CHAPTER-1

1.1 INTRODUCTION TO SINGLE CRYSTAL X-RAY DIFFRACTION

Crystallography is mainly concerned with the study of the atomic structure of matter in the crystalline state.

Single crystal X-ray diffraction over the last three decades, has revolution our insight about the molecular structures. The primary aim of the crystallographic studies is to obtain a detailed picture of the constituents of the crystal at the atomic level. A careful structure analysis provides a good deal of information about the bond lengths, bond angles, torsion angles, conformation and packing parameters, etc. These parameters are of utmost importance in establishing the relation of structural parameters to the chemical properties and it enables one to check on the nature of the theories of chemicals bonding. Starting with the study of the crystals containing few atoms in the early thirties, the single crystal X-ray diffraction technique has now been extended to the molecules of much greater complexity such as proteins, poly-nucleotides, enzymes, viruses, etc.

The brilliant experiment of Max von Laue in 1912, proved unmistakable that crystals behave like three dimensional gratings and that x-rays behave like wave. The x-ray crystallography is the only methods which give the stereochemistry of the molecule.

The basic principle of the diffraction of X-rays from the crystal specimen is used as a tool in the investigation of the crystal structures. In a typical X-ray diffraction experiment, a parallel, monochromatic beam of X-rays is incident on a photograph or by a counter. The record of the scattered radiation constitutes the experimental data. The intensity data so called depends essentially on the specimen used and on the geometry of the experimental set up.

The determination of a crystal structure normally proceeds in three distinct stages. The first is the measurement of the intensities of the Bragg reflections and the calculation of amplitudes from them, reduced to a common scale and corrected for various geometrical and physical factors. These amplitudes are known as 'Observed structure amplitudes' or 'observed structure factors'. The second stage is the solution of the phase problem: the phase of the reflections cannot be measured directly, and yet they must be derived in some way before the structure can be solved by Fourier methods. Because of uncertainties in the amplitudes and phases, this first structure determination consists of retaining the approximate atomic positions so as to obtain the best possible agreement between the structure factors and the 'calculated structure factors' i.e. those calculated from the approximate atomic positions of the successive stages of refinement.

With the help of high speed computers, it became very easy to determine the structure within reasonable time.

The present work deals mainly with the three dimensional structure analysis of some medicinal plant compounds by x-ray diffraction method.

1.2 SOME THEORETICAL ASPECT OF CRYSTAL STRUCTURE

1.2.1 THE CRYSTAL AND ITS SYMMETRY

The concept of 'Space lattice' i.e. the fundamental arrangement of identical pattern units, the screw axis, glide plans, the theory of point and space groups etc. are developed by the early crystallographers. Bravais showed from symmetry considerations that there are 14 possible types of space lattices of which seven are primitive and other seven are face centered or body centered within the seven crystal system. The unit cell is the basic structural unit of a crystal. The unit cell is defined by three unit translations $\vec{a}, \vec{b}, \vec{c}$ and three inter axial angles α, β, γ and the repetition of which in three

dimensions constitute the whole crystal. The origin of the unit cell is chosen at some symmetrically convenient position. Each lattice point represents an atom or a group of atoms which are related by symmetry elements, and the space lattice is built up by repeating these regular intervals in three dimensions.

1.2.1(i)POINT GROUPS

The unit of pattern associated with each lattice point may itself possess symmetry and this symmetry is closely related to that of the crystal as a whole. There are only thirty two difference combinations of the external symmetry elements of crystals. These thirty-two sets of symmetry elements are called point groups, because all the elements of any one group pass through one point which is at the origin of crystallographic axis chosen in conformity with morphological conventions.

Operation of any one of the symmetry elements of the point group will bring the crystal as a whole. That is the normal of the faces or the faces themselves if they are fully developed into a new orientation which is indistinguishable from the old. Repeated operation will ultimately return to its initial orientation. The external symmetry displayed by the crystal is dependent upon the atomic arrangement within the crystal itself, which in its turn depends upon the symmetry displayed by the atoms and molecules associated with each lattice point and which comprise what we have called the unit pattern. The unit of pattern may passes exactly the same combination of reflection planes, rotation and inverse rotation axes as does the crystal as a whole. When this occurs the point group symbol serves to designate both the internal grouping of the atoms round the lattice point and the external symmetry of the crystal

1.2.1(ii) SPACE GROUPS

However the unit of pattern may possess symmetry elements which relate every point of the pattern with another by operations which involve translating this type of symmetry elements will have no place in point groups which are not concerned with translations. There are two such additional symmetry elements, called glide plane and screw axis, in accordance with which the unit of pattern is unaltered by the operation of a reflection across a plane, combined which a translation parallel to the plane (glide) or by a rotation combined with a translation in the direction of the rotation axis (screw). By repeated operation of the transnational symmetry elements the unit of pattern is brought into coincidence, not with itself, but with the corresponding group in an adjoining unit cell, and so on into the next cell and the next through the crystal lattice. These are 230 different combinations of internal symmetry elements, which constitute the 230 different kinds of extended three-dimensional framework into which the unit of pattern associated with each lattice point may be fitted to produce a periodic crystal lattice. They are called space group. Although the space groups must account for the symmetry relations extisting within the unit pattern, it feels as nothing about the actual arrangements of the atoms.

1.2.2 RECIPROCAL LATTICE

The concept of reciprocal lattice was first developed by Ewald in 1913 who expanded the idea in 1921. References to reciprocal lattice theory are so common in discussions of X-ray diffraction from crystals that one is seriously handicapped without an understanding of it. From the well known Bragg equation we get

$$\sin\theta_{ukl} = \lambda / 2d_{hkl} \qquad (1)$$

This equation immediately suggests a reciprocal relationship between a d values in a crystal and the sine's of the Bragg angles. For a (100) plane the equation may be written as

$$\sin\theta_{100} = \frac{\lambda}{2d_{100}} = a \tag{2}$$

We also know that

$$d_{100} = d_{100} / h \tag{3}$$

Substituting the equation (3) in to equation (1)

$$\sin\theta_{100} = \frac{\lambda}{2d_{h00}} \tag{4}$$

We have $\sin\theta_{h00} = \mu\lambda / 2d_{100}$ \hfill (5)

We find the interesting relationship

$$\sin\theta_{h00} = \mu\sin\theta_{100} \tag{6}$$

equation (6) means that if one known from X-ray data the value of d $_{100}$ be could salve for sin θ_{100} from equation (2) and then one could solve for Sinθ_{h00}.

