2)	6972(310)	8743(347)	8286(361)		931(282)	
B(3)	6343(200)	7026(217)	10421(269)	- 535(223)	696(218)	- 769(174)
B(4)	8489(239)	8268(238)	7925(245)	- 728(218)	- 10(200)	-1638(205)
C(1)	6556(265)	10528(379)	9308(360)		1972(264)	
C(2)	7552(285)	8093(287)	7757(276)		97(226)	
C(3)	8140(211)	7066(197)	9788(239)	949(187)	- 2(183)	782(167)
C(4)	8437(340)	14037(469)	13186(495)		-1953(339)	
C(5)	8008(326)	13036(451)	10783(373)		-1303(282)	
C(6)	13499(332)	11605(312)	10468(265)	1398(260)	1570(239)	3256(259)
C(7)	10679(256)	9159(248)	12976(313)	-1315(223)	1977(241)	1223(220)

bond lengths ranged from 1.51 - 1.64Å, which is far greater than the final range of 1.552 - 1.570Å and illustrates the importance of including hydrogen atoms in the refinement of light atom compounds.

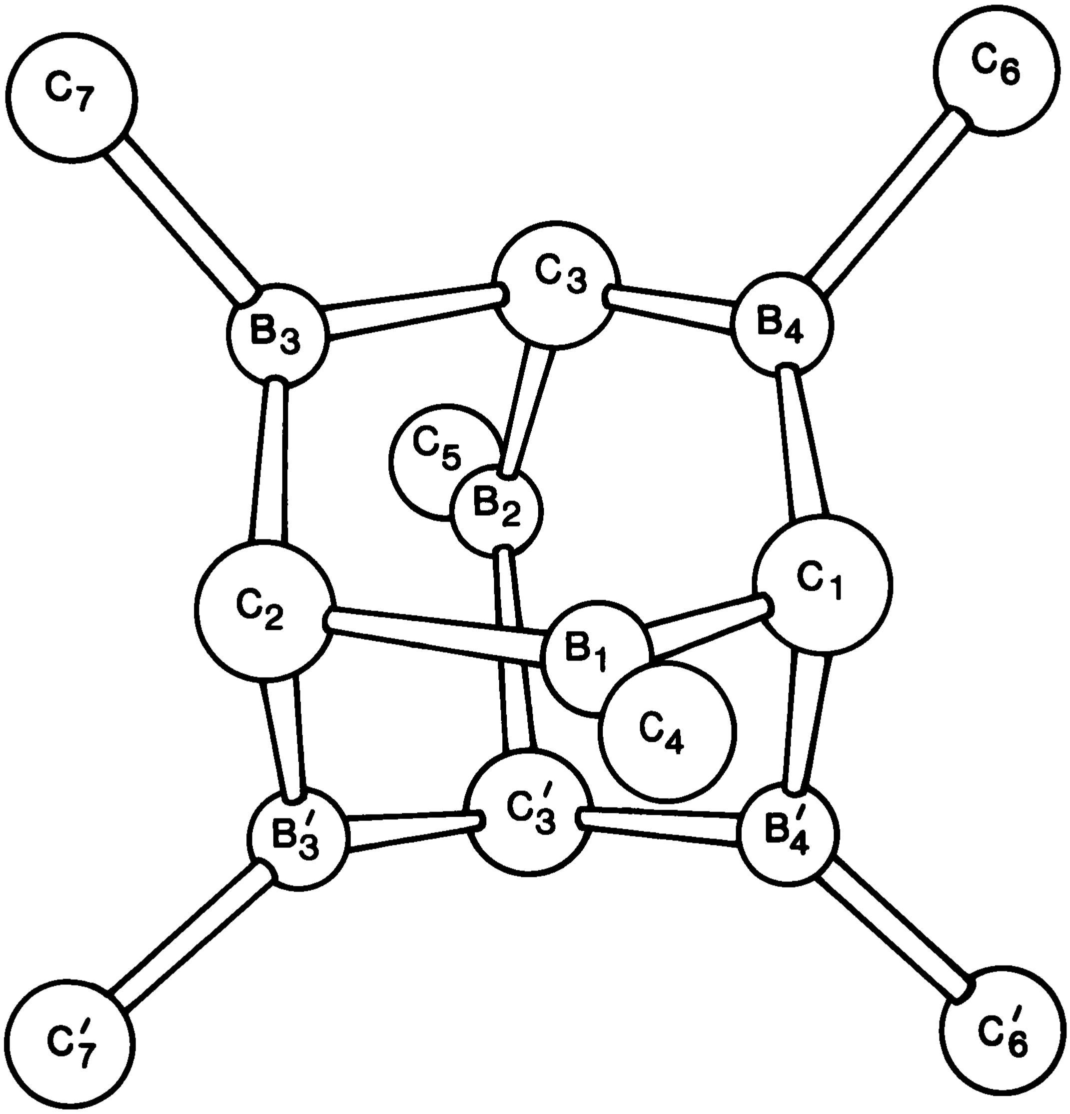
A difference map calculated at the end of the refinement showed no peaks greater than 0.2e.Å^{-3}. The weighting scheme used was

$$\sqrt{w} = 1/[P_1 + |F_o| + P_2|F_o|^2 + P_3|F_o|^3]^{\frac{1}{2}}$$

the parameters were varied until a uniform distribution of $w\Delta^2$ as a function of the magnitude of $|F_o|$ was obtained; the final values used were $P_1 = 5.5$, $P_2 = 0.015$ and $P_3 = 0.002$. The unobserved reflections were not included in the refinement. The final least squares totals and weighting analysis are given in table 8.1. The final calculated and observed structure factors are given in table 8.8. The scattering factors for boron and carbon were taken from International Tables Vol. III, and those for hydrogen from Stewart, Davidson, Simpson (1966). The atomic coordinates and anisotropic thermal parameters are given in tables 8.2 and 8.3 respectively.

8.5 Description of the Structure of $(BCH_3)_6(CH)_4$

The molecule has a structure resembling that of adamantane as previously proposed and as such is unlike a normal carborane. The framework of the molecule consists of four carbon atoms which lie near the corners of a tetrahedron bonded together by six boron atoms as shown in figure 8.1. These boron atoms lie above the six edges of the tetrahedron in an almost octahedral arrangement. There is a



$(BCH_3)_6(CH)_4$

Figure 8.1

(Excluding Hydrogen Atoms)

methyl group attached to each boron and a hydrogen to each framework carbon, so that the molecular symmetry approximates to $\bar{4}3m$. Each carbon atom exhibits its normal covalency of four and each boron atom a covalency of three. This is in complete agreement with the structure proposed from interpretation of its n.m.r. spectra. Intramolecular bond distances and angles are given in tables 8.4 and 8.5 respectively.

