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Chapter 5

Structural investigations of thiourea mixed ADP crystal

5.1 Introduction

It is well known that thiourea and ADP undergoes ferroelectric and antiferroelectric phase transitions. Thiourea has five polymorphic phases. Ferroelectric phases exist between 179K and 176K and below 168K while nonpolar forms are stable from 176K to 168K and 202K to 179K [1]. ADP undergoes para antiferroelectric phase transition at 148 K [2-4].

When ADP is cooled down to 148 K, a transition occurs which produces a large enough change in volume to shatter the crystal. It was generally believed that [5] this transition was due to an interaction of the NH$_4^+$ ions due to their deviation from a spherical symmetrical configuration. The para-electric phase of the hydrogen bonded ADP is isomorphous with that of the well-known ferroelectric prototype potassium dihydrogen phosphate (KDP). The para-electric structure of ADP has been established by X-ray and neutron diffraction measurements [6, 7]. The space group is $I4_2d$ with four molecules in the body centered tetragonal unit cell. The space group of antiferroelectric phase [8] is P2$_12_12_1$. We have made an attempt to mix thiourea and ADP in 1:3 ratio. But ADP takes maximum of 10mol% of thiourea. The inclusion of thiourea made drastic changes in the non-linear optical conversion efficiency of ADP. In this chapter, study made on the low temperature X-ray diffraction characteristics of thiourea mixed ADP single crystal is presented.
5.2 Single crystal x-ray diffraction technique

In single crystal or rotating crystal method a single crystal is mounted on a spindle with one of the crystal axis or some important crystallographic directions normal to a monochromatic X-ray beam. The crystal is rotated about the chosen direction and the intensity of the diffracted beam is measured directly by an area detector, which is the electronic equipment of X-ray film. The rotation of the crystal brings different atomic planes into positions for reflection. The reflected beams lie on the surface of imaginary cones coaxial with the rotation axis. The detector is a position-sensitive one and it is coupled to an electronic device for recording the data in computer readable form. The data so recorded include the intensity of a Bragg reflection and its precise direction. The image of the diffraction pattern appears as a series of spots of different intensities distributed along layer lines. The various crystal planes parallel to the rotation axis will produce Bragg reflections along the equatorial plane. Planes tilted with respect to the rotation axis will give reflection spots along layer lines above and below the equatorial plane. However, there will be no reflected beams from a plane, which always contains the incident beam during the whole rotation. Since the crystal is rotated about only one axis, the Bragg angle does not take all possible values between $0^\circ$ and $90^\circ$ for every set of planes. The chief use of the single crystal method is in the determination of unknown crystal structures and for this purpose it is the most powerful tool the X-ray crystallographer has at his disposal.
5.2.1 XRD Instrumentation

Single crystal X-ray diffractometer measures three-dimensional intensities of X-ray beams diffracted from different planes of a single crystal. The data is used for the elucidation of structural parameters of the crystalline solid. Fourier transform techniques are used to determine the exact positions of the atoms in the unit cell. Automatic diffractometers are used nowadays to record diffraction data. The automated instrument can move the crystal and the detector through angular ranges under computer control to the required setting angles that orient the crystal in such a way that Bragg diffraction can occur and be measured by the detector. Results are achieved rapidly and with much better precision. The modern apparatus available for measuring the intensities of Bragg reflections consist of

1. highly monochromatic and powerful source of X-rays.
2. the crystal which can diffract the X-rays, and
3. a system to detect the spatial direction and intensity of each Bragg reflection.

The sophisticated instrumentation now available for the measurement of Bragg reflections, when used with care and wisdom, can yield very precise intensity data. Electronic detectors can record the intensities of a large number of Bragg reflections simultaneously, in a manner analogous to that of X-ray film.