The real space 'γ' corresponds to the space of the scattering material and the reciprocal space γ* corresponds to the space the observed diffraction pattern. The reciprocal lattice is defined by the unit translation vector $\vec{a}^*, \vec{b}^*, \vec{c}^*$ and the interaxial angles by $\alpha^*, \beta^*, \gamma^*$ which are related to the direct lattice $\vec{a}, \vec{b}, \vec{c}$ by

$$\left.\begin{array}{l} \vec{a}.\vec{a}^* = \vec{b}.\vec{b}^* = \vec{c}.\vec{c}^* = 1 \\[3em] \vec{a}.\vec{b}^* = \vec{a}.\vec{c}^* = \vec{b}.\vec{c}^* = 0 \end{array}\right\} \tag{7}$$

The scattering vectors S can be defined in terms of the reciprocal lattice as

$$S = \mu \vec{a}^* + k \vec{b}^* + \gamma \vec{c}^* \qquad (8)$$

1.3 STRUCTURE AND ITS DETERMINATION FROM X-RAY DIFFRACTION DATA ANALYSIS

The crystal structure of a substance determines the diffraction pattern of that substance or more specifically, that the shape and size of the unit cell determines the angular positions of the diffraction lines and the arrangement of the atoms within the unit cell determines the relative intensities of the lines. Since structure determines the diffraction pattern, it should be possible to go in the other direction and deduce the structure from the pattern. It is possible, but not in direct manner. If the structure of a substance is known, then we can calculate its diffraction pattern in a very straightforward fashion. But the reverse problem, that of directly calculating the structure from the observed pattern, has not yet been solved. The procedure adopted is essentially one of trial and error. On the basis of an educated guess, a structure is assumed, its diffraction pattern calculated, and the calculated pattern compared with the observed one. If the two agree in all detail, the assumed structure is correct; if not the process is repeated as often as is necessary to find the correct solution.

The determination of an unknown structure proceeds in three major steps:

1) The shape and size of the unit cell are deduced from the angular positions of the diffraction lines. An assumption is first made on the basis of preliminary X-ray diffraction data to which of the seven crystal systems the unknown structure belongs to,

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and then, on the basis of this assumption, the correct Miller indices are assigned to each reflection. Once this is done, the shape of the unit cell is known and its size is calculable from the positions and Miller indices of the diffraction lines.

2) The number of atoms per unit cell is then computed from the shape and size of the unit cell, the chemical composition of the specimen, and its measured density.

3) Finally, the positions of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines with the help of the computation method.

Only when these three steps have been accomplished is the structure determination complete.

1.4 SOLUTION OF THE PHASE PROBLEM BY DIRECT METHOD

The aim of the crystal structure analysis by X-ray diffraction is to locate the position of the atoms within the unit cell given by the maxima of the electron density function. Therefore, if we know $|F_{hkl}|$ and ϕ_{hkl}, we can compute ρ (x, y, z) for all values to give a three dimensional electron density map. However, we can normally obtain only the structures factor amplitude $|F_{hkl}|$ and not the phase angle ϕ_{hkl}, directly from the experimental measurements. So, ϕ_{hkl} can be derived either from the values of A_{hkl} and B_{hkl} that are computed from trial structures or by purely analytical methods. The problem of getting estimates of phase angles so that an image of the scattering material can be calculated is called the phase problem and is one of the crucial one in the X-ray crystal structure analysis the phase problem exists because.

1) We are unable to monitor the wave completely and accurately due to very high frequency ($\approx 10^{18} Hz$) of X-ray.

2) If the phase measurement is to be meaningful the distance between the site at which we sample the diffracted wave and that at which we measure the reference wave, for comparison of two waves, must be known accurately.

3) We cannot detect the phases of the diffracted waves because the emission of X-ray occurs from a' incoherent source' in random event. As a consequence there are no two well-defined phase relationships between the incidents waves and this prevents us from measuring phase relationship between the diffracted waves.

To solve the phase problem, researchers have used various techniques such as Direct method[1], Isomorphous replacement method[2], Patterson Method[3], Heavy Atom Method[4], and Anomalous Scattering Method[5]

1.4.1 DIRECT METHODS

Direct methods try to evaluate phases ϕ_{hkl} directly from the measured diffraction intensities I_{hkl} by using relationships among the phases whose values are based on the intensities. Therefore aim of the direct methods is to identify as many relationships as possible. Next the origin is fixed by specifying the phases of a few suitable reflections numerically. Then using the phase relationships, new phase are calculated. In this way it is not possible to phase all strong reflections. Thus the unknown phases of the remaining strong reflections can then be calculated by selection of a few more starting reflections. Thus when most of the strong reflections have got a phase the numerical values of the unknown are evaluated and then using the following expression an image of the structure is produced.

$$\rho(x,y,z) = \frac{1}{v} \sum_{a|hkl|} \sum \sum |F_{hkl}| \cos\left(\left(2\pi(hx+ky+lz)-\phi_{hkl}\right)\right)$$

<div align="right">(9)</div>

$$C = \frac{R_P - R_b}{m}$$

$$Y = mX + C$$

$$R_p = mX + C$$

These phase determining technique make use of weak and strong structure factors, triplet relationships, structure invariants and origin fixing reflections and the process of phase determination.

1.4.2 STRONG AND WEAK STRUCTURE FACTORS

If in a crystal structure the atoms lie in the neighborhood of the set of planes (hkl), the reflection has a large intensity while the intensity is small if the atoms are randomly distributed. This also follows directly from the structure factor expression (10) because a large F_{hkl} will only

$$F = \sum_{J=1}^{N} f_j \exp(2\pi i r_j s)$$

<div align="right">(10)</div>

be found if the atoms lie near positions for which $(hx_j+ky_j+iz_j)$ a constant module 1 for all J. conversely, a strong intensity of (hkl) implies that the electron density will peak in planar region which lie d_{hkl} apart. The choice of the origin with respect to these planer regions of the electron density defines the phases ϕ_{hkl} in expression (10).

Large and small structure factor amplitudes thus may be used to predict where in the unit cell electron density can approximately be expected. Moreover the strong and weak reflections have different distribution when the space group is centric or non-centric. The centric space group is populated by weak reflections.