Table 8.4

$(BCH_3)_6(CH)_4$ Bond Distances(Å) and their Estimated Standard Deviations (Å x 10^3)

B(1) - C(1)	1.557(8)
B(1) - C(2)	1.563(7)
B(1) - C(4)	1.564(8)
B(2) - C(3)	1.566(4)
B(2) - C(5)	1.566(7)
B(3) - C(2)	1.564(5)
B(3) - C(3)	1.571(5)
B(3) - C(7)	1.566(5)
B(4) - C(1)	1.565(5)
B(4) - C(3)	1.552(5)
B(4) - C(6)	1.570(6)

In the cell the molecules lie across mirror planes at $y = {}^1/4$ and ${}^3/4$, with the atoms B(1), B(2), C(1) and C(2) of the molecular framework situated on the mirror plane at $y = {}^1/4$. The boron-carbon distances range from 1.552(5) - 1.571(5)Å and are all the same within experimental error. The mean terminal bond distance of 1.567(3)Å is not significantly different from the mean cage bond distance of 1.563(2)Å. The overall mean boron-carbon distance of

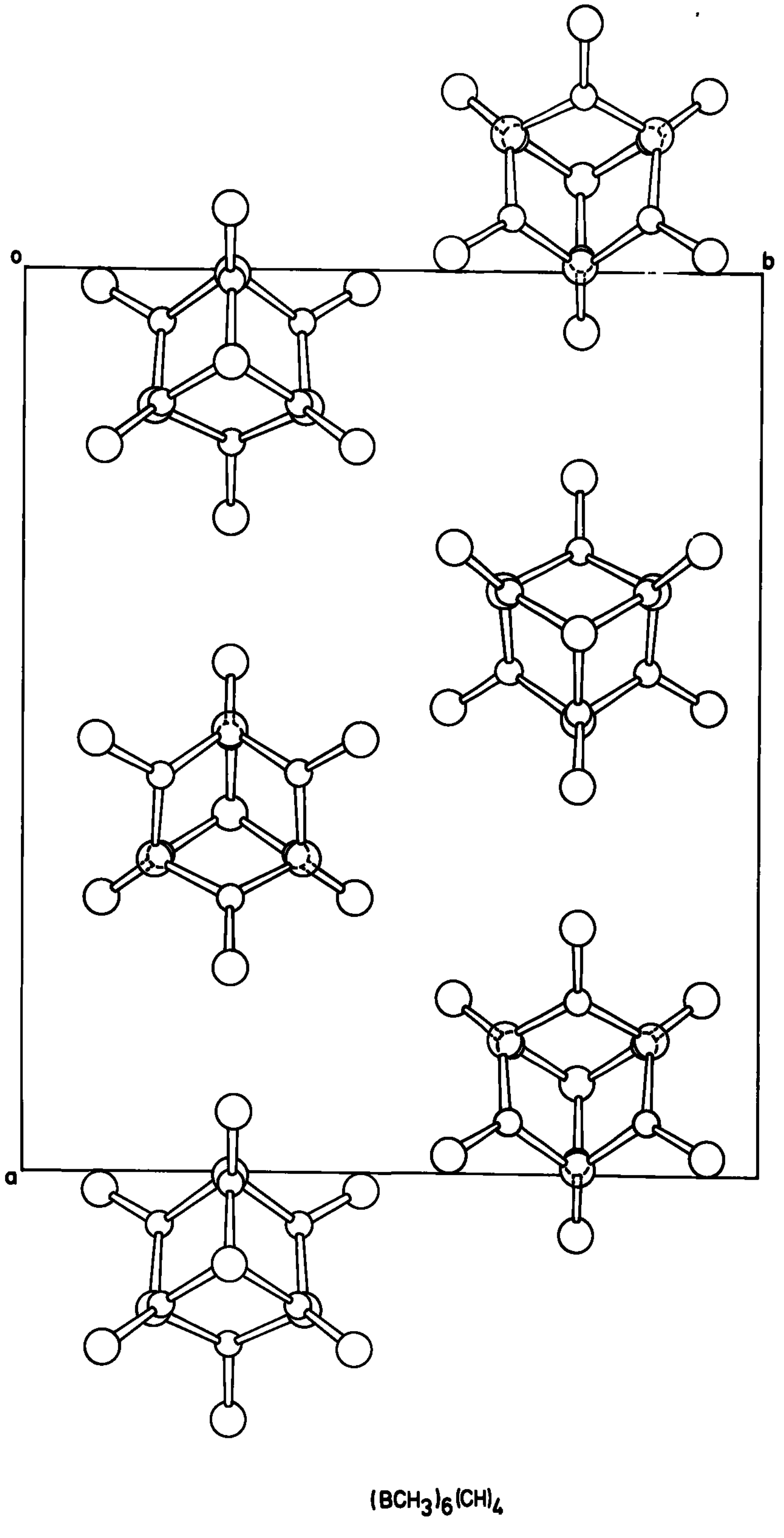
1.564(2)Å is similar to that of 1.578(1)Å in $B(CH_3)_3$ (Bartell and Carrol, 1965) but is shorter than that of 1.590(3)Å in tetramethyl diborane, $B_2H_2(CH_3)_4$ (Carrol and Bartell, 1968) this difference may be accounted for by the change in hybridisation at boron on changing from threefold to fourfold coordination.

In $(BCH_3)_6(CH)_4$ there are sufficient valence electrons available to allow the atoms to bond together by two-electron two-centre bonds. The B-C distances in carboranes are normally longer than such single bonds and are associated with a coordination at boron greater than three, eg. the B-C distance in $B_{10}C_2H_{12}$ (1,12 dicarbaclosododecarborane 12) is 1.710Å with a coordination of six at boron and five at carbon. (Bohn and Bohn, 1971).

The angles at boron within the cage vary from 116.8 - 117.5° and are all equal within experimental error with a mean of 117.2°, whilst the angles at carbon lie in the range 103.1 - 106.4°. All of these angles are less than those expected for atoms in sp^2 and sp^3 hybrid states respectively; this feature is dictated by the structure itself. In a molecule with ideal $\bar{4}3m$ symmetry an angle of 120° at boron necessitates an angle of 103°12' in the cage at carbon, whereas an angle of 109°28' at carbon requires the cage angle at boron also to be tetrahedral. The angles observed represent a compromise between these two extremes. The $C-B-CH_3$ angles vary from 120.6 - 121.9° and are the same within experimental error.

Departure from ideal symmetry occurs throughout the molecule. This is most evident in the distances between methyl carbon atoms, e.g. the edges of the octahedron, which ideally should be equal but vary from 4.529 - 4.797Å. These differences are mirrored in the corresponding boron-boron distances, but on a smaller scale. For comparison both sets of distances are given together in table 8.6. The greatest differences involve C(7) and the boron, B(3) to which it is attached, and from the distances given it can be deduced that C(7) is displaced towards $C(7^I)$ across the mirror plane at y = $^1/4$, and towards C(5). This distortion may be explained by the molecular packing. In the structure the shortest intermolecular contacts are close to 4Å which is the contact distance normally accepted for rotating methyl groups. As far as the distortion is concerned the important contact appears to be that of 4.001Å between C(7) and C(6) in the molecule at $\bar{x}$, $\bar{y}$, $\bar{z}$, (table 8.6). This distance would be decreased if the C(7) --- $C(7^I)$ separation was increased. This distortion accounts for the angles B(3) - C(2) - $B(3^I)$ and B(2) - C(3) - B(3) being less than the other cage angles at carbon, i.e. 103.1° and 103.8° as compared to 105.2 - 106.4° for the remaining angles. It also accounts for the observation that B(3) is not coplanar with the three carbon atoms to which it is attached, as shown in table 8.7. The movement of C(7) towards the mirror plane is accompanied by a similar but smaller movement of B(3) towards $B(3^I)$ so that B(3) lies 0.024Å above the plane of the three carbon atoms. Conversely the other boron atoms are coplanar with their attached carbon atoms.