The most recent technological advance in X-ray detection is the imaging plate [9-11], which is a storage phosphor. A latest image is produced on the plane when X-rays strike it, and this image is then exposed to laser light. Light of a different wavelength is emitted and is converted by a photomultiplier into an electrical signal. The imaging plate can store information for a considerable time period and can then be used again for another diffraction experiment.
The results of an X-ray diffraction experiment are only as good as the quality of the crystal and the intensity data that results from it. A polarizing microscope is a valuable tool that may aid in the choice of a good single crystal for diffraction studies. The crystal is examined under crossed polarizers to check for imperfections such as cracks or voids, and to make sure that there is complete extinction of light at certain angles of rotation of the stage. If the crystal is not single, it will cause problems when diffraction data are measured, the diffraction pattern will be a superposition of two or more patterns in differing orientations, and difficult to interpret. The crystal for study is glued into a thin glass fibre. The fibre, via a brass pin, is inserted into the goniometer head, which holds the crystal in place on a diffractometer and allows it to be oriented in the X-ray beam by means of translational and angular motions. The arcs and translations of the goniometer head are adjusted so that the crystal will be centered in the X-ray beam at all angles of study. The crystal should be small enough in order to be bathed totally in the X-ray beam and yet large enough to offer good diffraction [12]. A stationary crystal gives only few Bragg reflections. To overcome the paucity of Bragg reflections, the crystal is rotated or oscillated about an axis to give a range of crystal orientations suitable for diffraction.

To analyse the single crystal diffraction data collected by the imaging plate, computer programs are available. The four most important developments in the data analysis of diffraction measurements are

(i) auto indexing
(ii) profile fitting
(iii) transformation of data to a reciprocal-space coordinate system
and
(iv) the demonstration that a single oscillation image contains all the information necessary to derive the diffraction intensities from that image.

The analysis and reduction of single crystal diffraction data consists of seven major steps, which are as under:

(a) Visualization and preliminary analysis of the original, unprocessed diffraction pattern
(b) Indexing for the diffraction pattern
(c) Refinement of the crystal and detector parameters.
(d) Integration of the diffraction maxima
(e) Finding the relative scale factors between measurements
(f) Precise refinement of crystal parameters using entire data set
(g) Merging and statistical analysis of the measurements related by space group symmetry

A computer package with suitable programs perform these functions. The package can estimate Bragg intensities from single crystal diffraction data that are recorded on a position-sensitive X-ray detector such as the imaging plate scanner. The programs allow for data collection by oscillation and for random changes in the position and sensitivity of the detector between consecutive exposures. Also the package features profile fitting, weighted refinement, eigenvalue filtering, and a universal definition of detector geometry.

In the single crystal XRD studies the measurements were made on a SMART6000 (Bruker) with graphite monochromated MoKα radiations as the scanning X-ray beam. Image processing and data reduction were done by SHELX. The structure was solved and refined using SHELX.
SHELX is a program, which takes raw X-ray diffraction data from imaging plate and reduces it to a file containing the h, k, l indexes and intensity of the spots on the image, along with an estimate of the error. Depending on the number of spots on the image, a typical 7 to 18MB raw imaging plate data file will yield a reduced file of approximately 0.1 to 2 MB.

5.2.2 Single crystal XRD of TADP crystal

Thiourea mixed ADP crystals were grown by using slow evaporation solution technique. A small fragment of approximate dimensions 0.15 x 0.14 x 0.10 mm onto the tip of a 0.1 mm diameter glass fiber which was subsequently mounted on a SMART6000 (Bruker) and cooled to 116(2) K.

A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 30 frames. The data collection was carried out using graphite monochromatic MoKα radiation with a frame time of 2 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Six sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at -43° in 2θ. Final cell constants were calculated from the xyz centroids of 959 strong reflections from the actual data collection after integration (SAINT) [13]. The lattice constants are found to be a = b = 7.4996(4) Å, c = 7.4749(8) Å.

Pure ADP undergoes structural phase transition at T₁ = 148K [14]. The high temperature structure (space group: \textit{I}42d, Z=4) [8] is isothermal with the para-electric structure of KH₂PO₄ (KDP). In contrast to the ferroelectric activity in KDP, ADP has the antipolar structure in the low-temperature phase (space group P2₁2₁2₁, Z=4) [8] indicating the different fluctuating character between them. To understand the phase transition mechanism in ADP,
Nagamiya [15] considered that the lateral configurations of H₂PO₄ are lower than the up-down ferroelectric configurations. Since then many studies of ADP have been carried out mainly to reveal what kinds of Slater configurations exist in connection with the transition mechanism. [16-18] In thiourea mixed ADP phase transition does not occur at low temperature phase. Some of the hydrogen atoms of pure ADP are displaced by the hydrogen atoms of thiourea. Hence the bond length and bond distance of thiourea mixed ADP entirely different from pure ADP. The substitution of thiourea maintains the para-electric phase of ADP. This is basically from an assumption of hydrogen movements in the O-H...O bond system according to Nagamiya scheme [15]. Hence it is contributing to the increase in second harmonic generation. It follows that the disorder-like motion of the NH₄⁺ ion rather than the PO₄ tetrahedron dominates the mechanism of the phase transition.