1.4.3 UNITARY AND NORMALIZED STRUCTURE FACTORS

Equation (2) shows that the scattering factor of an atom reduces exponentially with the increase of $Sin^2\theta/\lambda^2$ As a result the high angle structure factors fall with $Sin^2\theta/\lambda^2$ to overcome this problem the atoms are assumed as the point–atoms on normalizing the structure factors. The unitary structure factor is defined as the ratio of the structure amplitude, $|F_{hkl}|$ to its maximum possible value, i.e. the value it would have if all atoms scattered exactly in phase. It is denoted by U. and $U_{hkl} = \dfrac{|F_{hkl}|}{\left|_{j}f_{j}\right|}$, where f $_{j}$ contains the

temperature expression

$$U_{hkl} = \frac{|F_{hkl}|}{\sum\limits_{j=1}^{N} f_j} = \sum n_j \exp\left(2\pi r_j . s\right) \qquad (11)$$

So that $|U_{hkl}| \le 1$ where n$_j$ is the unitary scattering factor defined by

$$n_j = \frac{f_j}{\sum\limits_{J=1}^{N} f_J} \qquad (12)$$

The normalized structure factors, E. introduced by Hauptman Karle[6] is convenient to use in the probabilistic methods given by them and is defined as

$$E_{hkl} = \frac{F_{hkl}}{\xi_{hkl}^{1/2}\left(\sum\limits_{J=1}^{N} f_J^2\right)^{1/2}} = \xi_{hkl}^{-1/2} \sum\limits_{J=1}^{N} V_J \exp\left(2\pi i r_J s\right) \qquad (13)$$

Where, $V_J = \dfrac{f_J}{\left(\sum\limits_{J=1}^{N} f_J^2\right)^{1/2}}$

The equation (13) is clearly the structure factor formulae of a point atom structure. The ξ_{hkl} is a small integer which makes the average E^2 unity for any given class of reflections. This factor depends on the crystal class[7] and corrects for systematic absences and the resulting redistribution in intensity. The quantity ξ_{hkl} includes both the scaling factor and statistical weight of structure factor, which emanated from the overlap of the atoms along various projections due to point group symmetry elements. Hence the ξ_{hkl} is space group symmetry dependent.

In case of equal atom structures,

$$E_{hkl} = (\xi_{hkl}N)^{-1/2} \sum_{J=1}^{N} \exp(2\pi i r_j s) \qquad (14)$$

In practice, the analytical methods of phase determination are carried out on normalized structure factors i.e. the values of structure factor, $|F|$, modified to remove the fall-off in the individual scattering factors I , with increasing angle 2θ .

1.4.4 WILSON STATISTICS (DISTRIBUTION OF INTENSITIES)

In general 50 space groups can be determined on examining the systematic absences in the diffraction pattern. For the identification of the remaining space groups, the intensity data statistics play a vital role . A.J.C. Wilson calculated two distribution functions, one for cetrosymmetric and the other for non-cetrosymmetric distribution of intensities by using the central limit theorem. This states that, "The sum of a large number of independent random variables will have a normal probability distribution with mean equal to the sum of the means of the independent variables and variance equal to the sum of their variances irrespective of the nature of distribution function of individual random variables". We consider, a number, N of independent random variables X_j (j=1 to N) which have means X_j and variance α_j^2

$$X = \sum_{J=1}^{N} x_J \quad , \overline{X} = \sum_{J=1}^{N} \overline{x}_J \text{ and } \alpha^2 = \sum_{J=1}^{N} x_J^2$$

Here, the real and imaginary parts of the contribution from all the atoms are considered as random variables.

$$X_j = f_j \cos\left(2\pi i r_j.s\right) \text{ and } y_j = f_j \sin\left(2\pi i r_j.s\right).$$

The quantity $2\pi r_j.s$ is assumed to be uniformly distributed between 0 to 2π. Hence x_j and y_j have equal chances of being positive and negative. . So $<x_j>=0$ and $<y_j>=0$

The probability that x_j lie between x and x+dx and y_j lies between y and y+dy is

$$P(x.y) \, dxdy = p(x)p(y) \, dxdy = \frac{1}{\pi\sum} \exp\left(-\frac{x^2+y^2}{\sum}\right) dxdy \tag{15}$$

In the absence of any symmetry element, the probability that the intensity ($I = x^2 + y^2$) lies between I and I+dI , derived from equation (18) is

$$_1 P(I)di = \sum \exp(-1/\sum) \tag{16}$$

where $\sum = \sum_{J=1}^{N} f_J^2$ is the sum of the square of atomic scattering factors of all atoms.

In the presence of an inversion center, the structure factor is real (i.e. $y_j = O$) and the distribution of intensities is calculated as

$$\sum_1 P(I)DI = \frac{1}{\left(2\pi\sum\right)^{\frac{1}{2}}} \exp\left(-\frac{1}{2\sum}\right) dI \tag{17}$$

After some simple arithmetic's [8], the probability distribution equation (18) and (20) can be expressed in terms of $|E|$'s as

$$_1 P(|E|)d|E| = 2|E|\exp\left(-|E^2|\right)d|E| \tag{18}$$

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$$\sum_{1} P(|E|)d|E| = \frac{2}{\pi}\exp(-\frac{E^2}{2})d|E| \qquad (19)$$

For any kind of distribution $\langle|E^2|\rangle = 1$ and the Wilson ratio is

$$P = \langle|E|\rangle^2 = \pi/4 \simeq 0.785 \text{ for n.c.s}$$

$$= 2/\pi \simeq 0.637 \text{ for c.s.} \qquad (20)$$

The cumulative function[9] N (z) the percentage of reflections with normalized intensity less than equal to z is defined as

$$N(z) = \int_0^z P(t)dt \qquad (21)$$

Where $z = 1/\langle1\rangle = |E|^2$ is the normalized intensity. Apart from the above types of distribution, hypercentric[10,11] intensity distribution arises when more than a molecule, each with a non-crystallographic center of symmetry occupy general position in a centrosymmetric space group. An experimental data set is considered to be centric, acentric or hypercentric distribution. Also the probability distributions of intensities along various projections provide vital information regarding the space group symmetry elements.

1.4.5 HARKER-KASPER INQUALITIES

An extensive system of inequalities exists for the coefficients of a Fourier series, which represents a positive function. Inequalities among structure factors were first discovered by Harker and Kasper[12]. In more general term it is the positiveness of the electron density function P(r) which allows the inequalities among unitary structure factors that allow for the determination of the phases of the certain intense reflections in a centrosymmetric crystal. To do this Harker and Kasper used the Cauchy's inequality and showed that for P1 space group.

$$U^2_{hkl} \leq \frac{1}{2}(1 + U_{2h,2k,2l})$$ (22)

This equation can be utilized to predict the sign of $U_{2h, 2k, 2l}$. The above inequality restricts the phase only of structure factors with indices of defined parity (2h,2k,2l in P1) . It is also possible to restrict phases of reflections of any parity by means of suitable in equalities.

1.4.6 TRIPLET PHASE RELATIONSHIPS

Sayer[13] derived an equality relationship between structure factors containing almost equal and well-resolved atoms and the electron density function P(r) and P^2(r) are alike and show peaks in the same position using the concept of the 'Squared density structure' the structure factors of such crystals must satisfy the relation

$$F_H = \frac{1}{V}\frac{f}{\gamma} \sum F_{H'} F_{H-H'}$$ (23)

Where γ is the scattering factor of the squared atom and depends only on the magnitude of the reciprocal vector H and f/v (=k) is the overall scaling factor. This is the Sayer's equation, valid for both centro and non centrosymmetric structures and provides an exact linkage among the phases and the result is not restricted by the assumption of positive electron density.