A projection along $\underline{c}$ of the contents of a unit cell is shown in figure 8.2.



$(BCH_3)_6(CH)_4$

projection on the [001] plane

Figure 8.2

Table 8.5 $(BCH_3)_6(CH)_4$

Bond Angles (degrees) and their Estimated Standard Deviation (deg. x 10^2)

C(1) - B(1) - C(2)	117.51(35)
C(3) - B(2) - C(3^I)	116.77(31)
C(2) - B(3) - C(3)	117.20(29)
C(1) - B(4) - C(3)	117.14(30)
B(1) - C(1) - B(4)	105.20(31)
B(4) - C(1) - B(4^I)	105.85(29)
B(1) - C(2) - B(3)	106.11(30)
B(3) - C(2) - B(3^I)	103.11(28)
B(2) - C(3) - B(3)	103.75(27)
B(2) - C(3) - B(4)	106.42(28)
B(3) - C(3) - B(4)	106.16(26)
C(1) - B(1) - C(4)	120.59(32)
C(2) - B(1) - C(4)	121.91(37)
C(3) - B(2) - C(5)	121.60(33)
C(2) - B(3) - C(7)	121.72(30)
C(3) - B(3) - C(7)	121.00(29)
C(1) - B(4) - C(6)	121.59(32)
C(3) - B(4) - C(6)	121.27(31)

I refers to the equivalent position at x, $^1/2$-y, z.

Table 8.6 $(BCH_3)_6(CH)_4$

Some Non-bonding intermolecular contacts (Å) with their Estimated Standard Deviations (Å x 10^3)

B(1) - B(3)	2.499(6)	C(4) - C(7)	4.797(6)
B(1) - B(4)	2.480(7)	C(4) - C(6)	4.681(7)
B(2) - B(3)	2.468(6)	C(5) - C(7)	4.564(6)
B(2) - B(4)	2.497(6)	C(5) - C(6)	4.754(6)
B(3) - B(4)	2.497(5)	C(6) - C(7)	4.770(6)
B(3) - B(3^{I})	2.450(5)	C(6) - C(6^{I})	4.728(6)
B(4) - B(4^{I})	2.497(6)	C(7) - C(7^{I})	4.529(5)

C(1) - C(2)	2.667(6)
C(1) - C(3)	2.660(5)
C(2) - C(3)	2.676(5)
C(3) - C(3^{I})	2.667(4)

Some Intermolecular Contacts < 4.3Å for nonhydrogen atoms

C(1) - C(5^{II})	4.068
C(3) - C(7^{III})	4.082
C(4) - C(5^{IV})	4.009
C(4) - C(6^{V})	4.218
C(5) - C(7^{VI})	4.163
C(6) - C(6^{VII})	3.979
C(6) - C(6^{VIII})	4.074
C(6) - C(7^{VII})	4.001
C(6) - C(7^{VI})	4.256

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

Table 8.7 $(BCH_3)_6(CH)_4$

Mean Planes

$0.5400X + 0.0Y - 0.8416Z - 1.0058 = 0$

Atom	B(2)	C(3)	C(3')	C(5)
P	-0.0100	0.0017	0.0017	0.0033
σ(P)	0.0052	0.0031	0.0031	0.0052

$-0.8343X - 0.5500Y - 0.0373Z + 3.1135 = 0$

Atom	B(3)	C(2)	C(3)	C(7)
P	0.0187	-0.0056	-0.0040	-0.0066
σ(P)	0.0033	0.0035	0.0029	0.0036

$-0.8342X - 0.5502Y - 0.0382Z + 3.1178 = 0$

Atom	B(3)†	C(2)	C(3)	C(7)
P	0.0241	0.0	0.0	0.0
σ(P)	0.0033			

$-0.2889X - 0.4954Y - 0.8192Z + 1.9674 = 0$

Atom	B(4)	C(1)	C(3)	C(6)
P	0.0025	-0.0008	-0.0005	-0.0010
σ(P)	0.0037	0.0041	0.0031	0.0041

P and σ(P) represent the distance and its estimated standard deviation of the atom from the mean plane. X, Y, and Z refer to orthogonal coordinates in Å parallel to *a*, *b* and *c*.

† signifies that this atom was not included in the calculation of the mean plane.

8.6 Discussion.

Carboranes have been defined as mixed hydrides of carbon and boron in which both carbon and boron atoms participate in a delocalised molecular framework, so that the compound discussed here is strictly not a carborane. It is exceptional in this field in that it possesses a constitution normally associated with delocalised bonding and yet is obviously held together by normal single bonds. This is possible because there is a boron:carbon ratio of 3:2 and does not require delocalisation in the bonding.

There is only one other known compound with this boron:carbon ratio, namely $C_2B_3H_5$. Its structure has been found by electron diffraction methods and has the form of a trigonal bipyramid with the apical positions occupied by carbon atoms (Macneil et.al., 1973). This is the shape predicted from the electron counting rule mentioned earlier. Its boron-carbon bond distance of 1.556Å is of the appropriate length for a normal single bond, and its B-B distance of 1.853Å is longer than that normally found in carboranes (e.g. 1.720Å in $C_2B_4H_6$ Macneil et. al., 1973). The authors think however that this B-B distance does not proclude B-B interactions but suggest that it is weaker than in normal carboranes, and thus it is not possible to clearly differentiate between the two types of bonding.

It is unlikely that the next member, $C_6B_9H_{15}$, will exist since for a structure based on normal covalent bonds, carbon must be tetravalent; this requires that the structure would be based on a trigonal prism of carbon atoms with boron atoms along its edges. This would require either large angles at boron or at carbon, which would reduce its stability.