**Structure solution and refinement:** Intensity statistics and systematic absences suggested the tetragonal space group I₄₂d and subsequent solution and refinement confirmed this choice. The structure was solved using SHELXS-97 and refined with SHELXL-97 [19]. A direct-methods solution was calculated which provided positions of non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed to locate the hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The unique hydrogen on the nitrogen and the half-weight hydrogen on the oxygen atom were refined as isotropic contributors in the final cycles of refinement. The final full matrix least squares refinement converged to R₁ = 0.0141 and wR₂ = 0.0391 (F², all data). The remaining electron density is located on bonds.
Table 5.1: Program for data file labeled TADP

<table>
<thead>
<tr>
<th>At. No.</th>
<th>At. Wt.</th>
<th>Abs. %</th>
<th>No.</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>30.974</td>
<td>7.970</td>
<td>26.93</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>15.999</td>
<td>1.220</td>
<td>55.64</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>14.007</td>
<td>0.845</td>
<td>12.18</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1.008</td>
<td>0.373</td>
<td>5.26</td>
<td>6</td>
</tr>
</tbody>
</table>

The density is 1.817 g/cc.
The volume is 420.42 Å³
Z = 4 and the molecular wt. is 115.03
F (000) = 240
The linear absorption coefficient = 5.356 reciprocal centimeters, and 1/4Mu = 0.4667mm.

Table 5.2: Crystal Data for thiourea mixed ADP

Empirical Formula: H6N04P
Color of Crystal: colorless
Crystal Dimensions were: 0.15 x 0.14 x 0.10 mm.
Space Group: I42d
Cell Dimensions (at 116(2) K; 959 reflections)
a = 7.4996(4) Å
b = 7.4996(4) Å
c = 7.4749(8) Å
Alpha = 90
Beta = 90
Gamma = 90
Z (Molecules/cell): 4
Volume: 420.42(6) Å³
Calculated Density: 1.817 gm/cm³
Wavelength: 0.71073 Å
Molecular Weight: 115.03
F(000): 240
Linear Absorption Coefficient: 0.536

Data were collected on a Bruker SMART 6000 sealed-tube system comprising a three-circle platform goniostat, an HOG crystal monochromator, a four kilo pixel by four kilopixel single-chip CCD-based detector, a K761 high voltage generator, and a PC interface running Bruker's SMART software. Detector to sample distance = 5.0 cm.
Take off angle = 6.0 deg.
Data collected by the omega scan technique according to the following parameters:
Frame width = 0.3 deg.
Time per frame = 2.0 sec.

Data processing statistics for 29.9 degrees maximum theta:
Total number of intensities integrated = 5486
Number of unique intensities = 315
Number with F > 4sigma(F) = 315
R for averaging = 0.02

Refinement results:
Final residuals are:
R (F) (observed data) = 0.0141
Rw (F²) (refinement data) = 0.0391

Final Goodness of Fit = 1.311
Maximum delta/sigma for the last cycle = 0.00
Table 5.3: Fractional Coordinates & Isotropic Thermal Parameters of TADP

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)</td>
<td>10000</td>
<td>0</td>
<td>0</td>
<td>7(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>11473(1)</td>
<td>-836(1)</td>
<td>1163(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>N(2)</td>
<td>15000</td>
<td>0</td>
<td>2500</td>
<td>19(1)</td>
</tr>
<tr>
<td>H(1)</td>
<td>1143(4)</td>
<td>-191(4)</td>
<td>120(5)</td>
<td>21(7)</td>
</tr>
<tr>
<td>H(2)</td>
<td>1407(3)</td>
<td>2(4)</td>
<td>187(2)</td>
<td>48(5)</td>
</tr>
</tbody>
</table>

Notes:
1) Fractional coordinates are $10^4$ for non-hydrogen atoms and $10^3$ for hydrogen atoms. Uiso values are all $10^3$.
2) Isotropic values for those atoms refined anisotropically are calculated as one third of the trace of the orthogonalized $U_{ij}$ tensor.
3) Parameters without standard deviations were not varied.