By multiplying both sides of equation (23) by F_H i.e. F_{-H} we obtain

$$|F_H|^2 = \frac{1}{V}\frac{f}{\gamma} \sum |F_{-H} F_{H'} F_{H-H'}| \exp\left[i(\phi_{-H}\phi_{H'}\phi_{H-H'})\right]$$ (24)

For large values of $|F_H|$,the left hand member will be large ,real positive. We may therefore, except that, the largest contributors to the summation on the right are also real and positive i.e. if $|F_{H'}|$ and $|F_{H-H'}|$ are large we get the relation

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$$\phi_3 = \phi_{-H} + \phi_H + \phi_{H-H''} = 0 \pmod{2\pi} \qquad (25)$$

which is known as 'sum of angles' formulae. Also the positivity of electron density criterion leads to the phase addition formulae as proposed by Karle and Karale[14-16] in the from of

$$\phi_H = \phi_H + \phi_{H-H''} \qquad (25a)$$

When several triplets are involved with a given H, the relation becomes,

$$\phi_H = \langle \phi_{H'} \phi_{H-H'} \rangle_{H'_r} \qquad (25b)$$

Where $< >_{H'_r}$ implies a restricted set vector summation involving $r|E|$ values. This equation is used in determining phases for non-centrosysmmetric structures.

For a centrosymmetric crystal the equation (25) reduces to

$$S(E_H)S(E_{H'})S(E_{H-H'}) \approx +1 \qquad (26)$$

Cochran and Zachariasen [17,18] individually showed that, even when $|E|$'s are smaller than the necessary to satisfy the inequality relation it could still be showed that equation (26) is probably true. The equation (25) and (26) are triplet relations expressed in a probabilistic way where S(H) represents the sign of reflexion. The vectors associated with these reflections d(H), d(H'), d(H-H') from a closed triangle. In practice it may be possible to form several such vector triplets for given (hk1). If two of the signs in (26) are known. The third can be deduced.

1.4.7 PHASE DETERMINING FORMULAE

Karle and Hauptman derived a number of relationships between the structure factors. For space group P1, the basic Hauptman and Karle formulae can be expressed as

$$\sum\nolimits_1 : s(E_{2H}) \approx s(E_H^2 - 1)$$

$$\sum\nolimits_2 : s(E_H) \approx s\left[\sum_H E_H, E_{H-H''}\right]$$

$$\sum\nolimits_3 : s(E_H) \approx s\left[\sum_H E_{H'}.(E_{\underline{H-H'}} - 1)\right] \qquad (27)$$

$$\sum\nolimits_4 : S(E_{2H}) \approx \left[\sum_{H'} (E_{H''}^2 - 1)(E_{H+H'}^2 - 1)\right]$$

Since only the magnitude of E's are known $\sum\nolimits_1$ and $\sum\nolimits_4$ can be used initially. But as soon as few more sign are known $\sum\nolimits_3$ beings to contribute and as more signs are available, $\sum\nolimits_2$ plays an important role. For a centrosymmetric space group the $\sum\nolimits_2$ formula takes the form

$$S(E_H) \approx S(\sum_{H_r}, E_H, E_{H-H''}) \qquad (28)$$

If all E's were large, (31) may be used in the from given by Zachariasen

$$s(E_H) \approx s\left[\sum_{H_r} s(E_H) s(E_{H-H'})\right] \qquad (29)$$

Cochran and Douglas [19], and Grant, Howells and Rogers [20] have used the triple product sign relationship in different forms to solve the phase problem.

If follows that we have to use probability theory in order to assess the reliability of (25) and (26).

The probability of $s(E_H)$ associated with equation (28) to be positive as given by Woolfson [21] and Cochran & Woolfson [22] for a structure with N equal atoms is defined as

$$P_+(E_H) = \frac{1}{2} + \frac{1}{2} \tanh(\frac{1}{\sqrt{N}} |E_H| \sum E_{H'} E_{H-H''}) \qquad (30)$$

This formulae can be extended to the case of non-equal atoms by substituting $1/\sqrt{N}$ with $\sigma_2\sigma_3^{-3/2}$ where $\sigma_n = \sum_{J=1}^{N} z_j^n$ where Z_j being the atomic number of the jth atom. When several terms contribute to, the summation with the same sign, then the argument of the tanh becomes large and P_+ tends to the extreme values 1.0 or 0.0 values of P_+ less than ½ are thus indications that the sign of F_{hkl} is negative with a probability P_- given by

$$P_- = 1 - P_+$$

For a non-centrosymmetric structure the phase (ϕ) can take any value between 0 to 2 and the probability density [23] of Φ_3 is

$$P(\Phi) = \frac{1}{2\pi I(x)}\exp(\cos\Phi_3) \qquad (31)$$

Where $I(x)$ is a modified Bessal function of order zero. This is the well known Cochran distribution. $P(\Phi_3)$ is a von Mises[24] function and its trend is smaller to that of Gaussian function. The parameter is derived from the normalized structure factor as

$$= \frac{2}{\sqrt{N}}\left|E_H E_{H''} E_{H-H'}\right| \qquad (32)$$

Cochran distribution (31) shows that, for higher values of χ the distribution peaks more sharp, which increase the reliability of the phase estimation.

For a non-centrosymmetric crystal structures additional formulae (25b) may be used to derive approximate values for the phase angle. The so called tangent formulae by Karle and Hauptman [25] is

$$\tan\phi_H \approx \frac{\sum_{H'}\left|E_{H'}\right|\left|E_{H-H'}\right|\sin(\phi_{H'}+\phi_{H-H'})}{\sum_{H}\left|E_H\right|\left|E_{H-H'}\right|\cos(\phi_{H'}+\phi_{H-H'})} \qquad (33)$$

and is used extensively to calculate and also to refine phases for non-centrosymmetric structures. The current phase determining procedures are based on the following weighted tangent formulae,

$$\tan \phi_H \approx \frac{\sum_{H} W_H |E_{H'}| |E_{H-H'}| \sin(\phi_{H'} + \phi_{H-H'})}{\sum_{H} W_H |E_{H'}| |E_{H-H'}| \cos(\phi_{H'} + \phi_{H-H'})} \tag{34}$$

Where $w_H = \tan^{-1}\left[N^{-1/2} |E_H| (A_H^2 + B_H^2) \right]$ (35)

Initially the weight w_H of phase are taken unity. The variance associated with the determination of ϕ_H can be derived from probability formulae of Cochran.

$$V = \frac{\pi^2}{3} + \left[I_0(\alpha) \right]^{-1} \sum_{n=1}^{\alpha} \frac{I_{2n}(\alpha)}{n^2} 4\left[I_0(\alpha) \right]^1 \sum_{n=1}^{\alpha} \frac{I_{2n+1}(\alpha)}{(2n+1)^2} \tag{36}$$

where

$$\alpha = \left\{ \left[\sum 2N^{\frac{1}{2}} |E_H E_{H'} E_{H-H'}| \cos(\phi_{H'} + \phi_{H-H'}) \right]^2 + \left[\sum 2N^{-\frac{1}{2}} |E_H E_{H'} E_{H-H'}| \sin(\phi_{H'} + \phi_{H-H'}) \right]^2 \right\}$$

and $I_n(\alpha)$ is the nth order modified Bessel function of imaginary argument.