Table 8.8 $(BCH_3)_6(CH)_4$

Final Calculated and Observed Structure Factors

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	34.0	36.4	8	12	0	-1.2	-0.2	7	5	1	2.1	2.7	8	12	1	0.0	-1.0
4	0	0	22.0	25.3	2	13	0	1.7	-1.5	8	5	1	12.4	-12.1	0	13	1	3.5	3.3
6	0	0	51.0	48.0	4	13	0	-0.6	0.4	9	5	1	8.0	8.5	1	13	1	0.0	0.0
8	0	0	6.2	-6.1	6	13	0	-0.6	-0.5	10	5	1	5.2	4.9	2	13	1	2.9	2.6
10	0	0	3.2	-2.8	0	14	0	2.3	1.5	11	5	1	12.0	-12.3	3	13	1	-0.7	0.1
12	0	0	5.6	4.8	1	0	1	61.6	69.9	12	5	1	-1.1	1.5	4	13	1	-1.3	-1.5
14	0	0	11.4	12.0	2	0	1	21.3	22.6	13	5	1	5.7	-6.1	5	13	1	0.0	-1.3
16	0	0	-0.8	1.2	3	0	1	9.6	-9.8	14	5	1	-1.4	-1.7	6	13	1	0.0	-0.3
2	1	0	76.4	-104.0	4	0	1	71.2	-75.6	15	5	1	-1.8	1.8	0	0	2	81.0	-86.3
4	1	0	24.9	24.9	5	0	1	17.9	18.3	1	6	1	16.5	12.8	1	0	2	43.0	-42.1
6	1	0	8.5	7.4	6	0	1	12.9	-13.0	2	6	1	8.8	-8.8	2	0	2	5.8	-5.8
8	1	0	35.2	-33.1	7	0	1	31.6	31.1	3	6	1	20.8	-20.3	3	0	2	5.1	5.8
10	1	0	3.0	-1.9	8	0	1	18.9	-17.7	4	6	1	-0.9	0.5	4	0	2	27.2	-25.4
12	1	0	6.9	-6.6	9	0	1	7.7	-6.6	5	6	1	10.5	-10.4	5	0	2	2.6	2.8
14	1	0	2.3	-2.0	10	0	1	8.1	8.3	6	6	1	7.7	-8.4	6	0	2	14.0	13.2
16	1	0	6.5	-6.8	11	0	1	3.5	-4.2	7	6	1	0.0	-0.6	7	0	2	15.5	-16.[illegible]
0	2	0	79.3	-99.6	12	0	1	2.5	2.2	8	6	1	12.0	12.8	8	0	2	3.1	2.9
2	2	0	17.3	-17.8	13	0	1	9.1	8.7	9	6	1	12.8	-13.1	9	0	2	12.5	12.4
4	2	0	11.3	11.9	14	0	1	4.6	4.8	10	6	1	0.0	-0.1	10	0	2	9.9	-9.7
6	2	0	14.8	14.3	15	0	1	4.5	4.2	11	6	1	9.8	-10.1	11	0	2	2.4	-3.0
8	2	0	8.4	-8.7	16	0	1	-1.1	0.3	12	6	1	2.0	-3.0	12	0	2	3.5	3.3
10	2	0	0.0	-1.1	17	0	1	0.0	-0.9	13	6	1	2.5	2.7	13	0	2	-1.7	1.2
12	2	0	6.1	-6.2	0	1	1	10.1	9.4	14	6	1	-1.2	0.9	14	0	2	0.0	1.5
14	2	0	6.8	-7.0	1	1	1	45.1	-48.6	15	6	1	0.0	-0.6	15	0	2	5.5	4.6
16	2	0	-1.8	-1.0	2	1	1	5.8	5.7	0	7	1	8.4	-8.2	16	0	2	2.1	1.4
2	3	0	44.8	-47.2	3	1	1	28.9	-30.5	1	7	1	4.9	-4.7	1	1	2	36.9	-36.4
4	3	0	23.9	23.1	4	1	1	46.4	-47.9	2	7	1	14.1	-13.8	2	1	2	6.6	-6.4
6	3	0	32.3	-32.1	5	1	1	11.3	11.8	3	7	1	4.3	-4.5	3	1	2	4.7	4.7
8	3	0	5.0	-4.9	6	1	1	7.4	-6.8	4	7	1	-0.9	1.3	4	1	2	7.3	6.5
10	3	0	3.0	2.4	7	1	1	21.0	-20.7	5	7	1	3.1	2.6	5	1	2	4.6	-4.0
12	3	0	13.3	13.1	8	1	1	2.3	2.2	6	7	1	7.7	7.7	6	1	2	6.2	-6.2
14	3	0	1.9	2.3	9	1	1	11.8	-10.3	7	7	1	0.0	1.4	7	1	2	18.1	19.2
16	3	0	2.1	-0.3	10	1	1	4.4	4.3	8	7	1	4.6	5.1	8	1	2	-1.3	0.4
0	4	0	12.2	12.1	11	1	1	6.6	6.7	9	7	1	2.3	-2.4	9	1	2	10.4	10.0
2	4	0	25.6	25.4	12	1	1	3.8	3.6	10	7	1	2.2	-2.5	10	1	2	1.7	2.1
4	4	0	34.4	33.1	13	1	1	2.6	3.3	11	7	1	4.7	4.6	11	1	2	2.3	-2.3
6	4	0	21.2	-19.7	14	1	1	-1.6	1.1	12	7	1	0.0	0.3	12	1	2	9.2	10.5
8	4	0	5.1	4.5	15	1	1	4.2	-4.1	13	7	1	2.8	2.8	13	1	2	4.1	3.6
10	4	0	23.4	23.1	16	1	1	-1.4	-1.6	14	7	1	-1.6	2.2	14	1	2	-1.5	-0.7
12	4	0	3.1	3.5	1	2	1	35.7	-37.7	1	8	1	8.8	8.9	15	1	2	3.3	-3.4
14	4	0	4.8	-4.9	2	2	1	-0.7	0.3	2	8	1	1.8	-0.6	16	1	2	2.3	0.7
16	4	0	2.6	2.8	3	2	1	2.3	2.7	3	8	1	0.0	-1.2	0	2	2	5.9	-5.5
2	5	0	23.7	23.0	4	2	1	12.9	-13.0	4	8	1	8.8	9.7	1	2	2	1.4	1.6
4	5	0	2.1	2.3	5	2	1	25.4	-25.0	5	8	1	7.1	7.2	2	2	2	16.2	-15.4
6	5	0	16.9	-16.5	6	2	1	9.8	9.1	6	8	1	2.2	-1.0	3	2	2	-1.0	-0.9
8	5	0	13.5	13.4	7	2	1	14.7	-15.2	7	8	1	5.0	5.0	4	2	2	20.7	-20.9
