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Molecular structural visualization and micro-structural features of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone

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ABSTRACT

The compound of selenium containing heterocycles namely (I) 4,6-dimethyl-3-cyanopyridine-(2H)-selenone ($C_8H_8N_2Se$) was used as model to investigate the structural and micro-structural features of some selected selenones. Visualization of molecular structure of selenium containing moiety was accurately investigated to clarify role of selenium ion in nucleation process of forming 3D-framenet of H-bonded of substituted selenones. Bond distances, torsions on angles of investigated compound were compared with others crystal data to confirm crystal structures of substituted selenones which is monoclinic crystal form with *P* 21/*n* space group.

KEYWORDS

Synthesis;
Selenium;
H-bond;
XRD;
SEM;
Visualization;
Crystal structure.

INTRODUCTION

Because of their high level of chemical diversity, ready availability, easy handling, and wide efficiency and applicability, organoselenium compounds are considered useful reagents for many synthetic transformations.[1-4] Although their chemical structure is closely related to that of the homologous sulfur analogous, the reactivity often presents marked differences[1]. An illustrative example is that of vinyl selenones. The electron-withdrawing effect combined with the excellent nucleofugal ability of the phenylselenonyl function makes the vinyl selenones useful substrates for interesting transformations, which have no parallel in sulfone chemistry.

A classic example is the *one-pot* synthesis of cyclopropanes by treatment of vinyl selenones with enolates, a Michael Initiated Ring Closure reaction (MIRC) in which the phenylselenonyl substituent plays a dual role as activating group in the conjugate addition and as leaving group in the cyclization according to[5-8]. Multistep syntheses of aziridines, based on ring closure reactions starting from β-aminoselenides are disposable in the literature,[9-15] but examples of direct transformation of vinyl selenones through tandem Michael addition–intramolecular nucleophilic substitution reactions are only sporadic.[16-18] As a consequence of the great synthetic and biological interest for the aziridine skeleton[19-22].

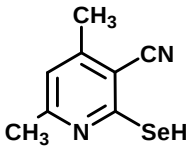
Organic compounds containing selenium are of considerable interest since they exhibit diverse biological activities with numerous therapeutic applications[23] and[24]. In addition, the presence of a heterocyclic ring as the organic moiety in these compounds alters their

properties to a great extent. A pharmacologically active hetero-cycle is the quinoline ring that occurs in several natural products and displays a broad range of biological activity[25] and[26] including anti-tumour, hypoglycemic, antihistamine and anti-carcinogenic properties[27], etc. Due to their importance as substructures in a broad range of natural and designed products, significant efforts have been directed into the development of new qui noline based structure[28].

Many research were devoted to understand crystal structure, effect of substituent's on the different crystallographic data obtained from single crystal data and their biological and catalytic activity of substituted pyridine[29-36].

The major goal of the present is to visualize and compare the crystallographic data of some selected selenium containing simplest hetero-cycles such as substituted pyridine nucleus with experimental data. Beside confirming the validity of using XRD- powder diffraction as quantitative tool for estimating different phases for small nucleus of organic compound. Furthermore accurate investigations of micro-structural parameters that responsible for their biological activity.

EXPERIMENTAL PROCEDURES



Compound (I) 4,6-dimethyl-3-cyanopyridine-(2H)-selenone ($C_8H_8N_2Se$)

The compound of selenium containing heterocycles namely (I) 4,6-dimethyl-3-cyanopyridine-(2H)-selenone ($C_8H_8N_2Se$), was carefully synthesized and structurally established by one of the authors themselves see ref.[37-39] according to the following briefs.

A compound **(I)** 4,6-dimethyl-3-cyanopyridine-(2H)-selenone ($C_8H_8N_2Se$) was synthesized by mixing a mixture of the corresponding chloroquinoline derivative 1 (1.66 g, 10 mmol), selenium metal (1.0 g, 12 mmol) and sodium borohydride (1.2 g, 32 mmol) was refluxed in ethanol (50 mL) for 5 h. The mixture was cooled and poured in cold HCl. The solid precipitate was filtered, dried, and re-crystallized from ethanol. The details of data was reported in ref.[37,38].