1.4.8 STRUCTURE INVARIANTS AND SEMIINVARIANTS

Structure Invariants: The phases ϕ_H depend upon both the atomic positions as well as the choice of origin where as the amplitudes $|E_H|$ ' are independent of the origin and the function of only the structure. If we shift the origin by a vector Δ, all the atomic vectors change to $r_j - \Delta$ and F_H become $F_{H, given}$ by

$$F_H' = \sum f_j = \exp\left[2\pi i H(r_j - \Delta) \right] = F_H \exp(-2\pi i H\Delta) \tag{37}$$

$$= |F_H| \exp\left[i(\phi_H - 2\pi H\Delta) \right]$$

We see that phase changes by an amount $-2\pi H\Delta$ while the amplitude is invariant as directed by the physical reason. There exist certain linear combinations of phases

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(triplets and quarters) whose values are independent of the choice of origin and are known as structure invariants [26] i.e.

$$\Phi_3 = \phi_{H_1} + \phi_{H_2} + \phi_{H_3} \tag{38}$$

A triplet structure invariant is uniquely associated with the three reciprocal lattice vectors if

$$H_1 + H_2 + H_3 = 0 \tag{39}$$

The first neighborhood [27] of the triplet (38) satisfying the condition (39) consists of three magnitudes $|E_{H_1}|, |E_{H_2}|, |E_{H_3}|$ when all the three magnitudes are large then

$$\Phi_3 \approx 0 \text{ (Cochran distribution)} \tag{40}$$

The eee group does not change its sign with change of origin and these structure factors are, therefore called structure semi invariants. If three groups are taken, such as oee, eoe and ooe where adding the parity of the indices gives eee, then the product of three such structure factors is also a structure invariant.

Similarly, a quartet [28] phase relationships Φ_4 is defined as

$$\Phi_4 = \phi_{H_1} + \phi_{H_2} + \phi_{H_3} + \phi_{H_4} \tag{41}$$

$$\text{When } H_1 + H_2 + H_3 + H_4 = 0 \tag{42}$$

First neighborhood of the quartet (41) consists of four magnitudes

$$|E_{H_1}|, |E_{H_2}|, |E_{H_3}|, |E_{H_4}| \tag{43}$$

$$\text{In favourable condition } \Phi_4 \approx 0 \tag{44}$$

The second neighborhood of the quartet (44) consists of the four magnitudes in (43) and three additional cross terms

$$|E_{H_1+H_2}|, |E_{H_2+H_3}|, |E_{H_3+H_4}| \tag{45}$$

If all the seven magnitudes are large then the condition (44) is favoured [29]. when the cross terms (45) are small and the four magnitudes are large the estimation [30,31] is

$$\Phi_4 \approx \pi \qquad (46)$$

The Quartets (46) are known as negative or zero quartets. The estimation of the negative quartets, which includes the contributions from observed weak reflections (cross terms), are entirely different from those of active triplets, but the weights associated with the quartets are small in comparison to that of active triplets. Therefore, the negative quartets are not used for finding the initial phases, but play a significant role in the figures of merits (FOM).

Structure semi invariants: The linear combinations of phases which are independent of the choice of the permissible origins are called structure semi invariants. Form equation (37) we get

$$\phi_H{}' = \phi_H - 2\pi H\Delta \qquad (47)$$

For all permissible origins $\phi_H{}' = \phi_H$ i.e. $H\Delta$ is an integer. The structure invariants Φ_H, defined by equation (47) is known as one phase semi invariant.

The linear combinations of two phases $\phi_{H_1} + \phi_{H_2}$ is a structure semi invariants if $(H_1 + H_2)\Delta$ is an integer and so on for higher structure semi invariants. Analogous to the structure invariants, the structure semi invariants can be estimated using the nested neighborhood principle [32]

1.5 REFINEMENT OF STRUCTURE

Once a trial model of the structure has been proposed, it is necessary to refine it. A common measure of the extent to which refinement of the atomic positions has

progressed is to compute the reliability factor (R) which measures the agreement between observed and calculated structure factors. The R-factor can be defined as

$$R = \frac{\sum\limits_{hkl} \left| |F_0| - |F_C| \right|}{\sum\limits_{hkl} |F_0|} \qquad (48)$$

Where $|F_0|$'s and $|F_c|$'s the observed and calculated structure factors respectively. The value of R depends on the accuracy of structure determination.

The differential Fourier synthesis can be used for refinement of a structure, but the main disadvantage of this method is that it is not possible to refine the scale and thermal parameters of the structure.

An analytical method of refinement of great power and generality is based on the principle of least- squares and has been described by Whittaker and Robinson [33]. In this method the refinement of crystal structures are based on the minimization of the squares of the properly weighted differences between the calculated and observed structure factors with respect to some parameters of the structure. The most commonly used function is,

$$\sum\limits_{hkl} w_{hkl} \left(|F_0| - |F_C| \right)^2 \qquad (49)$$

Where w_{hk1} is the weight of the observation and usually expressed as

$$W_{hkl} = \frac{1}{\sigma^2 (hkl)} \qquad (50)$$

Where $\sigma(hk1)$ is the standard deviation $|F_0(hkl)|$

Cruickshank [34] and Rollet [35,36] have discussed methods for solving the equations involved in the least- squares refinement. The parameters generally involved in the refinement process are:

1) One or more scale factor

2) The three positional parameters and six anisotropic thermal parameters for each heavy atom and three positional parameters and one isotropic thermal parameter for each hydrogen atom.

1.5.1 ESTIMATED STANDARD DEVIATIONS FROM LEAST –SQUARES

The estimated standard deviations (e.s.d.) for any parameter p_i is

$$\sigma\left(P_i\right) = \left[\left(b_{ii}\right)\left(\sum_{hkl} w\Delta^2\right) / \left(m-n\right)\right]^{\frac{1}{2}} \qquad (51)$$

Where b is the ith diagonal element of the inversion matrix, w is the weight, m is the number of observations and n is the number of parameters. Refinement of the parameters may be considered to be complete when the shifts in the parameters are smaller than their e.s.d.'s.