10	5	0	4.6	-4.5	8	2	1	0.0	0.3	8	8	1	0.0	0.8	5	2	2	-0.7	1.6
12	5	0	30.9	-31.5	9	2	1	-0.9	-0.8	9	8	1	2.4	1.1	6	2	2	30.8	-28.3
14	5	0	-1.5	-0.4	10	2	1	17.2	-17.7	10	8	1	7.2	7.4	7	2	2	-0.8	0.0
16	5	0	-1.1	-0.2	11	2	1	4.0	-3.4	11	8	1	2.9	2.9	8	2	2	0.0	1.0
0	6	0	42.3	-41.2	12	2	1	-0.8	-1.6	12	8	1	2.0	2.3	9	2	2	4.1	-4.0
2	6	0	10.3	-9.9	13	2	1	2.6	-2.5	13	8	1	-1.4	1.2	10	2	2	1.9	-1.8
4	6	0	43.4	-43.5	14	2	1	9.3	-9.6	0	9	1	-1.6	0.8	11	2	2	2.5	2.2
6	6	0	3.0	-2.6	15	2	1	3.3	-3.4	1	9	1	11.9	-12.2	12	2	2	-1.1	-0.2
8	6	0	-1.1	-0.5	16	2	1	0.0	1.0	2	9	1	14.7	14.8	13	2	2	-0.7	-0.4
10	6	0	30.6	-30.9	0	3	1	19.8	-19.2	3	9	1	3.9	-3.8	14	2	2	-1.1	0.0
12	6	0	2.7	-2.6	1	3	1	9.4	10.0	4	9	1	-1.3	-1.4	15	2	2	-1.4	-1.9
14	6	0	4.1	4.7	2	3	1	89.2	-101.4	5	9	1	3.7	4.5	16	2	2	2.4	-2.4
2	7	0	4.7	-4.9	3	3	1	9.0	-9.4	6	9	1	2.3	1.6	1	3	2	-1.3	3.0
4	7	0	6.3	-5.9	4	3	1	6.0	5.3	7	9	1	6.1	-6.3	2	3	2	8.2	8.0
6	7	0	1.6	1.5	5	3	1	10.4	10.0	8	9	1	7.8	8.2	3	3	2	11.4	12.6
8	7	0	8.5	-9.0	6	3	1	4.9	5.2	9	9	1	2.3	-2.4	4	3	2	9.4	-7.8
10	7	0	-1.2	1.2	7	3	1	11.6	11.5	10	9	1	-0.7	0.3	5	3	2	9.6	-9.2
12	7	0	15.1	15.2	8	3	1	12.1	-12.2	11	9	1	2.0	1.8	6	3	2	28.7	28.2
14	7	0	0.0	0.8	9	3	1	5.2	-5.1	12	9	1	3.3	3.3	7	3	2	3.2	-2.7
0	8	0	16.9	16.5	10	3	1	1.7	1.1	13	9	1	0.0	1.0	8	3	2	-0.6	-0.7
2	8	0	3.6	4.1	11	3	1	7.8	7.2	1	10	1	12.7	-12.9	9	3	2	0.0	-0.9
4	8	0	-0.9	-1.6	12	3	1	5.6	-5.5	2	10	1	1.7	-0.6	10	3	2	3.1	2.8
6	8	0	3.7	-3.5	13	3	1	3.1	2.8	3	10	1	4.9	4.8	11	3	2	0.0	0.1
8	8	0	4.6	4.8	14	3	1	-1.3	-0.2	4	10	1	2.5	2.4	12	3	2	0.0	-0.4
10	8	0	3.3	3.4	15	3	1	0.0	-0.6	5	10	1	4.7	-4.5	13	3	2	0.0	-0.5
12	8	0	4.2	4.0	16	3	1	-1.1	0.7	6	10	1	7.1	6.9	14	3	2	-1.5	-0.5
14	8	0	3.7	3.0	1	4	1	7.4	-7.4	7	10	1	5.8	-6.0	15	3	2	-1.4	0.1
2	9	0	13.4	-12.8	2	4	1	2.3	2.3	8	10	1	-1.3	0.3	16	3	2	-1.8	1.7
4	9	0	3.1	-3.2	3	4	1	27.9	29.1	9	10	1	3.1	2.9	0	4	2	26.1	-25.4
6	9	0	9.7	10.0	4	4	1	11.7	12.7	10	10	1	2.7	-2.9	1	4	2	4.4	4.4
8	9	0	6.5	-6.8	5	4	1	25.7	25.8	11	10	1	-1.2	1.1	2	4	2	6.2	6.5
10	9	0	-1.2	0.4	6	4	1	2.1	-2.2	0	11	1	3.0	-2.4	3	4	2	11.6	11.2
12	9	0	2.1	2.1	7	4	1	1.6	-1.3	1	11	1	7.2	7.2	4	4	2	15.7	14.7
0	10	0	33.1	-32.2	8	4	1	6.5	-6.5	2	11	1	2.5	2.2	5	4	2	12.7	14.1
2	10	0	6.4	-6.0	9	4	1	15.1	15.9	3	11	1	3.6	4.0	6	4	2	14.6	14.5
4	10	0	5.8	6.0	10	4	1	7.4	7.7	4	11	1	6.2	6.3	7	4	2	4.3	3.9
6	10	0	5.9	-6.1	11	4	1	12.9	12.4	5	11	1	1.8	-2.0	8	4	2	-1.4	1.4
8	10	0	-1.3	-1.5	12	4	1	2.0	1.5	6	11	1	0.0	-1.5	9	4	2	-1.0	0.1
10	10	0	5.5	5.7	13	4	1	5.1	-5.0	7	11	1	3.8	4.1	10	4	2	4.8	4.5
12	10	0	-1.4	-2.3	14	4	1	4.6	4.5	8	11	1	2.0	-1.7	11	4	2	5.2	-4.8
2	11	0	17.5	17.5	15	4	1	-1.5	1.1	9	11	1	3.2	3.1	12	4	2	-0.9	0.2
4	11	0	2.8	-2.5	16	4	1	3.8	-3.2	10	11	1	-1.1	-1.3	13	4	2	3.1	-3.1
6	11	0	-1.1	1.5	0	5	1	8.0	7.3	1	12	1	4.3	4.6	14	4	2	-0.9	0.5
8	11	0	7.9	8.5	1	5	1	23.6	23.4	2	12	1	4.1	3.9	15	4	2	-0.9	-1.2
10	11	0	-0.3	0.6	2	5	1	7.3	7.2	3	12	1	0.0	0.4	1	5	2	-1.3	1.1
0	12	0	20.9	20.7	3	5	1	18.5	20.7	4	12	1	3.6	-3.5	2	5	2	17.4	15.9
2	12	0	1.7	2.0	4	5	1	15.7	-14.4	5	12	1	2.3	2.2	3	5	2	12.5	13.3
4	12	0	-0.7	1.1	5	5	1	16.1	-15.6	6	12	1	-1.6	-1.8	4	5	2	-0.8	-0.5
6	12	0	9.0	9.4	6	5	1	14.6	-14.8	7	12	1	2.7	2.3	5	5	2	8.8	-8.6