The interest here is to find the structure property relationship of TADP crystal. ADP is a good non-linear inorganic crystal. Inclusion of thiourea results in three times increase in its SHG conversion efficiency. In TADP crystals the antiferroelectric phase transition is absent.

Table 5.4: Anisotropic Thermal Parameters for TADP

<table>
<thead>
<tr>
<th>Atom</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)</td>
<td>7(1)</td>
<td>7(1)</td>
<td>8(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(1)</td>
<td>13(1)</td>
<td>11(1)</td>
<td>18(1)</td>
<td>5(1)</td>
<td>-8(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>N(2)</td>
<td>23(1)</td>
<td>23(1)</td>
<td>11(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Form of the anisotropic thermal parameter:
$$\exp\{-2i^2[\ h^2 (a^*)^2 U_{11} + \ldots + 2hk a^* b^* U_{12} ]\},$$
All values are $10^3$
Table 5.5: Bond Distances for TADP

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)</td>
<td>O(1)#1</td>
<td>1.5389(6)</td>
</tr>
<tr>
<td>P(1)</td>
<td>O(1)</td>
<td>1.5389(6)</td>
</tr>
<tr>
<td>P(1)</td>
<td>O(1)#2</td>
<td>1.5389(6)</td>
</tr>
<tr>
<td>P(1)</td>
<td>O(1)#3</td>
<td>1.5389(6)</td>
</tr>
<tr>
<td>O(1)</td>
<td>H(1)</td>
<td>0.81(3)</td>
</tr>
<tr>
<td>N(2)</td>
<td>H(2)</td>
<td>0.843(17)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

#1 y+1,-x+1,-z  #2 -y+1,x-1,-z,  #3 -x+2,-y,z

Table 5.6: Bond Angles for TADP

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)#1</td>
<td>P(1)</td>
<td>O(1)</td>
<td>108.60(3)</td>
</tr>
<tr>
<td>O(1)#1</td>
<td>P(1)</td>
<td>O(1)#2</td>
<td>111.23(6)</td>
</tr>
<tr>
<td>O(1)</td>
<td>P(1)</td>
<td>O(1)#2</td>
<td>108.60(3)</td>
</tr>
<tr>
<td>O(1)#1</td>
<td>P(1)</td>
<td>O(1)#3</td>
<td>108.60(3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>P(1)</td>
<td>O(1)#3</td>
<td>111.23(6)</td>
</tr>
<tr>
<td>O(1)#2</td>
<td>P(1)</td>
<td>O(1)#3</td>
<td>108.60(3)</td>
</tr>
<tr>
<td>P(1)</td>
<td>O(1)</td>
<td>H(1)</td>
<td>114(2)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

#1 y+1,-x+1,-z  #2 -y+1,x-1,-z,  #3 -x+2,-y,z

These changes occurred because of the effect of thiourea on the structure of ADP. So an attempt was made to study the structure property relation by comparing data of TADP crystals with pure ADP. The Positional parameters
x, y, z (fraction) and thermal parameters $U_i (\times 10^{-2} \text{Å}^2)$ of the average structure of pure ADP at 152K in the high-temperature phase is already reported and it is given in table 5.7 [20]. It is found that there is a remarkable change in the positional parameters x, y, z (fraction) and thermal parameters of Pure at 152K and TADP at 116K (Table 5.3 and 5.4). The difference in oxygen parameters (table 5.8) stands for the absence of antiferroelectric phase and enhancement of SHG conversion efficiency.

