

## X-ray diffraction study of low symmetry organic molecular solids for learning use of on-line computer program and practice

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### Abstract

Crystallographic studies of low symmetry organic molecular crystalline solids were performed by using XRD diffraction method. The well defined peaks appeared in the XRD profile of solids was indexed by using  $\sin^2$  ratio method to understand the planes producing these peaks. The hkl values and d-spacing of the planes obtained from XRD file of diffractometer machine are feed into the software programme 'CellCalc' downloaded from internet website. Software has given crystallographic parameters, crystal angles and unit cell volumes which are further used to calculate number of molecules per unit cell. The XRD data analysis found to be successful when  $\sin^2$  ratio and software programme procedure are used together. The reliability of the analysis was indicated by the match observed for crystallographic parameter with the reported. Present article involves the details on the XRD experiments and data analysis of model compound p-terphenyl belonging to monoclinic lattice. The estimated value of number of molecules per unit cell 2 of p-terphenyl is same with the value reported in literature. This experiment can also incorporate into undergraduate and postgraduate laboratory curriculum and it is beneficial to the students for the comparative study of ordinary method and use of software for the motivation towards the study.

**Keywords:** XRD, low symmetry lattices, organic molecular solids, lattice parameters

### INTRODUCTION

The X-ray diffraction (XRD) technique is one of the most non-destructive powerful scientific tools for crystal structure determination, phase quantification and phase transfer analysis of crystalline materials [1]. Unending importance of this technique has vital role in the fields of material science, geology, forensic science and biomedical etc [1-4]. This is clear cut method for understanding nature of the materials. The indexing, structure determination and phase transformational analysis using powder XRD data is significantly challenging as

compared to the single crystal XRD methods. Extensive literature is available on XRD studies of high symmetry inorganic metals, alloys, inorganic salts and hybrid solid materials[5-7]. However, such studies on aromatic organic molecular materials of significance in optoelectronic devices are less attended may be because of low symmetry and rigorous mathematical calculations in data estimations[8].

The XRD pattern of low symmetry materials (monoclinic, triclinic) shows large number peaks, some with extensive overlap, some of low intensity and which

limits to complexity of structures that can be solved as compared to the simple high symmetry materials (cubic, hexagonal). Therefore indexing of the peaks in XRD pattern by conventional  $\sin^2$  ratio method based on use of lattice parameters available in literature and using quadratic form of Bragg's equation for low symmetry crystals is of immense challenge without any software programme [9]. Hence it is customary to use an autoindexing programme such as ITO, TREOR and DICVOL etc [10].

We have contributed significantly by characterizing pure and mixed organic molecular polycrystalline system of importance in optoelectronic devices by XRD studies [9, 11]. Currently the large input in Research and Development of XRD analysis has evolved commercially computerized expensive autoindexing programmes and specific computer system required there in. Some autoindexing programmes are also available online free of charge [12,13]. Use of such programmes after confirming their reliability of the crystallographic data obtained will be of worth significance for low symmetry crystal characterization.

The present article is an attempt to show how  $\sin^2$  ratio method based on trial and error procedure described for organic aromatic monoclinic crystals has provided reliable data by comparison with similar crystallographic data obtained using autoindexing software programme

'CellCalc' downloaded from the internet [12]. The detailed procedure for indexing of the distinct peaks and determination of lattice parameters for p-terphenyl as model aromatic molecular crystal by  $\sin^2$  ratio method and by using 'CellCalc' programme are described and illustrated.

The crystallographic data obtained by both methods are in close agreement. It is therefore suggested that the Industrially and Technologically important aromatic molecular crystals and their polycrystals can be undertaken for crystallographic studies by using available software. The concerned University and College Teachers can have to generate interest in the students by giving laboratory experiments on interpretation of powder XRD pattern of low symmetry lattice and crystallographic analysis.