H	K	L	FO	FC
6	5	2	-1.1	-0.6
7	5	2	3.6	-3.6
8	5	2	5.4	5.5
9	5	2	2.3	-2.7
10	5	2	-1.2	1.5
11	5	2	5.6	-5.7
12	5	2	6.6	7.1
13	5	2	-1.4	1.6
14	5	2	-1.1	0.6
15	5	2	-0.9	-0.5
0	6	2	35.1	33.5
1	6	2	12.8	12.4
2	6	2	-0.3	1.4
3	6	2	16.4	-15.8
4	6	2	5.3	5.6
5	6	2	15.1	-14.8
6	6	2	1.9	-2.1
7	6	2	0.0	-0.1
8	6	2	-0.9	-1.7
9	6	2	5.5	-5.3
10	6	2	3.3	3.6
11	6	2	4.7	5.1
12	6	2	0.0	-0.4
13	6	2	2.6	2.1
14	6	2	-1.6	-0.8
1	7	2	1.5	-0.6
2	7	2	1.8	-0.8
3	7	2	11.4	-10.8
4	7	2	-1.0	-0.8
5	7	2	2.4	1.8
6	7	2	3.8	3.6
7	7	2	-0.9	-1.3
8	7	2	1.9	2.1
9	7	2	0.0	0.6
10	7	2	0.0	0.8
11	7	2	2.7	2.4
12	7	2	4.5	-4.5
13	7	2	-1.5	-0.9
14	7	2	0.0	-0.1
0	8	2	5.2	5.4
1	8	2	2.7	-3.3
2	8	2	2.1	1.6
3	8	2	0.0	0.2
4	8	2	3.6	4.4
5	8	2	-1.6	1.8
6	8	2	11.1	11.5
7	8	2	2.0	2.3
8	8	2	0.0	0.8
9	8	2	-0.3	0.9
10	8	2	-1.1	0.0
11	8	2	-0.6	-0.3
12	8	2	0.0	-0.6
13	8	2	-1.6	1.0
1	9	2	3.6	-4.4
2	9	2	4.5	-4.5
3	9	2	-1.5	-1.8
4	9	2	5.6	6.0
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6	9	2	4.4	-5.2
7	9	2	2.6	2.9
8	9	2	1.9	-2.0
9	9	2	2.5	2.6
10	9	2	0.0	-0.8
11	9	2	-1.0	1.0
12	9	2	2.2	1.8
0	10	2	-1.7	1.7
1	10	2	2.6	2.2
2	10	2	-0.9	1.4
3	10	2	2.8	2.8
4	10	2	0.0	0.1
5	10	2	3.2	2.3
6	10	2	5.0	-4.8
7	10	2	1.8	1.4
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9	10	2	2.1	-2.1
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6	11	2	-1.3	-0.5
7	11	2	4.4	-4.5
8	11	2	2.0	-0.3
9	11	2	2.7	-2.7
0	12	2	6.7	-6.6
1	12	2	2.6	-2.5
2	12	2	0.0	0.4
3	12	2	-1.4	0.7
4	12	2	0.0	0.3
5	12	2	-1.9	-1.3
6	12	2	-0.9	-0.1
7	12	2	2.2	-2.3
1	13	2	-0.3	0.2
2	13	2	2.3	1.9
3	13	2	-1.5	0.7
4	13	2	0.0	-0.5
1	0	3	1.5	-1.9
2	0	3	37.5	-36.6
3	0	3	12.1	-12.3
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6	0	3	5.0	-5.5
7	0	3	6.9	-6.5
8	0	3	3.3	3.3
9	0	3	2.4	1.8
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14	0	3	-0.6	1.3
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2	1	3	10.3	-9.4
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6	1	3	4.3	-4.6
7	1	3	6.0	6.1
8	1	3	7.4	6.4
9	1	3	2.0	1.9
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11	1	3	3.1	-2.8
12	1	3	-0.4	-1.5
13	1	3	3.7	-3.2
14	1	3	-1.4	-1.7
15	1	3	-1.2	1.5
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3	2	3	8.7	-9.4
4	2	3	3.0	3.4
5	2	3	6.7	6.4
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7	2	3	1.8	1.1
8	2	3	2.2	2.9
9	2	3	2.6	-2.8
10	2	3	6.6	7.2
11	2	3	0.0	-0.1
12	2	3	2.2	2.6
13	2	3	3.2	-2.7
14	2	3	3.1	3.3
15	2	3	-1.4	0.7
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7	3	3	8.8	-10.0
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9	3	3	4.0	4.1
10	3	3	7.6	7.3
11	3	3	5.5	-3.3
12	3	3	3.6	3.6
13	3	3	-1.3	0.3
14	3	3	1.7	-2.0
15	3	3	-0.5	0.1
1	4	3	4.0	3.1
2	4	3	7.1	6.8
3	4	3	3.8	2.9
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5	4	3	10.2	-10.1
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7	4	3	3.7	-3.4
8	4	3	8.1	8.3
9	4	3	2.8	-3.1
10	4	3	5.0	-5.7
11	4	3	3.3	-3.3
12	4	3	8.5	-8.9
13	4	3	3.2	3.9
14	4	3	3.3	-2.8
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5	5	3	1.6	1.9
6	5	3	1.8	2.4
7	5	3	0.0	-1.1
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10	5	3	14.4	-13.9
11	5	3	2.8	3.1
12	5	3	-1.5	-1.8
13	5	3	2.2	2.0