1.6 EXPERIMENTAL PROCEDURE

1.6.1 SELECTION OF SUITABLE CRYSTALS

The selection of a single crystal of a proper size and shape is very important, since the success of entire process of crystal and molecular structure determination depends on the selection of an appropriate crystal. Using a polarizing microscope a crystal of proper size and shape may be selected. The crystal is mounted at the end of a thin glass fiber by some adhesive and mounted on a goniometer head. The goniometer head consists of two adjustable graduated arcs at right angles to each other and two other perpendicular adjustable screws used for horizontal and vertical shift of the crystal.

The size of the selected crystal should be such that it can produce a noticeable diffraction pattern with the minimum absorption of x-rays.

1.6.2 PRELIMINARY INVESTIGATIONS BY X-RAY PHOTOGRAPHIC TECHNIQUE

Preliminary studies, includes to find the unit cell dimension and space group of the crystal are usually done by photographic methods. The photographic methods involve the rotation, oscillation, Wessenberg methods.

The rotation photographs can give information about the dimension of the unit cell of a crystal provided it is allowed to rotate in the requisite direction, but it is not possible to get any symmetry information.

Some of the limitations of the rotation photographs can be overcome in the oscillation photographs. In the oscillation method the crystal is oscillated over a limited range resulting in fewer diffraction spots, which can be indexed two –dimensionally.

The problems of indexing and overlapping of diffraction spots have been removed in the Weissenberg method where a single layer of reciprocal lattice points are recorded separately. In this method only one layer line of reflections is allowed to be recorded by allowing in through an adjustable metal screen as a layer line screen and photographic film co-axial with the oscillation axis is given a translational motion parallel to the oscillation axis, synchronized with the oscillatory motion of the crystal. The distance traveled by the film is linearly related to the angle of rotation. This results in spreading of the reflected spots over the surface of the film on characteristic straight lines and curves. The Weissenberg photograph produces an image of the reciprocal lattice.

1.6.3 DETERMINATION OF SPACE GROUPS

Careful examination of oscillation and Weissenber photograph can lead to the identification of the Laue group and to the crystal class. Presence of symmetry elements,

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except the center of symmetry, can also be detected from the photographs. The observation of systematic absences in the Weissenberg photographs indicate the presence of symmetry operations involving translation, e.g. screw axes, glide planes and non-primitive lattices. The information thus obtained can be used to identify the space group of the crystal. There are a number of space groups which exhibit the same systematic absences and cannot be determined unambiguously. For heavy atom derivatives this ambiguity of space groups can be resolved from the occurrence of Harker line and Harker section vectors in the Patterson map.

Sometimes information about the presence or absence of center of symmetry can also be obtained from physical properties viz.piezo electricity, pyro electricity and the optical activity. The statistical distribution of E-values can also be used to detect the presence of the center of symmetry.

1.6.4. COLLECTION OF INTENSITY DATA

Photographically, intensity data is usually collected using the equi-inclination 'multiple films' Weissenberg method. In this method to cover the entire range of intensities it is often necessary to collect two sets of data for each year, one with long exposure and the other with a short exposure. The intensities are estimated either visually by using a calibrated scale or by the photographic method.

The intensity data is collected in a Bruker-Nonius SMART CCD-3circle diffractometer. It employs the kappa geometry instead of standard Eulerian geometry used in most of the 3-circle diffractometers. The $W/2\theta$ scan technique has been used for data collection. The profile of the reflecton is recorded by scanning it in 96 steps. The first and last 16 steps record the left backgrounds (LBG) and right background (RGB).

The net count is given by, ((INT)-2(LBG+RBG)) and the standard deviation of the counts is given by (INT+4(LBG+RBG)), where INT is the total count produced by intensity profile. During the data collection periodic checks are carried out with certain "orientation" and 'intensity' control reflections to ensure the stability of the crystal, the stability of the X-ray beam, and the orientation of the crystal.

The intensity data are collected by scanning the asymmetric part of the reciprocal lattice in a zig-zag manner, so that the mechanical movements of the diffractometer can be minimized. In the Bruker 3-circle diffractometer a graphite crystal with a mosaic spread of about 0.4° is positioned to produce 002 reflections and is used as monochromator.

1.7 FACTORS AFFECTING X-RAY INTENSITY

In X-ray diffraction the amount of energy E_{hkl} diffracted by the crystal which is rotating uniformly about an axis normal to the x-ray beam can be written as

$$E_{hk1} = KL_{hkl}P_{hkl} \left| F_{hkl} \right|^2 \qquad (52)$$

where K is a scale factor and it is constant for the experiment but L_{hkl} and P_{hkl} are the Lorentz and polarization factors and varying from reflection to reflection.

The Lorentz factor, which is a measure of the time for which a reciprocal lattice point is in the reflecting position, is dependent on the distance of the point from the origin. The Lorentz factor (L) is given by

$$L = \frac{Sin\theta}{Sin\theta(Sin^2\theta - Sin^2\mu)^{\frac{1}{2}}} \qquad (53)$$

Where θ is the Bragg angle and μ is the equi-inclination setting angle.

The expression (L) for diffractometer using the equitorial geometry is given by,

$$L = 1 / Sin2\theta \qquad\qquad (54)$$

The origin of the polarization factor lies in the attenuation of the reflected beam which occurs due to the polarization at the reflecting surfaces and given by,

$$P = \frac{1 + \cos^2 2\theta}{2} \qquad\qquad (55)$$

The polarization factor for the diffractometer using the crystal monochromator is given by,

$$P = (P \frac{\cos^2 2\theta_m + \cos^2 2\theta_c}{1 + \cos^2 2\theta_m} + (1 - P) \frac{\cos 2\theta_m + \cos^2 2\theta_c}{1 + \cos 2\theta_m}) \qquad\qquad (56)$$

Where P= 0, for an ideally imperfect crystal monochromator

= 1, for an ideally perfect monochromator

θ_m is the Bragg-angle for the 002 reflection of graphite and θ_c is the Bragg angle for the reflection being measured[37].P is arbitrarily chosen as 0.5 in all cases

1.7.1 ABSORPTION AND EXTINCTION EFFECTS

The absorption of X-rays in passing through a crystal is one of the major sources of errors in highly refined structures. This effect can be minimized by selecting a suitable radiation and a crystal of suitable size. Various methods have been suggested for correcting the effects of absorption [38-40]

There are two types of extinctions, primary and secondary. Primary extinction results from the destructive interference between the primary and secondary beams. Primary extinction is pronounced in perfect crystals and can be minimized by dipping the crystal in liquid air. In any case, most crystals are imperfect to some extent, and one can imagine an ideally imperfect crystal in which the perfect regions are so small that primary 'extinction' is inappreciable.