Structural measurements

(A) X-ray diffraction (XRD)

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground 4,6-dimethyl-3-cyanopyridine-(2H)-selenone in the range ($2\theta = 10\text{-}70^{o}$) using Cu-K$\alpha$ radiation source and a computerized [Steo-Germany] X-ray diffracto-meter with two theta scan technique. A visualized studies of crystal structure were made by using Diamond Molecular Structure version 3.2 package, Germany and Mercury 2.3-BUILD RC4-UK. A visualization study made is concerned by matching and comparison of experimental and theoretical data of atomic positions, bond distances, oxidation states and bond torsion on the crystal structure formed.

(B) Scanning electron - microscope (SEM)

Scanning electron microscope (SEM) measurements were carried out using small pieces of prepared samples on different sectors to estimate the actual molar ratios by using "TXA-840, JEOL-Japan" attached to XL30 apparatus with EDX unit, accelerant voltage 30kv, magnification 10x up to 500.000x and resolution 3. nm. The samples were coated with gold.

RESULTS AND DISCUSSIONS

Structural measurements

(A) Structural identification

The X-ray diffraction of pure 4,6-dimethyl-3-cyanopyridine-(2H)-selenone ($C_8H_8N_2Se$) which re-crystallized from ethanol was performed and supported by single crystal data supplied from ICSD-data bank Karlsruhe Germany see TABLE 1.

Analysis of the corresponding 2θ values and the interplanar spacing d (A^{o}) by using computerized program proved that the compound is mainly belongs to monoclinic crystal structure with *P21/n* space group as confirmed in crystallographic data in TABLE 1.

Figure 1a Shows the experimental XRD-profile recorded for highly pure solid product of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone. The most intense reflection peaks of monoclinic phase was marked with green squars as clear in Figure 1a. The indexed peaks are representing the major monoclinic phase in case of

powder diffraction while the non-indexed reflections refer to impurity phases. To confirm the validity of using XRD- powder diffraction as quantitative tool for estimating different phases for small nucleus of organic compound a visualized XRD- for single crystal of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone was constructed depending up on lattice coordinates of pure single crystal as clear in Figure 1b.

The comparison between the fundamental fingerprints of experimental lines (those with green squares) for 4,6-dimethyl-3-cyanopyridine-(2H)-selenone in Figure 1a with those in Figure 1b one can observe that the most intense reflection peaks (lines with [110] and [100]) are located nearly in the same position at two theta ~ 15-17. The differences between the two positions attributable to different kind of hydrogen bonding inside the unit cell of packing 4,6-dimethyl-3-cyanopyridine-(2H)-selenone. These results are in full agreement with those reported by[40,41] who were confirming that there are strong relationship between the intermolecular H-bonding and solid crystal structure of the investigated compound.

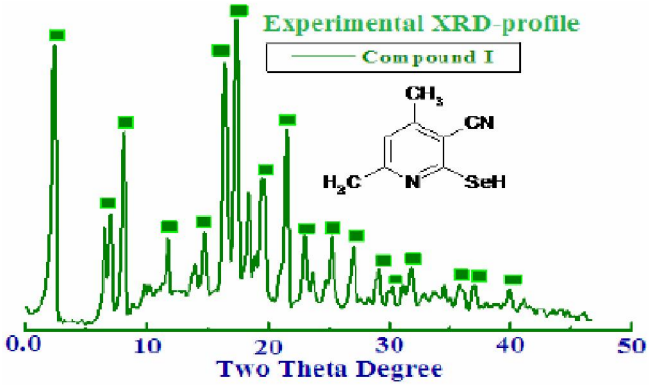


Figure 1a : Experimental x-ray diffraction pattern of of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