14	5	3	3.7	3.2
1	6	3	9.7	-9.6
2	6	3	3.5	-3.4
3	6	3	5.5	4.8
4	6	3	10.2	-10.1
5	6	3	-1.0	-0.4
6	6	3	2.5	2.3
7	6	3	4.3	4.4
8	6	3	11.4	-11.9
9	6	3	3.8	3.7
10	6	3	-1.6	1.6
11	6	3	2.9	2.7
12	6	3	6.5	7.0
13	6	3	-1.5	-0.8
0	7	3	4.0	3.5
1	7	3	2.6	2.7
2	7	3	3.3	3.7
3	7	3	2.6	1.9
4	7	3	-0.8	-0.7
5	7	3	2.7	-3.0
6	7	3	0.0	0.3
7	7	3	-0.7	-1.1
8	7	3	-1.2	-0.7
9	7	3	-1.2	1.8
10	7	3	6.7	6.7
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12	7	3	-1.5	0.9
13	7	3	-1.1	-1.4
1	8	3	0.0	0.3
2	8	3	5.1	-4.8
3	8	3	-1.0	0.7
4	8	3	-1.7	-1.4
5	8	3	4.2	-4.3
6	8	3	-1.1	-0.3
7	8	3	-0.8	2.2
8	8	3	-0.6	-0.6
9	8	3	1.9	0.8
10	8	3	3.1	-3.6
11	8	3	2.7	-2.4
12	8	3	2.7	-2.4
0	9	3	12.5	-12.3
1	9	3	5.0	5.2
2	9	3	8.8	-8.2
3	9	3	-1.3	-0.6
4	9	3	1.8	2.4
5	9	3	3.3	3.0
6	9	3	3.4	-3.2
7	9	3	4.4	4.8
8	9	3	1.7	-1.7
9	9	3	2.5	-2.2
10	9	3	-1.3	-0.2
11	9	3	2.1	0.8
1	10	3	3.2	4.0
2	10	3	8.5	8.2
3	10	3	-1.1	0.2
4	10	3	0.0	-1.1
5	10	3	2.7	2.6
6	10	3	0.0	-0.6
7	10	3	0.0	0.1
8	10	3	-1.2	0.9
9	10	3	-1.1	-1.0
0	11	3	8.4	8.8
1	11	3	2.0	-1.9
2	11	3	0.0	-0.3
3	11	3	2.3	-2.3
4	11	3	3.8	-4.0
5	11	3	-0.9	-1.0
6	11	3	-0.7	0.7
7	11	3	2.0	-1.3
8	11	3	2.2	-2.4
1	12	3	-1.5	-1.7
2	12	3	4.0	-4.5
3	12	3	0.0	-0.3
4	12	3	-0.7	1.0
5	12	3	0.0	0.3
0	0	4	9.2	9.0
1	0	4	10.0	-9.8
2	0	4	0.0	0.8
3	0	4	15.1	-15.1
4	0	4	4.5	4.4
5	0	4	8.9	7.7
6	0	4	-1.6	-0.7
7	0	4	5.3	-5.4
8	0	4	11.2	11.9
9	0	4	13.0	-12.5
10	0	4	6.7	6.7
11	0	4	6.4	6.8
12	0	4	-1.5	1.7
13	0	4	-1.3	1.2
14	0	4	-1.1	-0.1
1	1	4	15.8	-15.4
2	1	4	4.9	4.4
3	1	4	4.8	5.1
4	1	4	-1.1	-1.1
5	1	4	7.4	-7.9
6	1	4	10.4	10.6
7	1	4	16.8	-15.8
8	1	4	-0.9	0.5
9	1	4	0.0	-0.4
10	1	4	2.5	-2.4
11	1	4	2.9	2.7
12	1	4	4.1	-4.2
13	1	4	5.6	-5.6
14	1	4	-1.0	-1.8
0	2	4	5.5	5.5
1	2	4	9.0	8.1
2	2	4	4.8	4.4
3	2	4	5.5	5.7
4	2	4	7.5	7.3
5	2	4	-1.5	-1.4
6	2	4	9.2	8.7
7	2	4	7.8	8.1
8	2	4	6.1	-5.9
9	2	4	3.0	3.1
10	2	4	-0.4	-1.3
11	2	4	0.0	-0.5
12	2	4	2.5	-2.5
13	2	4	0.0	0.7
14	2	4	0.0	-0.2
1	3	4	6.3	5.6
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3	3	4	4.7	4.8
4	3	4	6.2	6.6
5	3	4	15.3	15.6
6	3	4	10.4	-10.7
7	3	4	2.2	2.0
8	3	4	-0.8	-2.1
9	3	4	6.2	6.5
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13	3	4	0.0	-0.9
14	3	4	0.0	-0.6
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1	4	4	6.8	6.9
2	4	4	3.8	3.4
3	4	4	2.4	2.3
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5	4	4	11.0	-11.3
6	4	4	9.8	-10.6
7	4	4	2.2	-2.8
8	4	4	-0.8	-1.0
9	4	4	4.8	5.2
10	4	4	2.3	-2.2
11	4	4	4.0	-4.5
12	4	4	0.0	1.0
13	4	4	2.7	-2.7
1	5	4	6.6	6.9
2	5	4	6.2	-6.2
3	5	4	15.9	-16.2
4	5	4	11.5	-11.7
5	5	4	5.2	-5.4
6	5	4	-1.3	-1.6
7	5	4	3.3	3.0
8	5	4	-1.2	-2.2
9	5	4	8.2	-7.9
10	5	4	-0.8	0.3
11	5	4	4.5	-4.6
12	5	4	0.0	0.2
13	5	4	-1.9	2.1
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2	6	4	8.9	-8.6
3	6	4	-0.9	0.5
4	6	4	2.8	-3.2
5	6	4	10.4	9.9
6	6	4	4.9	4.5
7	6	4	0.0	-0.3
8	6	4	0.0	-1.1
9	6	4	-1.4	-1.2
10	6	4	-1.1	1.1
11	6	4	3.3	3.1
12	6	4	0.0	-0.1
1	7	4	-0.8	0.2
2	7	4	-1.7	1.8
3	7	4	8.7	8.2
4	7	4	5.7	5.0
5	7	4	5.6	5.6
6	7	4	3.9	-3.9
7	7	4	-1.5	1.8
8	7	4	-0.8	0.3
9	7	4	4.3	4.5
10	7	4	0.0	-0.2
11	7	4	2.7	2.9
0	8	4	-1.6	-1.7
1	8	4	2.0	-2.5
2	8	4	-0.5	-1.2
3	8	4	-1.0	-0.7
4	8	4	4.3	-4.3
5	8	4	0.0	0.4
6	8	4	4.3	-4.3
7	8	4	3.7	-3.7