#### **Background of XRD:**

The students should know the essential basic knowledge of the crystallography and X-ray diffraction phenomenon [14, 15]. Perfect crystals are comprised of repeating smallest unit into which crystal can be imagined as subdivided without losing its essential properties called unit cell and such a repeating unit cells form lattice structure. Characteristic X-ray beam exposed on such a perfect crystal, it impinge with planes (regular, repeating atoms of crystals), a part of the beam transmitted, a part absorbed by

samples, part is refracted and scattered and some are diffracted. The diffracted beams are followed by the Bragg's equation,

$$2d \sin\theta = n\lambda \quad (1)$$

where  $n$ ,  $\lambda$ ,  $d$  and  $\theta$  are an integer value, wavelength of the monochromatic X-ray radiation, distance between atomic layers and angle of diffraction respectively. If  $n = 1$ , the reflection is said to be first order and  $n = 2$ , it is termed second order, and so on. The second-order reflection for a plane of spacing  $d$  appears at the same angle as a first-order reflection from planes of spacing  $d/2$ . Thus second-order reflections from (100) planes of a simple cubic crystal should be indistinguishable from first-order reflections from a hypothetical set of (200) planes. It is more convenient to treat the order of a reflection in this alternative way and to write the Bragg condition as

$$\lambda = 2d_{hkl} \sin\theta \quad (2)$$

where  $d_{hkl}$  is the distance between the  $hkl$  planes of the lattice. The integers  $h$ ,  $k$ , and  $l$  are the Miller indices. A more detailed discussion of these issues may be found in the available standard sources.16-18

## **EXPERIMENTAL PROCEDURES**

### **Recording of XRD Pattern**

The fine grained crystalline powder was packed firmly into sample holder and then mounted in the chamber provided on goniometer and gradually rotated (30 rpm) while being bombarded with X-ray ( $\text{Cr} = 2.2897\text{\AA}$ ) producing X-ray diffraction. The XRD pattern was scanned between  $2\theta$  angles of  $0^\circ$  to  $100^\circ$  by monitoring the parameter in close control. Each X-ray spectrum takes 30 minutes for complete scanning. During the scan, the computer collects the diffracted X-ray intensity at equally spaced divisions of  $2\theta$  and records these data, as well as other relevant information's, into a file that is named by the user. The XRD pattern of samples such as anthracene, p-terphenyl and perylene belonging to monoclinic lattice were recorded on Powder X-Ray Diffractometer (Philips, Model PW-3710, Holland). The XRD pattern of p-terphenyl shown in Figure 1. is interpreted for crystallographic analysis using conventional  $\sin^2$  ratio method and 'CellCalc' software downloaded from the internet [12]. The XRD pattern of anthracene and perylene were studied in similar manner and results are tabulated.

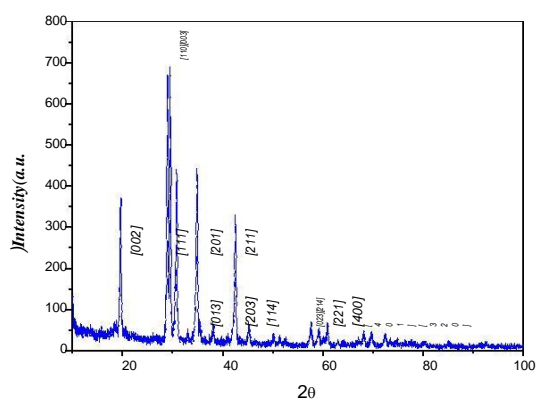


Fig. 1: Figure Caption

**HAZARDS**

The organic polynuclear molecular solids are carcinogenic and affects on skin and inhalation during purification by sublimation and hence use of safety goggles, hand gloves and lab coat are recommended during experiment..

