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Determination of six unit cell parameters of 1-Tosyl-2-Ethyl Pyrrolidine

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Abstract
A highly clean and efficient and eco-friendly method for the synthesis of 1-Tosyl-2-Ethyl-pyrolidine which is an alkaloid is taken for investigation. The synthesis of this compound is done by using THF and LAH. Numbers of experimental methods are used for alignment and centring of said compound. Six cell parameters, three axial lengths a, b, c and three interaxial angles α, β, and ϒ are determined to see that compound taken under investigation belong to which crystal system. To investigate X-ray diffraction technique is used. The purpose of working on the compound is that it has pharmacological as well as botanical importance. Weissenberg camera is used for the purpose.

Keywords: 1-Tosyl-2-Ethyl-Pyrrolidine, LAH (lithium aluminium hydride) THF (tetrahydrofuran), pyrrolinole, template, diffraction, cell parameters, reciprocal lattice, crystal system, axial lengths, interaxial angles

Introduction
The compound under investigation is obtained from Regional Research laboratory Jammu. The compound is given the name M_2 by the scientists of RRL Jammu. The titled compound is an Alkaloid. Alkaloids have a complex structure with atom involved in heterocyclic ring. Today about 2000 alkaloids are known. They are found in about 10-15% of all vascular plants. The most common constituents of an alkaloid are carbon, hydrogen, oxygen and nitrogen. The classification of an alkaloid can be made only on the basis of its chemical, pharmacological and botanical properties.
Broadly, alkaloids have been classified into various groups of which the following groups have been studied in laboratory such as 1) Pyrrolizidines Alkaloid 2) Pthalideisoquinoline Alkaloid 3) Pyrrolidine Alkaloid. Pyrrolidine have been undertaken in the laboratory during my M.Phil under the supervision of late prof.K.N Goswami department of physics university of Jammu.

Isolation of 1-tosyl-2-ethyl pyrimidine
The compound under investigation has been obtained from chemistry department of regional research laboratory jammu (BHUTANI, 1990). The literature survey for pyrrolidine type of compound reveals that synthesis of titled compound exists in the literature (Kostynovsky, 1974). The titled compound is extracted by the reduction of L-pyrrolidine by stirring and cooling, resulting in the formation of L-pyrolinole. L-pyrolinole is then added to P-Toluene sulphochloride giving to the formation 0f N-DITOSYL-Pyrolinole. Further N- Ditosyl-Pyrolinole is added in 200ml THF results 1-Tosyl-2-Ethyl Pyrrolidine ($C_{13}H_{19}SO_2N$). Finally, the compound is purified by column chromatography on SiO_2 with benzene. The reaction mechanism for this compound is shown in fig.1.Few pieces of finally purified material were picked for their X-ray studies. The chemical structure of M_2 crystal is shown in fig 2.

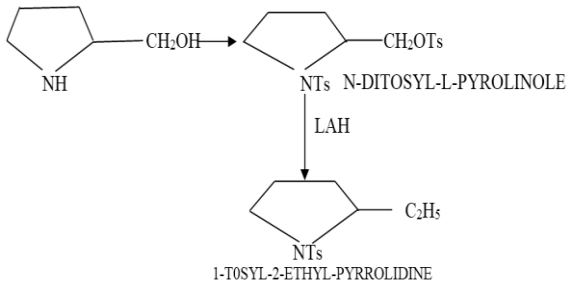

Fig 1: Reaction Mechanism of M_2 Crystal

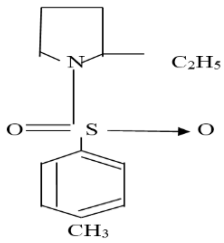

Fig 2: Chemical Structure of M_2 Crystal

Selection, Mounting, Crystalization and Centering Of Crystal
The title compound crystallizes into small sized rectangular shaped crystals. These crystals are examined under polarizing microscope so as to ensure that they do not possess any defect like twinning, cracks etc. After careful examination of all the crystal pieces, a crystal with no defects and of suitable size is chosen. The ultimate evidence of good crystal is normally furnished by a diffraction pattern.
The selected crystal is mounted on goniometer head. One of the axes of crystal is chosen as axis of rotation. The alignment of the crystal is roughly made by microscope fitted with the base of goniometer. One of the prominent faces is made

parallel with the horizontal crosswire. This process is repeated many times until the crystal remains fixed with respect to crosswire when it is rotated through 360^0. Thus the crystal is approximately aligned. The exact centring of the crystal is finally achieved by taking Oscillation Photograph.

