CHAPTER II

EXPERIMENTAL WORK ON PYRIDINE PICRATE

2.1 Introduction:

Pyridine picrate (Fig. 2.1) belongs to the well-known group of crystalline complexes containing stoichiometric proportions of polynitro-aromatic substances and aromatic hydrocarbons, bases and their derivatives.

![Pyridine Picrate Structure](image)

FIG. 2.1.

Constituent molecules of these addition compounds are held together in some cases by affinity arising due to charge-transfer and are known as charge-transfer complexes, viz., anthracene picrate, naphthalene picrate etc. In others, the binding takes place through the mechanism of hydrogen bonds. These complexes are mostly chemically unstable. Owing to their chemical instability, the problem of structure determination by chemical methods is a difficult one as it
is impossible to make any study of the chemical properties characteristic of these complexes themselves. The only alternative way for structural investigation is therefore the application of physical methods in the solid state of these complexes. Williams and Wallwork (1966) have determined the structure of a molecular complex of 1,3,5-trinitrobenzene and 2,4,6-tri(dimethylamine)-1,3,5-triazine from X-ray diffraction data. However, structure analysis of any picrate complex does not appear to be reported. Interest in the problem is drawn also from other considerations. Pyridine picrate has a unit cell (Section 2.2) suitable for structural investigation in projection. It is composed of atoms having nearly the same scattering power. Moreover it has structural groups in the form of ring configurations. All these render the structural investigation of pyridine picrate an attractive problem for application of the techniques of optical transform methods (Chapter I) in which the department is particularly interested at this moment. A complete structure analysis of the compound from X-ray diffraction data is therefore undertaken by application of a combined strategy of optical transform approach and usual Fourier methods.
2.2 Physical and X-ray data:

The crystals of pyridine picrate crystallises from alcohol, in the form of soft yellowish laths elongated along the b-axis. The melting point is 167°C. X-ray rotation, oscillation and Weissenberg photographs, calibrated with silicon (a = 5.4305 Å) powder lines show that the crystals are monoclinic with the lengths of the laths parallel to the symmetry axis b and that the dimensions of the unit cell are,

\[
\begin{align*}
  a &= 12.15 \pm 0.02 \text{ Å} \\
  b &= 3.78 \pm 0.01 \text{ Å} \\
  c &= 26.60 \pm 0.02 \text{ Å} \\
  \beta &= 93.0°
\end{align*}
\]

The density of the crystals measured by method of flotation in a mixture of carbon-tetrachloride and bromoform is found to be 1.62 g. cm⁻³. The calculated density with four molecules in the unit cell is 1.67 g. cm⁻³.

**Space group:**

Zero-layer-line Weissenberg photographs taken along a, b and c axis reveal the following systematic absences.

- \( h0i \) absent for \( l \) odd
- \( o0k \) absent for \( k \) odd.

This uniquely establishes that the space group is \( P2_1/c \).
The symmetry of special projections are,
\[(100) \text{pgg} : b' = b, c' = c.\]
\[(010) \text{p2} : c' = c/2, a' = a.\]
\[(001) \text{pgm} : a' = a, b' = b.\]

**Intensity measurement:**

For intensity measurement, zero-layer-line a and b-axis Weissenberg photographs are taken. Maximum exposure times of 30 hrs. (\(\sim 600 \text{ ma. hrs}\)) and 45 hrs. (\(\sim 900 \text{ ma. hrs}\)) are used for hkl and okl reflexions respectively. The multiple-film technique (Robertson, 1943) is used to record the two zones of reflexions and the intensities are measured by visual comparison with calibrated diffraction spots of known relative exposures obtained from the same crystal. Such diffraction spots of relatively graded exposure times are obtained by photographing selected reflexions from zero-layer-line in successive positions of the film by moving the camera laterally and adjusting exposure times by counting number of oscillations of the crystals under investigation within convenient range (Buerger, 1960). These graded series of spots obtained from the specimen crystal under investigation has the advantage that the calibrated X-ray diffraction spots and spots on the photographs for intensity measurement have identical shape and size. This ensures accuracy in the intensity estimation.
The cross-sections of the crystal specimens chosen for recording both sets of weissenberg photographs are approximately rectangular in the plane perpendicular to the axis of oscillation. The cross-sectional dimensions are 0.06 mm x 0.08 mm. (for b-axis specimen) and 0.12 mm x 0.08 mm. (for a-axis specimen). In view of the low linear absorption co-efficient \( \mu = 11.5 \text{ cm}^{-1} \) for CuKα = 1.5405 Å, no absorption correction is considered necessary. No significant variation of spot shape in both the zones of reflexions are observed to call for any correction in this regard. Intensities are then corrected for Lorentz and polarisation factors and two sets of observed structure factors on relative scale are obtained.

2.3 The determination of the absolute scale of the intensities:

A statistical method as suggested by Wilson (1942) is then applied to place the \( F_{\text{obs}} \) values upon an absolute basis and determine the temperature factor parameter.