**Table No. 1**

Pea k	d-value	2θ	sin <sup>2</sup> θ Expt.(Obs.)	sin <sup>2</sup> θ (Estimate d)	hkl
1	13.096	10.030	0.007642	0.007082	[001]
2	9.6302	13.655	0.01413	0.019972	[100]
3	6.7654	19.485	0.028635	0.02832	[002]
4	4.5894	28.890	0.062225	0.061625	[110]
5	4.5093	29.415	0.06445	0.06373	[003]
6	4.3322	30.715	0.07014	0.067868	[111]
7	4.0422	32.905	0.08021	0.07988	[200]
8	3.8326	34.76	0.08926	0.085293	[201]
9	3.5897	37.915	0.10553	0.105387	[013]
10	3.1665	42.39	0.13071	0.126946	[211]
11	2.9862	45.085	0.14697	0.138592	[203]
12	2.7102	49.975	0.1784	0.171571	[114]
13	2.3820	57.45	0.23098	0.230346	[023]
14	2.3233	59.045	0.2428	0.228139	[214]
15	2.2585	60.915	0.2569	0.251905	[221]
16	2.0478	67.980	0.3125	0.319554	[400]
17	2.0056	69.615	0.32583	0.323282	[401]
18	1.9400	72.330	0.34823	0.346361	[320]
19	1.8368	77.11	0.3884	0.381959	[031]
20	1.6970	84.85	0.45511	0.454766	[230]

**Table No. 2**

Monoclinic (beta < > 90)

Reciprocal Lattice Parameters

a*	b*	c*	α*	β*	γ*	V*
0.1223	0.1794	0.0727	---	86.762	-	0.001594
Da*Db*		Dc*	Dα*	Dβ*	gamma*	DV*
0.0003	0.0003	0.0006	----	0.756	---	0.000014

Lattice Parameters

a	b	c	alfa
8.18872	5.57350	13.76926	----
Da	Db	Dc	Dalfa
0.02161	0.01043	0.11506	----

Observed Data

H	K	l	d <sub>obs</sub>	d <sub>calc</sub>	d <sub>o-dc</sub>	Q <sub>o</sub> -Q <sub>c</sub>
0	0	1	13.096	13.74728	-0.65128	+0.00054
1	0	0	9.6302	8.17565	+1.45461	-0.00418
0	0	2	6.7654	6.87364	-0.10824	+0.00068
1	1	0	4.5894	4.60519	-0.01579	+0.00032
0	0	3	4.5093	4.58243	-0.07313	+0.00156
1	1	1	4.3322	4.32544	+0.00274	+0.00007
2	0	0	4.0422	4.08782	+0.04557	+0.00136
2	0	1	3.8326	3.85918	+0.002651	+0.00093
0	1	3	3.5897	3.53965	+0.05005	-0.00221
2	1	1	3.1665	3.17282	+0.00626	+0.00039
2	0	3	2.9862	2.96832	+0.01788	-0.00135
1	1	4	2.7102	2.71329	-0.00309	+0.00031
0	2	3	2.3820	2.38103	+0.00106	-0.00016
2	1	4	2.3233	2.32661	-0.00331	+0.00053
2	2	1	2.2585	2.25928	-0.00078	+0.00014
4	0	0	2.0478	2.04391	+0.00389	-0.00091
4	0	1	2.0056	2.00528	+0.00032	-0.00008
3	2	0	1.9400	1.94841	-0.00841	+0.00229
0	3	1	1.8368	1.84110	-0.00430	+0.00138
2	3	0	1.6970	1.69135	+0.00565	-0.00232

Residual ...0.00004413

**RESULTS AND DISCUSSION**

**Indexing of the XRD Pattern**

**1) Sin<sup>2</sup> Ratio Method:**

The organic solids selected in present experiments belong to monoclinic system with lattice parameters  $a \neq b \neq c$  and  $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ . The values of lattice parameters are obtained from the JCPDS (Joint Committee on Powder Diffraction Standards) data cards (*p*-terphenyl, perylene and anthracene cards number 39-1727, 39-1848 and 04-0412 respectively). The indexing method involves calculation of  $\sin^2\theta$  values for probable planes using quadratic equation of monoclinic system [19].