Oscillation Photograph

In the present study, all X-rays photograph have been taken using copper radiation filtered through nickel foil. The generator is operated at 10mA and 30 KV. The crystal is exposed for 50 minutes to X-ray radiation. The oscillation range of crystal is set at 17^0. From the photograph, it is found that crystal is slightly misaligned. Since the distance between the layers is very small, so the alignment of crystal by double oscillation is not possible. The exact centring of crystal is finally achieved by repeatedly taking single oscillation photographs and correcting the tilt and a bow error of the crystal till is perfectly aligned.

Rotation method

The rotation photograph is taken when the crystal is perfectly aligned. We can determine one axial length of crystal from this method. The axis of rotation of crystal is chosen as (b). The range of crystal rotation is fixed at 210^0 and an exposure of five hours is given to the crystal. The value of (b) of M_2 crystal has been calculated and is given in TABLE-1.

Zero-layer weissenberg photograph

The rotation photograph contains information about one dimensional layer line. In 1924, Weissenberg removed this problem by suggesting useful method. The principle involved in this method is, that a single line is selected by a slotted screen which allows only those diffracted beams from the particular layer chosen during the rotation of crystal. The layer line screen is used for selecting only one-layer line at a time.

In zero-layer photograph, the angle of inclination (μ) is set equal to zero and the layer line screen is so adjusted so that crystal is clearly observed through a small gap left between the two slots of layer-line screen. The translation and rotation are coupled by means of split pins and the crystal is rotated through an angular range, usually set below 220^0 and in the present case, the range fixed for rotation is 215^0. To check the zero-layer setting, a test photograph of one-hour exposure is taken. Then the final photograph of 7 hours' exposure is taken.

Table 1: Calculation of identity period (b) when crystal is rotated about b-axis.

s.no.	layer-line no. n	y_n (mm)	$£_n = \sin\tan^{-1}(y_n/r)$	identity period along b- axis $b = (n\lambda/£_n)A^0$	mean value of identity period (b)
1	FIRST	3mm	0.1041	$14.804\ A^0$	
2	SECOND	6.2mm	0.2082	$14.807\ A^0$	
3	THIRD	9.4mm	0.3117	$14.837A^0$	
4	FOURTH	13.1mm	0.4158	$14.830A^0$	$14.809A^0$

Here Y_n =Perpendicular distance between zero-layer and nth layer on the film.
R =Radius of cylindrical camera having fixed value =28mm.

Indexing of zero-layer photograph

The indexing of Weissenberg photograph is always reduced to the identification of diffracted spots as lying on the intersection of two festoons. The diffracted spots on the photograph are traced on the trace paper. It is apparent from the inspection of trace paper that some reflections lie on the prominent slanting straight lines running across the film, but the other spots are found to form festoons in nature. These prominent straight lines are taken as the axis of the crystal imprinted on the film.

Marking spots above and below the central region (spot free region) along the prominent axial lines, the central line is drawn which divides the photograph into two halves, upper half and lower half. To draw the festoons usually a template devised by Buerger (1966) is used. The traced copy is kept over the template in such a way that two axes which are 9cm apart coincide with the engraved axes of template. The traces of reciprocal lattice lines parallel to the will fall on or between the festoons of template. When the festoons are drawn; the spots are assigned proper indices depending upon the nature of the axes chosen. The same procedure is followed for both the halves of traced picture and thus the indexing of whole photograph is completed as shown in fig.3.

The axes on the upper half of zero-layer Weissenberg photograph of the M_2 crystal are taken as c^*, a^* and $-c^*$, while the reflections on the axes are indexed as 001, h00 and 001.

Determination of A and C

Since the Weissenberg photograph is a map of reciprocal lattice layer, the most straight-forward method for obtaining cell constants is to obtain the reciprocal lattice constants and then to convert them into direct lattice.