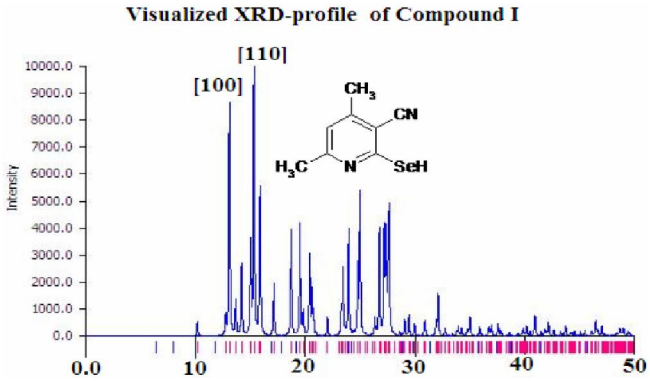


Figure 1b : Visualized x-ray diffraction pattern of of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

For accurate identification of peak position in both cases experimental and visualized XRD-profiles Figures 2a, 2b were constructed as high resolution zoom in diffractogram. It was concluded that the differences between experimental and visualized intense reflection peaks (lines with [110] and [100]) was one theta degree (2theta =15,15.5 and 16-16.5 for visualized one) which is due to wide range of H-bond possibilities inside the crystal lattice of compound **(I)** namely 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

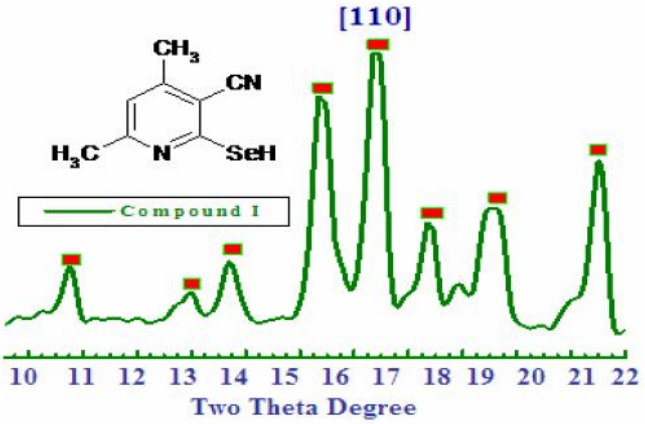


Figure 2a : High-resolution zoom in XRD-profile of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone, red squares refer to pure monoclinic phase with P21/n space group.

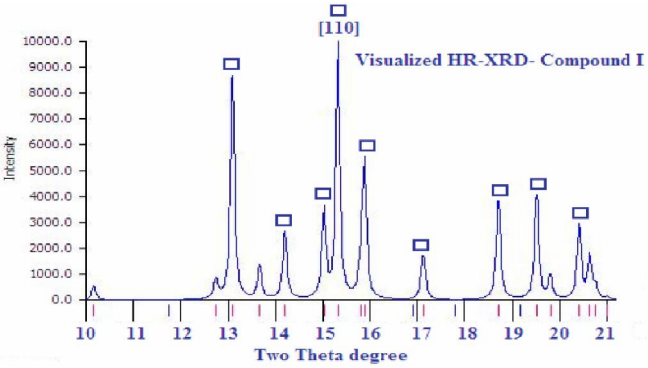


Figure 2b : Visualized XRD-profile of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

Figure 3 displays the different types of hydrogen bonding that could be found together in the 3D-unitcell of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone causing the small difference between the two diffractogram of experimental and visualized one.

From Figure 3 one can indicate that there are four types of H-bonding two are intra-H-bond in the same molecule of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone which are Se…H….CN and Se….H….N while the others two inter-H-bond are Se…H…..N

and Se….H….Se. These four types of hydrogen bonding are responsible for forming 3D-framnet of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone as solid array material.