$$\sin^2 \theta = \frac{\lambda^2}{4 \sin^2 \beta} \left[ \frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} + \frac{k^2}{b^2} \right] \quad (3)$$

Sr. No	Name of organic compound	Reported lattice parameters (Å)				Unit cell volume $V(\text{Å}^3)$	Observed lattice parameters (Å)				Unit cell volume $V(\text{Å}^3)$
		<i>a</i>	<i>b</i>	<i>c</i>	$\beta$		<i>A</i>	<i>B</i>	<i>c</i>	$\beta$	
1	<i>p</i> -terphenyl	8.106	5.6130	13.613	92.02°	618.99	8.189	5.573	13.769	93.238°	627.423
2	Perylene	11.277	10.826	10.263	100.55°	1252.95	11.08	10.67	10.20	99.551°	1190.49
3	Anthracene	9.4746	6.0163	8.5243	103.58°	472.32	9.475	5.856	8.4560	102.92°	457.338

where *h*, *k*, *l* are Miller indices of the probable planes and  $\lambda$  is wavelength of monochromatic X-ray beam [Chromium source ( $K\alpha_1$ ) = 2.2897 Å]. The  $\sin^2\theta$  values calculated using above equation are given in Table 1. and compared with experimental values of  $\sin^2\theta$  obtained from XRD profile.

The observed match determines the Miller indices of the planes from which peaks are produced in the XRD pattern and given in the same Table 1.

## 2) Use of 'CellCalc' Software for Data Analysis:

The 'CellCalc' programme was used for further data analysis. The software was opened for monoclinic system and the *h*, *k*, *l* values along with *d*-values of the planes were feed into the programme and executed. The data on lattice parameters *a*, *b*, *c*, crystal angle  $\beta$  and unit cell volume (*V*) shown on the dialogue box of the software were noted and presented in Table 2. It is seen that, the lattice parameters given by software matches with those reported. The negligibly small residual value (0.00004413) given

$$Z = \frac{V \times N}{V_m} \quad (4)$$

where  $V_m$  is molar volume and *N* is the Avogadro's number. The molar volume is obtained from the density and molecular weight (*M* = 230.31 gm per mole). The density was determined experimentally using reported procedure [20]. The value of number of molecules per unit cell *Z* = 2 was found to be same as reported in the literature [21,22]. This observation confirms the reliability of the present data analysis procedure based on use of the software. The similar procedure was used for XRD data analysis of perylene and anthracene. The estimated crystallographic data are summarized in the Table 3. The concurrency between estimated and literature data led us to conclude that the present data analysis procedure developed by us is applicable to the any crystalline materials of all lattice type.

Table No.3

## 2.0 CONCLUSION

The XRD data analysis of high symmetry crystalline solids such as cubic and hexagonal is simple and can be done manually by using  $\sin^2$  ratio method. However application of this method for XRD data analysis of low symmetry crystalline compounds involves complicated calculations whose solution without computer software is highly impossible. The present procedure of data analysis from XRD pattern of monoclinic organic molecular solid using  $\sin^2$  ratio method coupled with use of free of charge 'CellCalc' software programme can be successfully applied to any low symmetry lattice system. It is recommended that such experiments on the XRD data analysis of the organic molecular solids be introduced in curriculum of graduate and postgraduate courses. Further use of this procedure in studies of substitutional solid systems would help to identify the position of different impurity molecules in the host lattice and to correlate structure with the electrical, magnetic and optical properties of the materials.

## ASSOCIATED CONTENT Supporting Information

Instructor note, brief background of XRD, sample preparation process and recording of XRD patterns, details calculation of  $\sin^2$  ratio method and use 'CellCalc' software for further determination of crystallographic data, density measurement and number of molecules per unit cell.