Let $2Y_n$ be the perpendicular distance between the corresponding reflections on the axial lines, then

$£_n = 2\sin Y_n$

The dimensions of given cell along given axes are given by

$a \text{ or } c = n\lambda/£_n = n\lambda/2\sin Y_n$

Where, n represents layer line number, and λ is the wavelength of light used

The values of cell parameters, a and c are calculated and given in TABLE-2 and TABLE-3

Table 2

S.NO.	Spot No.	L_n(mm)	$Y_n = L_n/2$	$£_n = 2\sin Y_n$	$a = n\lambda/£_n$	Mean(a)
1	2	15.4mm	7.7mm	0.2679	$11.501A^0$	$11.547A^0$
2	4	31.0mm	15.5mm	0.5344	$11.540A^0$	
3	6	47.0mm	23.5mm	0.7974	$11.601A^0$	

Table-3

S.NO.	Spot No.	L_n(mm)	$Y_n=L_n/2$	$£_n=2\sin Y_n$	$c= n\lambda/£_n$	Mean(c)
1	4	23.5mm	11.75mm	0.4072mm	15.142A^0	
2	6	36.0mm	18.00mm	0.6180mm	14.968A^0	15.055 A^0

Determination of Interaxial Angles

The angle β^* between the reciprocal axes a^* and c^* is given by

$\beta^* = X_\beta^*/X_{180}\times 180^0$

Where X_β^* is the distance between the two axes and X_{180} is the distance between two traces of single axis along the central line of the film.

For M_2 crystal,

$X_\beta^* = 45mm$ and $X_{180} = 90mm$

So, $\beta^* = 45/90\times 180^0 = 90^0$

Hence the angle between a and c is given by

$B = 180^0 - \beta^* = 180^0 - 90^0 = 90^0$

The other two inter-axial angles are determined by using the mathematical expressions

$a: b: c = \sin\alpha/a^*: \sin\beta/b^*: \sin\Upsilon/c^*$

Where α, β and Υ are the interaxial angles between a, b and c respectively

I.e. $a: b = \sin\alpha/a^*: \sin\beta/b^*$

$$\text{Or } \sin\alpha = \frac{a^* \times a}{b^* \times b}\sin\alpha \quad \ldots\ldots 1)$$

And $b: c = \sin\beta/b^*: \sin\Upsilon/c^*$

$$\text{So } \sin\Upsilon = \frac{c^* \times c}{b^* \times b}\sin\beta \quad \ldots\ldots 2)$$

On substituting the values of a, a*, b, b*, c, c* and sinβ in equation 1) and 2), we get $\alpha = 90^0$, $\beta = 90^0$, $\Upsilon = 90^0$,

Results Obtained From the Priliminary X-Ray Study of M_2 Crystal

CHEMICAL FORMULLA: $C_{13}H_{19}SO_2N$

RADIATION USED: CuKα ($\lambda = 1.5418A^0$)

CELL PARAMETERS: $a= 11.501A^0$, $b= 14.819A^0$, $c= 15.055A^0$ $\alpha= 90^0$, $\beta= 90^0$, $\Upsilon= 90^0$

CRYSTAL SYSTEM: Orthorhombic

No. Of molecules per unit cell (Z) 8

Conclusion

Experimental methods like oscillation method, rotation method, zero layers Weissenberg method were performed in the laboratory and the x-ray diffraction technique was used to find the six unit cell parameters and the crystal system of the compound which was given the name M_2 crystal. Out of six cell parameters, one parameter i.e. "b" was determined by rotation method. This parameter is calculated in Table.1. Then the indexing of Weissenberg photograph was done by using Buerger Template to identify the diffracted spots. These spots on the photo graph were traced on trace paper as shown in fig.3. By analysing the figure the other unit cell parameters were determined. The values of cell parameters (a, b, c, α, β, Υ) calculated from rotation and zero layers Weissenberg photograph were taken as raw data and were fed to computer for refinement. Firstly the programme calculated the reciprocal cell parameters with their estimated standard deviations (e.s.ds). After this the programme calculated the direct cell parameters with their e.s.ds. This process was repeated four cycles. For each cycle of refinement, the shifts and reciprocal cell parameters were printed out with estimated standard deviations. Then the direct cell parameters with e.s.ds were printed out. The data obtained from experiment was in close agreement with the refined data of computer. From the study it is proved that

$a \neq b \neq c$ and $\alpha= \beta= \Upsilon= 90^0$

so crystal is orthorhombic

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