H	K	L	FO	FC
8	8	4	2.2	2.1
9	8	4	0.0	-0.2
10	8	4	-1.9	-1.1
1	9	4	6.3	-5.6
2	9	4	-1.6	1.2
3	9	4	4.0	4.1
4	9	4	-0.8	-0.3
5	9	4	6.2	-5.5
6	9	4	5.6	5.5
7	9	4	4.1	-4.4
8	9	4	-1.1	0.4
9	9	4	0.0	-0.5
0	10	4	-1.2	1.1
1	10	4	5.4	5.4
2	10	4	-0.8	1.3
3	10	4	2.0	2.3
4	10	4	0.0	1.1
5	10	4	4.0	-3.7
6	10	4	-0.3	0.9
7	10	4	2.7	2.7
1	11	4	4.2	4.0
2	11	4	-1.7	-1.0
3	11	4	2.5	-1.7
4	11	4	0.0	-0.2
5	11	4	0.0	1.0
1	0	5	6.2	-6.5
2	0	5	4.8	-5.2
3	0	5	3.6	4.0
4	0	5	4.3	4.0
5	0	5	2.0	-2.1
6	0	5	4.2	4.1
7	0	5	13.0	12.7
8	0	5	13.2	-13.4
9	0	5	3.7	3.9
10	0	5	2.2	-2.1
11	0	5	0.0	-0.8
12	0	5	-1.0	0.6
0	1	5	9.4	-9.4
1	1	5	3.0	2.6
2	1	5	1.8	-0.7
3	1	5	0.0	0.8
4	1	5	4.5	-4.6
5	1	5	2.8	2.5
6	1	5	12.1	-12.5
7	1	5	3.4	3.3
8	1	5	7.3	-7.8
9	1	5	4.1	-4.1
10	1	5	3.0	3.1
11	1	5	2.3	1.6
12	1	5	2.4	-2.9
1	2	5	4.2	3.9
2	2	5	2.5	-2.2
3	2	5	-0.4	1.1
4	2	5	3.1	-2.4
5	2	5	0.0	-0.8
6	2	5	3.2	-2.6
7	2	5	4.6	-4.8
8	2	5	4.5	4.6
9	2	5	-1.6	-1.1
10	2	5	-1.0	-0.4
11	2	5	0.0	-0.2
12	2	5	0.0	-1.1
0	3	5	4.5	-5.2
1	3	5	3.1	2.9
2	3	5	0.0	-0.9
3	3	5	0.0	-0.5
4	3	5	6.6	6.9
5	3	5	3.3	3.5
6	3	5	0.0	-0.6
7	3	5	2.6	1.7
8	3	5	2.0	1.6
9	3	5	-0.5	-1.3
10	3	5	0.0	0.0
11	3	5	-0.7	-0.5
12	3	5	0.0	0.6
1	4	5	-0.6	0.4
2	4	5	8.6	8.0
3	4	5	5.4	5.3
4	4	5	6.5	-7.2
5	4	5	-0.9	0.9
6	4	5	4.3	-4.8
7	4	5	-0.6	-0.4
8	4	5	0.0	-0.2
9	4	5	0.0	-0.4
10	4	5	-0.9	0.6
11	4	5	-1.7	0.0
0	5	5	2.3	1.4
1	5	5	2.6	3.3
2	5	5	9.6	-9.1
3	5	5	3.8	-4.0
4	5	5	14.0	-14.0
5	5	5	8.5	-8.5
6	5	5	-1.0	0.8
7	5	5	0.0	0.3
8	5	5	0.0	-0.4
9	5	5	-1.1	-0.6
10	5	5	-1.9	-2.4
11	5	5	-1.7	2.0
1	6	5	0.0	0.3
2	6	5	5.4	-6.1
3	6	5	8.2	-8.3
4	6	5	5.9	6.4
5	6	5	2.5	2.5
6	6	5	5.4	5.7
7	6	5	-1.1	-1.1
8	6	5	1.8	1.6
9	6	5	-1.6	0.7
10	6	5	-1.8	0.3
0	7	5	0.0	0.0
1	7	5	1.9	-1.9
2	7	5	2.8	2.6
3	7	5	-1.2	2.1
4	7	5	7.0	7.0
5	7	5	3.4	3.7
6	7	5	-1.7	1.6
7	7	5	0.0	0.1
8	7	5	2.0	1.5
9	7	5	-1.0	0.6
1	8	5	-1.4	-0.7
2	8	5	-1.7	1.5
3	8	5	0.0	0.2
4	8	5	-1.6	1.2
5	8	5	0.0	1.2
6	8	5	-1.3	1.1
7	8	5	-1.5	1.3
8	8	5	2.0	-1.9
0	9	5	-1.4	-1.1
1	9	5	0.0	-1.1
2	9	5	-1.5	1.7
3	9	5	-0.9	1.3
4	9	5	0.0	0.3
5	9	5	0.0	0.6
6	9	5	3.1	-3.3
1	10	5	-1.5	0.9
2	10	5	-1.6	1.4
3	10	5	-0.9	0.1
0	0	6	5.7	-5.8
1	0	6	-1.3	-2.2
2	0	6	2.3	-2.8
3	0	6	3.7	3.4
4	0	6	3.0	-2.2
5	0	6	5.2	5.5
6	0	6	2.9	2.9
7	0	6	2.2	1.7
8	0	6	-1.3	-0.1
9	0	6	-1.0	-1.6
10	0	6	2.2	-1.8
1	1	6	0.0	-1.1
2	1	6	-1.3	1.9
3	1	6	0.0	0.5
4	1	6	2.9	3.3
5	1	6	-1.3	0.2
6	1	6	0.0	0.8
7	1	6	4.1	-4.6
8	1	6	-0.8	-0.7
9	1	6	-1.8	-2.0
10	1	6	-0.8	-0.6
0	2	6	0.0	1.6
1	2	6	1.9	-1.5
2	2	6	2.4	-2.8
3	2	6	-1.1	-0.4
4	2	6	-1.2	-2.5
5	2	6	-1.3	-1.2
6	2	6	3.1	-3.2
7	2	6	3.0	-3.0
8	2	6	-1.4	-1.0
9	2	6	-1.6	1.8
1	3	6	0.0	1.1
2	3	6	1.8	-2.1
3	3	6	4.4	5.4
4	3	6	-1.6	0.7
5	3	6	4.0	-4.2
6	3	6	2.4	2.3
7	3	6	0.0	0.7
8	3	6	0.0	1.1
9	3	6	0.0	0.0
0	4	6	2.9	-2.7
1	4	6	2.3	2.1
2	4	6	3.0	3.4
3	4	6	2.3	-2.3
4	4	6	3.1	2.7
5	4	6	3.8	-3.9
6	4	6	1.7	1.4
7	4	6	-1.2	1.4
8	4	6	-0.7	0.1
1	5	6	3.9	-4.2
2	5	6	2.5	2.9
3	5	6	4.8	-5.3
4	5	6	0.0	0.5
5	5	6	-1.0	1.0
6	5	6	-1.7	-1.2
7	5	6	-1.7	1.9
8	5	6	0.0	1.1
0	6	6	3.4	3.6
1	6	6	-0.9	0.6
2	6	6	-1.1	-0.2
3	6	6	-0.4	1.3
4	6	6	-1.1	-0.5
5	6	6	2.3	3.0
6	6	6	-0.9	0.3
7	6	6	0.0	-0.3
1	7	6	-0.9	2.1
2	7	6	0.0	-1.1
3	7	6	-1.6	1.9
4	7	6	-0.6	0.1
5	7	6	-1.7	-1.3
0	8	6	-1.1	0.2
1	8	6	0.0	0.4
2	8	6	2.4	2.1
1	0	7	-0.6	1.4
2	0	7	-1.1	1.9
3	0	7	-1.1	-0.7
4	0	7	-1.7	0.7
5	0	7	-0.6	-0.3
0	1	7	4.2	3.7
1	1	7	-0.5	-0.1
2	1	7	0.0	0.2
3	1	7	0.0	-0.6
4	1	7	2.7	2.2
5	1	7	-1.2	-0.5
1	2	7	-0.9	-1.0
2	2	7	0.0	0.4
3	2	7	-1.8	0.0
4	2	7	0.0	0.9
5	2	7	-1.7	0.5
0	3	7	-1.3	1.8
1	3	7	-1.7	-0.6
2	3	7	2.8	2.8
3	3	7	0.0	0.3
4	3	7	-1.5	0.0
1	4	7	0.0	0.1
2	4	7	-0.8	-1.4
3	4	7	-1.2	-1.5

APPENDIX

APPENDIX

Computer Programmes

The extensive calculations necessary for the work described in this thesis were carried out primarily on the University of Cambridge I.B.M.370/165 computer in conjunction with the N.U.M.A.C. I.B.M.360/67 and Durham I.B.M.1130 computers. I would like to thank the staff of the Computer unit, especially the computer operators for their help and advice.

The major programmes used in the structure determinations and refinements were written by F.R. Ahmed and his associates (N.R.C. Crystallographic Programs for the I.B.M.360 System, World List of Crystallographic Programs, 2nd edn., Appendix p.52) and I am grateful for permission to use these programmes.

I have personally written and amended several smaller programmes as was necessary. These include a programme written in conjunction with Dr H.M.M. Shearer to translate diffractometer data from card images of paper tape, stored on disc into planes on cards.

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