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## Supplemental materials for Instructors

These materials are written for the Graduate and Postgraduate students desiring to undertake studies on X-ray powder diffraction analysis of low symmetry organic molecular solids. The major essential part in this study the peaks in XRD pattern are indexing by using  $\sin^2$  ratio method and software. The software when feed with data of  $\sin^2$  ratio method given sufficient information required to estimate crystallographic parameters like number of molecules per unit cell, volume of unit molecule cell which further helps to understand the impurity molecule doping site and to correlate lattice structure with optical and electrical properties.

### Chemicals

Perylene (Alfa Aesar), Anthracene (Laboratory Rasayan, India) and p-terphenyl (Fluka) were used in the study as received after confirmation of purity.

Sr. No.	Experimental Chemicals	CAS Number
1	Perylene	198-55-0
2	p-terphenyl	92-94-4
3	Anthracene	120-12-7

### Background of XRD:

The following basic concepts should be introduced to the syllabus in order to maximize the knowledge of students essential to the understanding and interpretation of XRD pattern.

1. Crystal system
2. Bragg's equation of XRD from crystalline materials
3. Feature of XRD pattern
  - i) number of peaks
  - ii) Positions of peaks
  - iii) Peak Intensity
  - iv) Indexing of the peaks

### Experimental Procedure:

The success of structural analysis of crystalline powders by diffraction of X-ray absolutely depends upon the crystal type, and experimental conditions

#### 1. Process of Sample Preparation

The requirements of sharp and well defined peaks for comprehend of XRD pattern can be fulfilled by fine grained samples of size of about  $\sim 10 \mu\text{m}$  or less.



## 2. Recording of XRD Pattern

The fine grained crystalline powder is packed in the sample holder and placed in the sample chamber of diffractometer. Before the recording of XRD pattern of samples, the instrument was standardized by using standard reference as a silicon wafer. When X-ray focused on crystalline powders, the diffracted X-ray was scanned directly on a plot of intensity of diffracted X-ray against  $2\theta$  angles. The instrument given XRD pattern and Excel spread sheet contains detailed information of the results.

### Indexing of XRD by $\sin^2$ Ratio Method:

The Crystallographic data of the materials undertaken in the experiment were taken from JCPDS card. For p-terphenyl JCPDS card number is 39-1727.

For monoclinic crystal system the quadratic form of Bragg equation as given below [1].

$$\sin^2 \theta = \frac{\lambda^2}{4 \sin^2 \beta} \left[ \frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} + \frac{k^2}{b^2} \right] \quad (1)$$

Calculations for (002) plane using above equation given,

$$\sin^2 \theta = \frac{2.2897^2}{4 \sin^2 92.02} \left[ \frac{0^2}{8.106^2} + \frac{0^2}{13.613^2} - \frac{2 \times 0 \times 2 \times \cos 92.02}{8.106 \times 13.613} + \frac{2^2}{5.61^2} \right]$$

$$\therefore \sin^2 \theta = 0.028635 \quad (2)$$

Thus the values of  $\sin^2 \theta$  should be calculated for all possible planes such as [100], [110], [111], [120], [102] and so on. The  $\sin^2 \theta$  values were also calculated from the  $\theta$  values of the excel spread sheet provided by the instrument.

$$\sin^2 \theta = \sin^2 \left( \frac{2\theta}{2} \right) \quad \text{i.e.} \quad \sin^2 \theta = \sin^2 \left( \frac{2 \times 19.485}{2} \right)$$

$$\sin^2 \theta = 0.02832$$

( 2 )

( 2 )

(3)

The observed value of  $\sin^2 \theta = 0.02832$  matches well with  $\sin^2 \theta$  values calculated for (002) plane thus the peak appeared at  $2\theta = 19.485^\circ$  is produced due to X-rays diffracted from (002) crystal planes. Thus the match between observed and calculated  $\sin^2 \theta$  values decide the miller index of the plane from which diffracted X-ray appears on the profile as shown in Table 1.

**Table 1.** Estimated and experimental values (observed values in XRD) of  $\sin^2\theta$  and corresponding  $hkl$  values.