Wilson has shown that the mean value of \(|F|^2\) is equal to the value of \( \Sigma f_j^2 \) at a particular value of \( \theta \), that is,

\[
|F|^2 = \Sigma f_j^2 \quad \ldots \quad (2.1)
\]

Again, \(|F_{\text{obs}}|^2 = K|F|^2\), where \(|F_{\text{obs}}|^2\)'s are the structure amplitudes on an arbitrary scale and \(|F|^2\)'s are the
corresponding values on absolute scale.

\[ |F_{\text{obs}}|^2 = K \Sigma f_j^2 \]  \hspace{1cm} (2.2)

If Debye-Waller temperature correction is taken into consideration, then equation (2.2) may be written as

\[ \frac{|F_{\text{obs}}|}{\Sigma f_j^2} = Ke^{(2\pi \sin^2 \theta)/\lambda^2} \]  \hspace{1cm} (2.3)

Taking logarithms of both sides of equation (2.3),

\[ \log_e \left( \frac{|F_{\text{obs}}|^2}{\Sigma f_j^2} \right) = \log_e K - \frac{2\pi \sin^2 \theta}{\lambda^2} \]

or

\[ 2.303 \log_{10} \left( \frac{|F_{\text{obs}}|^2}{\Sigma f_j^2} \right) = 2.303 \log_{10} K - \frac{2\pi \sin^2 \theta}{\lambda^2} \]

or

\[ \log_{10} \left( \frac{|F_{\text{obs}}|^2}{\Sigma f_j^2} \right) = \log_{10} K - \frac{2\pi \sin^2 \theta}{2 \cdot 2.303 \lambda^2} \]  \hspace{1cm} (2.4)

Equation (2.4) takes the form \( y = mx + c \). From the slope of the \( \log_{10} \left( \frac{|F_{\text{obs}}|^2}{\Sigma f_j^2} \right) \) vs. \( \sin^2 \theta \) graph, \( B \) may be calculated.
Again, as $\theta \to 0$,

$$
\log_{10} \left( \frac{|F_{\text{obs}}|^2}{\sum f_j^2} \right) \to \log_{10} K.
$$

Thus the value of $K$ may be readily derived from the same graph.

The reciprocal lattice is divided into five $\sin^2 \theta$ zones and $|F_{\text{obs}}|^2$ values corresponding to each of these zones are determined as shown in the Table 2.1.

| $\sin^2 \theta$ range | $\sin^2 \theta$ middle | $\sum |F_{\text{obs}}|^2$ | Total no. of reflexions (N) | $\frac{\sum |F_{\text{obs}}|^2}{N}$ |
|------------------------|------------------------|------------------------|----------------------------|----------------------------------|
| 0.0-0.100              | 0.050                  | 637.01                 | 89                         | 71.60                            |
| 0.100-0.200            | 0.150                  | 5483.56                | 85                         | 64.50                            |
| 0.200-0.350            | 0.275                  | 1066.10                | 126                        | 8.46                             |
| 0.350-0.550            | 0.450                  | 1785.69                | 138                        | 12.90                            |
| 0.550-0.900            | 0.725                  | 381.37                 | 139                        | 2.74                             |

Assuming $f_c = f_n = f_0$, a Table of $\sum f_j^2$ is prepared as shown below.
Table 2.2.

<table>
<thead>
<tr>
<th>sin^2θ range</th>
<th>sin^2θ middle</th>
<th>f_c</th>
<th>f_c^2</th>
<th>(\sum f_j^2 = 88f_c^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.100</td>
<td>0.050</td>
<td>4.35</td>
<td>18.92</td>
<td>1664.96</td>
</tr>
<tr>
<td>0.100-0.200</td>
<td>0.150</td>
<td>2.95</td>
<td>8.70</td>
<td>765.60</td>
</tr>
<tr>
<td>0.200-0.350</td>
<td>0.275</td>
<td>2.20</td>
<td>4.84</td>
<td>425.92</td>
</tr>
<tr>
<td>0.350-0.550</td>
<td>0.450</td>
<td>1.85</td>
<td>3.42</td>
<td>300.96</td>
</tr>
<tr>
<td>0.550-0.900</td>
<td>0.725</td>
<td>1.60</td>
<td>2.56</td>
<td>225.28</td>
</tr>
</tbody>
</table>

Table 2.3 gives the values of \(\log_{10}\left(\frac{F_{\text{obs}}^2}{\sum f_j^2}\right)\) corresponding to each sin^2θ (middle) value.

Table 2.3.

<table>
<thead>
<tr>
<th>sin^2θ range</th>
<th>sin^2θ middle</th>
<th>(\frac{F_{\text{obs}}^2}{\sum f_j^2})</th>
<th>(\sum f_j^2)</th>
<th>(\log_{10}\left(\frac{F_{\text{obs}}^2}{\sum f_j^2}\right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.100</td>
<td>0.050</td>
<td>71.60</td>
<td>1664.96</td>
<td>0.0431 -1.3656</td>
</tr>
<tr>
<td>0.100-0.200</td>
<td>0.150</td>
<td>64.50</td>
<td>765.60</td>
<td>0.0842 -1.0747</td>
</tr>
<tr>
<td>0.200-0.350</td>
<td>0.275</td>
<td>8.46</td>
<td>425.92</td>
<td>0.0198 -1.7034</td>
</tr>
<tr>
<td>0.350-0.550</td>
<td>0.450</td>
<td>12.90</td>
<td>300.96</td>
<td>0.0428 -1.3686</td>
</tr>
<tr>
<td>0.550-0.900</td>
<td>0.725</td>
<td>2.74</td>
<td>225.28</td>
<td>0.0121 -1.9173</td>
</tr>
</tbody>
</table>

Values of K and B are then calculated from readings of the graph as shown in Fig. 2.2 and are found to be 0.084 and 3.0 respectively.