Table 5.7: Positional parameters x, y, z (fraction) and thermal parameters $U_i (\times 10^{-2} \text{Å}^2)$ of the average structure of pure ADP at 152K in the high-temperature phase

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.80(1)</td>
<td>0.80(1)</td>
<td>1.35(1)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>N</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>1.84(1)</td>
<td>1.84(1)</td>
<td>1.28(2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O</td>
<td>0.0846(1)</td>
<td>0.1478(1)</td>
<td>0.1153(1)</td>
<td>1.13(1)</td>
<td>1.26(1)</td>
<td>1.82(1)</td>
<td>0.17(1)</td>
<td>-0.31(1)</td>
<td>-0.56(1)</td>
</tr>
</tbody>
</table>

Table 5.8 Comparison of oxygen parameters of Pure ADP and TADP crystals

<table>
<thead>
<tr>
<th></th>
<th>Pure ADP Ref [20]</th>
<th>Present Paper (TADP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>0.085</td>
<td>1.1473(1)</td>
</tr>
<tr>
<td>y</td>
<td>0.146</td>
<td>-0.0836(1)</td>
</tr>
<tr>
<td>z</td>
<td>0.115</td>
<td>1.163(1)</td>
</tr>
</tbody>
</table>
The bond length, bond angle and thermal parameters of pure ADP are reported [21]. Table 5.9 gives a comparison between the bond length and bond angles pure ADP and TADP crystals. One finds a remarkable similarity in the P-O bond (i.e., H$_2$PO$_4$ systems in the two crystals). The only significant difference occurs in the bond angle of P-O-H. This one might expect from differences in c-direction packing (compare cell dimensions a=b= 7.502Å, c= 7.546 Å for Pure ADP and a=b= 7.4996(4), c = 7.4749(8) for TADP). However, it would seem from the difference in ADP between this bond angle and the angle between N-H and O-H that the structure 'wants' to assume an angle more nearly equal to that observed in TADP, but is prevented from doing so by the shape of the ammonium ion. The tetrahedral ammonium ion is found to be slightly distorted, presumably as a result of hydrogen bonding with neighboring PO$_4$ groups. The distortion is not so great, however, as to result in linear N-H...O bonds. The molecular structure, crystal packing and space filling drawings are shown in figure 5.1 to 5.3.

Table 5.9: Comparison of Interatomic distances and bond angles of Pure ADP and TADP

<table>
<thead>
<tr>
<th></th>
<th>Pure ADP Ref [21]</th>
<th>Present paper [TADP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-O</td>
<td>1.53Å</td>
<td>1.5389(6) Å</td>
</tr>
<tr>
<td>N(2)-H(2)</td>
<td>1.00 Å</td>
<td>0.843(17) Å</td>
</tr>
<tr>
<td>O-P-O</td>
<td>108.1°</td>
<td>108.6°</td>
</tr>
<tr>
<td>O-P-O(2)</td>
<td>108.62°</td>
<td>111.23°</td>
</tr>
<tr>
<td>O-H</td>
<td>1.07 Å</td>
<td>0.81(3)</td>
</tr>
<tr>
<td>P-O-H</td>
<td>116.28°</td>
<td>114(2)</td>
</tr>
</tbody>
</table>
Figure 5.1: Molecular structure of thiourea mixed ADP

Figure 5.2: Arrangement of hydrogen atom to maintain para-electric phase of TADP
5.4 Conclusion

It was found that the thiourea mixed ADP maintains its para-electric phase at 116(2) K. In addition to this, thiourea mixed ADP exhibits better non-linear optical properties than pure ADP crystal. The second harmonic generation efficiency of ADP enhances three fold when it is crystallized in the presence of thiourea. Hence it is necessary to investigate the influence of thiourea on the crystal structure of ADP. The structure of thiourea mixed ADP is solved and established by the single crystal X-ray diffraction method. Thiourea mixed ADP crystallizes in a non-centrosymmetric space group. The lattice constants are found to be $a = b = 7.4996(4) \, \text{Å}$, $c = 7.4749(8) \, \text{Å}$. The observed increase in SHG is attributed to the hydrogen movements in the O-H...O bond system.
References

13. SAINT 6.1, Bruker Analytical X-Ray Systems, Madison, WI.

19. SHELXTL-Plus V5.10, Bruker Analytical X-Ray Systems, Madison, WI.