Peak No.	$d$ -value	$2\theta$	$\sin^2\theta$ Expt.(Obs.)	$\sin^2\theta$ (Estimated)	$hkl$
1	13.096	10.030	0.007642	0.007082	[001]
2	9.630255	13.655	0.01413	0.019972	[100]
3	6.7654	19.485	0.028635	0.02832	[002]
4	4.5894	28.890	0.062225	0.061625	[110]
5	4.5093	29.415	0.06445	0.06373	[003]
6	4.33227	30.715	0.07014	0.067868	[111]
7	4.04225	32.905	0.08021	0.07988	[200]
8	3.83267	34.76	0.08926	0.085293	[201]
9	3.5897	37.915	0.10553	0.105387	[013]
10	3.16656	42.39	0.13071	0.126946	[211]
11	2.9862	45.085	0.14697	0.138592	[203]
12	2.7102	49.975	0.1784	0.171571	[114]
13	2.38209	57.45	0.23098	0.230346	[023]
14	2.3233	59.045	0.2428	0.228139	[214]
15	2.2585	60.915	0.2569	0.251905	[221]
16	2.0478	67.980	0.3125	0.319554	[400]
17	2.0056	69.615	0.32583	0.323282	[401]
18	1.9400	72.330	0.34823	0.346361	[320]
19	1.8368	77.11	0.3884	0.381959	[031]
20	1.6970	84.85	0.45511	0.454766	[230]



**Use of Software for XRD Data Analysis**

The 'Cellcalc' software available online ([http://homepage2.nifty.com/~hsc/soft/cellcalc\\_e.html](http://homepage2.nifty.com/~hsc/soft/cellcalc_e.html)) free of cost was shows dialogue box as in below Figure 1. The software was opened and calculated hkl values, experimental (d<sub>obs</sub>) interplanar spacing values, sample name, lattice etc data were feed and executed using calculation option. The results on data analysis such as reciprocal lattice parameter, lattice parameter along with volume of unit cell and residual values were read on the dialogue box shows in Figure 2.