Secondary extinction leads to the reduction of intensity of the primary X-ray beam, even in an ideally imperfect crystal. This results from the diversion of the energy from the primary beam by reflection from the planes preceding it and any absorption in the path of it. It is very difficult to eliminate this effect by any treatment of the crystal. Sometimes the extinction parameter may be incorporated as an additional parameter in the least squares refinement of the crystal structure.

1.7.2 SCALING OF DATA

Once of the various corrections have been applied to the observed intensities of reflections, it is necessary to convert them to the 'absolute scale' and a scale factor is required for the conversion.

According to Wilson[41] the expectation value of the intensity for the hkl reflection is given by,

$$\langle I(hkl) \rangle = \sum G_j \tag{57}$$

Where G_j is the scattering factor of the jth atom taking into account the attenuation due to thermal vibration. If a common isotropic temperature factor. B is attribute to all atoms, then

$$\langle I(hkl) \rangle = \exp(-\frac{2B\sin^2\theta}{\lambda^2}) \sum f_j^2 \tag{58}$$

If K is the scale factor which relates the observed intensities to the absolute intensities, then

$$\langle I(hkl)_{obs} \rangle = K \exp(-\frac{2B\sin^2\theta}{\lambda^2}) \sum f_j^2 \tag{59}$$

Therefore, $\quad \ln\left(\frac{\langle I(hkl)_{obs} \rangle}{\sum f_j^2}\right) = -\frac{2B\sin^2\theta}{\lambda^2} + \ln K \tag{60}$

So a plot of $\ln\left(\dfrac{\langle I(hkl_{obs})\rangle}{\sum f_j^2}\right) vs. \dfrac{\sin^2\theta}{\lambda^2}$

Would give a straight line from which both K and B can be found out. This plot is known as Wilson plot.

The corrected intensities are converted to the absolute scale by dividing them with the scale factor 'K' obtained from the Wilson plot.

1.8 CALCULATION OF INTERATOMIC DISTANCES AND ANGLES

A molecule can be represented either by a set of external or internal parameters. The parameters of a molecule are the coordinates of the various atoms as determined in the structure analysis and are usually given w.r.t. the crystallographic axis, in terms of fractional coordinates. The internal parameters of a molecule are parameters that characterize the molecular conformation and hence are known as conformational parameters. There are three conformational parameters in a structure, which are bond length, bond angles and torsion angles etc.

1.8.1 BOND LENGTHS

The distance between two covalently bonded atoms is known as bond length and is represented by the symbol L. The expression for the bond length between two bonded atoms A&B is given by

$$L(AB) = ((X_B - X_A)^2 + (Y_B - Y_A)^2 + (Z_B - Z_A)^2)^{\frac{1}{2}} \tag{61}$$

Where $X_A, Y_A, Z_A, \& X_B, Y_B, Z_B$ are the coordinates of the atoms A&B. This conformational parameter gives an idea about the nature and strength of any covalent bond.

In general, any two atoms in a structure are neither completely correlated, so the error in positional parameters and unit cell parameters also contributes to the error in bond length and hence give rise to the standard deviation in bond length which is expressed by an equation,

$$\sigma_L = (\sum_{i=1}^{n}\sum_{j=1}^{n}(\frac{\partial L}{\partial P_i})(\frac{\partial L}{\partial P_j})V_{ij}) + (\sum_{i=1}^{6}\sum_{j=1}^{6}(\frac{\partial L}{\partial a_i})(\frac{\partial L}{\partial a_j})u_{ij}) \qquad (62)$$

Where L is the bond length, P_i, P_j are positional parameters, a_i, a_j are unit cell parameters, V_{ij} is related to the element b_{ij} of the inverse matrix element of the refinement by the equation,

$$V_{ij} = (\sum_{r=1}^{m}\frac{w_r \Delta F_r^2}{m-n})b_{ij} \qquad (63)$$

Similarly, U_{ij} is related to the number of parameters of the matrix that define the lattice

$$u_{ij} = \sum_{r=1}^{m'}\frac{w_r \Delta\theta_{2r}}{m'-n'}b'_{ij} \qquad (64)$$

Where w_r and w_r are weights of the rth F_0 and θ_0, ΔF_r is, $|F_0|-|F_C|$, $\Delta\theta_r$ is $\theta_0 - \theta_c$, m & m' are the number of measured F_0's and θ_0's.

1.8.2. BOND ANGLES

The angles between the two bonds meeting at a common atom are called as bond angles. This is represented by the symbol θ. The angle θ subtended by bonds AB & AC from the law of direction cosines, be represented as

$$\theta \cos^{-1}(\frac{(AB)^2 + (AC)^2(BC)^2}{2(AB)(AC)}) \qquad (65)$$
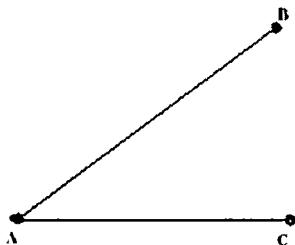
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Figure 1.1: Bond angle

If the axes of the unit cell are orthogonal, the angles may be calculated from the direction

cosines of the line segments AB & AC

$$\theta = \cos^{-1}(l_1 l_2 + m_1 m_2 + n_1 n_2) \qquad (66)$$

Where l_1, m_1, n_1, & l_2, m_2, n_2 are the direction cosines of AB & AC respectively.

The standard deviation in a bond angle is given by the expression,

$$\sigma(\theta) = \left(\sigma B^2 / (AB)^2 + \sigma A^2 (BC)^2 / (AB)^2 (AC)^2 + \sigma c^2 / (AC)^2\right)^{\frac{1}{2}} \qquad (67)$$

Where A, B, C are the standard deviation in the positions of the atom A, B, C.

1.8.3 TORSION ANGLES

The torsion angle about the bond B-C in a series of bonded atoms A-B-C-D is defined as
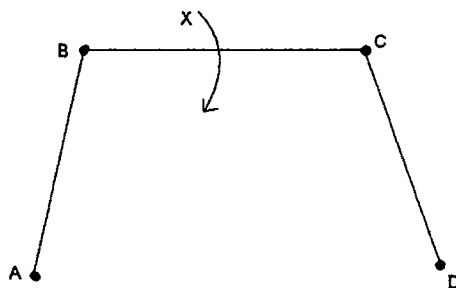
the angle of rotation needed

Figure.1.2: Torsion angle

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to make projection of the B-A bond coincide with projection of C-D bond. The range of X is from -180° to +180°. For a given molecule, different conformation are obtained through rotations about single bond and the parameters i.e. different from one confirmation to another is the torsion angle. Thus the torsion angles is the most important and informative parameters in the field of molecular conformation.