**Figure 1.** Before use of Software

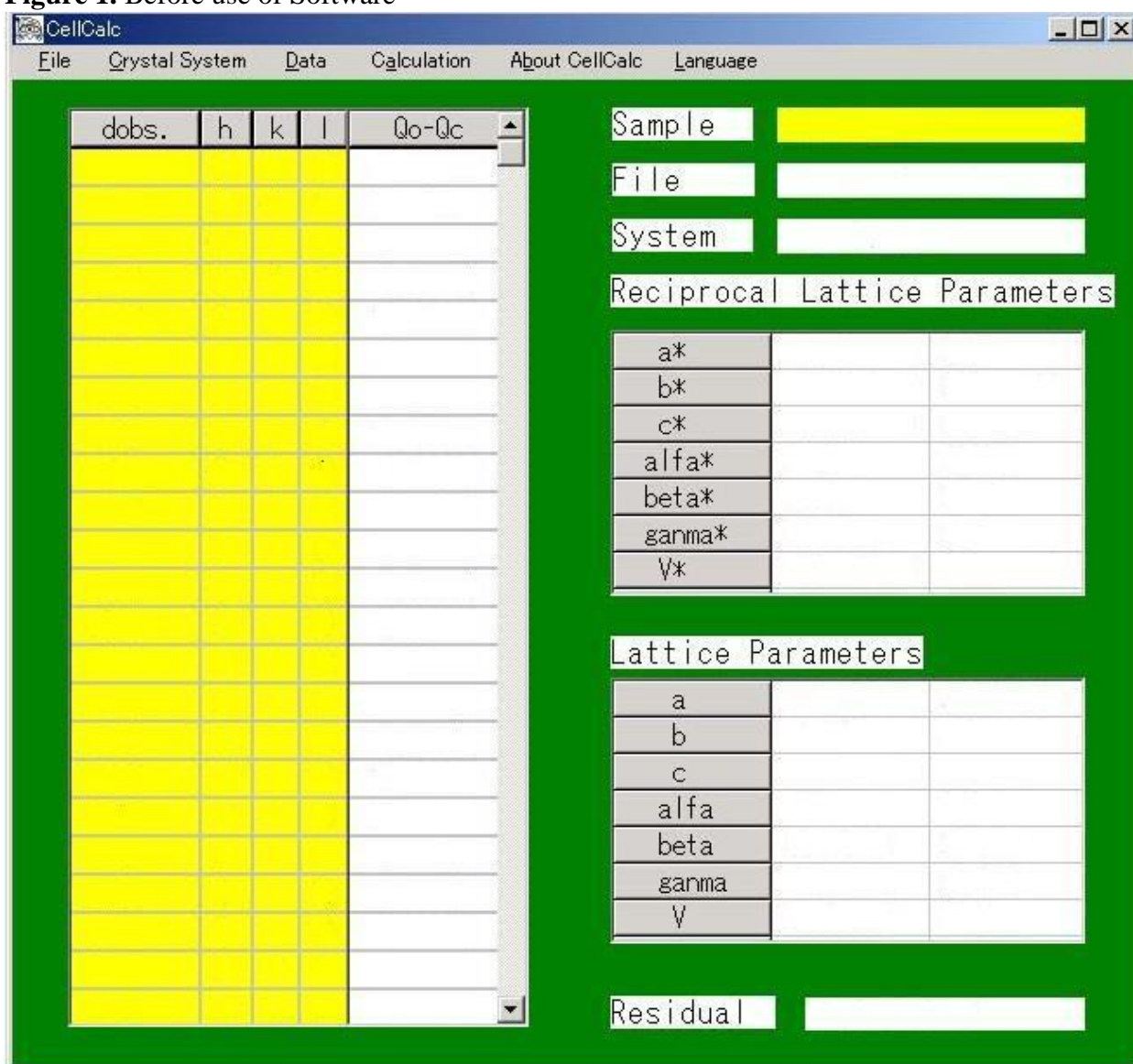


Figure 2. After Use of Software



The values of lattice parameter obtained from software were found in close agreement with those reported in JCPDS card. The molecular volume was used further to calculate density of crystal system. The calculated density was also found concurrent with the experimental and theoretical density ( $\rho$ ) value. Finally the characteristic parameter ( $Z$ ), the number of molecules per unit cell was also calculated and the value of 'Z' two molecules per unit cell is as per the expectation. All details of calculation are given for the more information of instructor.

### Determination of Density of Crystalline Materials:

Determination of number molecules per unit cell needs known value of density of materials. Density of materials was calculated by using reported procedure as mentioned [2].

#### Procedure:

- 1) Weight of empty pycnometer ( $w_1$ ) = 18.3574 g
- 2) Weight of pycnometer + sample ( $w_2$ ) = 20.3684 g
- 3) Weight of pycnometer + sample + water ( $w_3$ ) = 26.8442 g
- 4) Volume of liquid ( $v$ ) = 8.1366 ml (at 25°C,  $\rho = 0.99705$ )

$$\rho = \frac{\rho_L (w_2 - w_1)}{\rho_L V + w_2 - w_3}$$
$$\rho = \frac{0.99705(20.3684 - 18.3574)}{(0.99705 \times 8.1366) + 20.3684 - 26.8442}$$
$$\rho = 1.22 \text{ g dm}^{-3}$$

### Determination of Number of Molecules per Unit Cell

The number of molecules per unit cell is calculated by using following equation [3],

$$Z = \frac{V \times N}{V_m}$$

The volume of unit cell ( $V$ ) obtained from software and molar volume ( $V_m$ ) obtained from molecular weight divided by density. These values are substituted in above equation to obtain,

$$Z = \frac{627.423 \times 0.6023}{230.30}$$
$$Z = 2.00126$$

The reported value of  $Z$  for p-terphenyl is 2, matches well with experimental value.<sup>3</sup>

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