1.9(a) COMPUTER PROGRAM USED

Computer program based on the principle of direct methods are used for the solution of the crystal structure. For the generation of phase, different workers suggest number of ways for the same. But the software developed for the generation of phase in SHELX computer programmed has advantages compared to other methods.

1.9(a).1 SHELX-76

SHELX-76 is a very versatile software package for the automatic solution of crystal structure [42]. It is written in an extremely simple subset of ASA FORTAN which does not trouble any Fortran compiler, provide that integers are at least 24 bits long. This program runs comfortably in 24K fast core on various computers. Overlay is not essential if virtual memory is available.

This package consists of fifteen subroutines namely, INIT, XDRED, FREAD, SMERG, ATFIX, XREF, SELS, ABOND, XCEN, XTPR, CONV, PHEX, QUAT, XMAP, XPLAN, XPRR all these subordinates are linked together in such a way that the structure can be had in a single computer job.

The following main operations are required to be performed for carrying out the structure solution.

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1.9(b) SHLEX 97

SHLEX-97 is the most upgraded version of the computer program package for the determination of crystal structure. The program is due to Prof.G.M.Sheldrick[43]of the University of Gottingen, Germiny.This program package is released in the year 1997.There are six executable programs. They are SHELXS, SHELXL, CIFTAB, SHELXA, SHELXPRO and SHELXWAT.

The refinement program SHELXL includes many new features to make it easier to use for macromolecules, even at moderate resolution. It has been used in the present work for the refinement of all the structures. This program carries out full matrix least squares refinement of the positional parameters temperature factors.

It also calculates the torsion angles least squares planes dihedral angles hydrogen bond geometry etc.

1) NORMALIZATION

Normalization of structure factors are calculated by K-curve.

2) INVARIANTS AND SEMIINVARIANTS

Triplet relations generated are followed by negative quartet estimation Quartets are employed as figures of merit (FOM) only. Sigma-1 type formulae are used to estimate the one-phase semi-invariants.

3) STARTING SET

The most tightly linked 200 reflections are selected and a starting set of phase is derived from this by means of pseudo tangent refinement. This is a phase less tangent formulae expansion system somewhat comparable to divergence mapping As an alternative, conventional convergence mapping is used.

4) PHASE EXTENSION AND REFINEMENT

Phase permutation is employed by using "Magic Integers" which feed a Hull-Irwin[44]-weighted tangent refinement procedure figures of merit are the out put. Generally the COM-FOM, if the start of structural calculation is correct, will give the maximum frequency of occurrence.

SHELX-76 program is provided with five test jobs whose CPU time ranges from (13-90) seconds.

1.10 (a).2 SHELXS-86

The direct method strategies in SHELX –86 [45,46] are based on random start, multi-permutation, single solution procedure. For computational efficiency, a reflection subset (NS) is used for estimation of α's and initial refinements. Out of the possible phase permutation the best 10 %(by default) subset phase permutations are selected with the use of FILTER (F) derived on the basis of early FOM s as

$$F = R_\alpha + \max(0,(0.25 + NQUEST)^2) \qquad (68)$$

Where the negative quarters are used to calculate NQUEST-FOM. These phase permutation are refined for NTAN tangent refinement cycles with subset reflections. One phase structure estimates are evaluated which are used in the FOM calculations and can also be incorporated in starting set with the command PHAS. The phase refinements of NP phase permutations are performed by a modified tangent formula.

$$\text{new } \phi_H = \text{Phase of} \left(\sum \alpha - \eta \right) \qquad (69)$$

In which the triplets and quartets are respectively

$$\alpha = N^{\frac{1}{2}} \sum 2 |E_H| E_{H'} E_{H-H'} \qquad (70)$$

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and $\eta = N^1 \sum g \left| E_{H_1} \right| E_{H_2} E_{H_3} E_{H_4}$ (71)

Where 'g' is a positive constant and 'N' is the number of atoms per unit cell.

The figures of Merits used are

I) R^{47} which shows the consistency of active triplets is defined as

$$R_\alpha = \frac{\sum_H w(\alpha - (\langle \alpha_{est} \rangle))^2}{\sum_H w \langle \alpha_{est} \rangle^2}$$ (72)

Where the weight $w = \dfrac{1}{(\alpha_{est} + 5)}$

II)   The FOMNQUAL[48] (instead of NQUEST[49]) defined as

$$NQUAL = \frac{\sum_H Re(\alpha - \eta)}{\sum_H |\alpha| \cdot |\eta|}$$ (73)

Is used to check the internal consistency of negative quartets as well as triplets.

From the above two figure of Merits, R and NQUAL, the CFOM is calculated as,

$$CFOM = \left| \begin{matrix} R_\alpha \\ R_\alpha + (NQUAL)^2 \end{matrix} \right. \qquad \text{if Q>NQUAL}$$ (74)

otherwise

Where Q is a structure dependent constant.

For a correct phase set, NQUAL approaches to –1, M (ABS) close to 1.0 and CFOM is below 0.08. Also for the best solution, both FILTER and RESID have their minimum values. The structure corresponding to the phase set with the best of FOMs is improved by an E-Fourier partial structure extension procedure [50] applied on point atoms and peaks. In this cyclic process,

$$RE = 1 - \frac{(\sum E_0 {}^1 E_0)^2}{\sum E_0^{2^1} \sum E_0^2}$$ (75)

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is minimized . Here the phase of E_0's calculated from all the atoms and peaks; where the atoms contribute to the phase E_0's only.

1.10 (b) 2 STATISTICAL TEST

Some statistical tests are carried out in order to examine the accuracy of the result.

(1) GOODNESS OF FIT (S)

Goodness of fit (S) is calculated by the SHELX-97 programmed with the help of the formulae,

$$S = \left| \sum w \left(|F_0| - |F_0|^2 \, /(m-n) \right) \right|^{\frac{1}{2}} \tag{76}$$

Where , m = number of observed reflection

n = number of parameters

(2) SHELXS 86 programme calculates the values of R_{int} and R_σ by averaging

equivalent reflection using

$$R_{int} = \sum \left| F^2 - (F^2) \right| mean1 / \sum F^2 \tag{77}$$

$$R_\sigma = \sum \sigma(F^2) / \sum F^2 \tag{78}$$

2) ORTEP

This program by C.K.Johnson (1976) has been used for drawing the molecular structures showing the thermal ellipsoids, the stereoscopic view of the molecule and molecular packing.

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