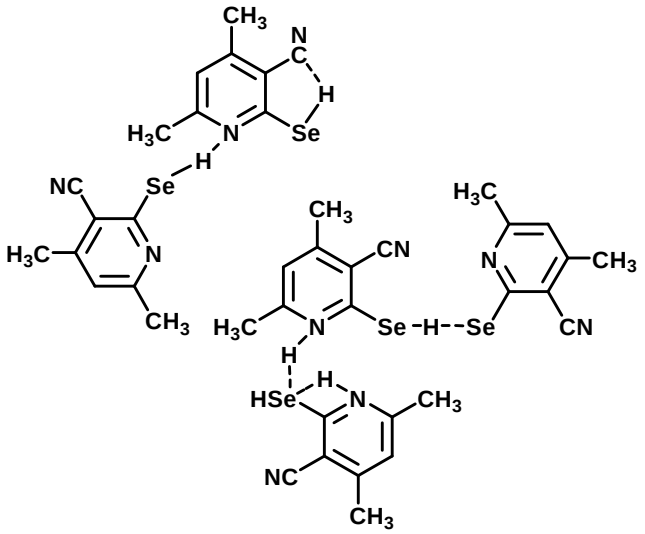


Figure 3 : Possibilities of H-bonding inside 3D-unit cell of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

Venkatachalam et al.[42] repoted that the are strong correlation between structural variation imparts molecular anisotropy (H-bonding) in solid state by preferentially forming intermolecular and intramolecular hydrogen bonds. In particular examination of crystal structure of a group of structurally similar compounds revealed the importance of the individual groups in their structure and how they influence the molecular lattice framework.

Structural visualization of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone

To confirm the crystallographic data obtainable from experimental XRD and single crystal data reported in TABLE 1 a visualized unit cell with minimum 120 atoms was constructed by using both of DIAMOND – IMPACT CRYSTAL-Germany /and MERCURY 2.3Build RC4-UK visualizer - see Figure 4 and TABLES 2, 3 and 4.

The study concerned by matching and comparison of lattice constants, torsion of bonding, bond lengths and lattice volume. Figure 4 shows the 3D-packing monoclinic with 10 molecules in unit cell with $P2_1/n$ space group built up via MERCURY-package version 2.3 RC4-UK depending up on pyridine ring has four different substituent R_1= Se…H, R_2= CN^-, R_3=R_5=CH_3 and the plans of symmetry represented by cyan and violet color. The molecules are linked in strongly hydrogen-bonded two-dimensional sheets. The mean separation between the sheets of molecules is ~ 4.321 (7) A °, corresponding to fifth of the c axis. There are no stacking interactions in this structure. The molecules form a mesh and the symmetry-related molecules in the adjacent planes lie above or below the gaps in the mesh. There are no strong interactions visible between the molecular layers inside unit cell.

It was observed that selenium anion has important role as nucleation center such that selenium can form four types of H-bonding as clear in Figure 3 two are intra-H-bond in the same molecule of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone which are Se…H….CN and Se….H….N while the others two inter-H-bond are Se…H…..N and Se….H….Se.

The observed changes in the Se….H distances in

TABLE 1 : Crystallographic data and measurements of compounds I.

Formula	Compound I : $C_8H_8N_2Se$
Assymetric unit	$C_8H_8N_2Se$
Formula weight	301
Crystal Size	0.15x0.2x0.4
T/K	100(1)
Crystal system	Monoclinic
Space group	*P* 21/*n*
a/Å	6.112(4)
b/Å	7.474(5)
c/Å	22.779(6)
β/°	94.345(5)
V/Å ^{3}	1039.26(10)
Z	4
Absorption coefficient/mm$^{?1}$	7.095
D_{calc}/g cm^3	2.107
F(0 0 0)	632.0
2*θ*/°	57.56
Index ranges	?8 < *h* < 6; ?9 < *k*<9; ?30 < *l* < 23
Reflections collected [R_{int}]	6378 [0.0745]
Reflections unique	2552
Parameters	137
GOF	1.134
R_1/wR_2 [$I > 2\sigma(I)$]	0.0716/0.1933
R_1/wR_2 (all data)	0.0933/0.2683
Largest res. peak/e Å$^{?3}$	0.935

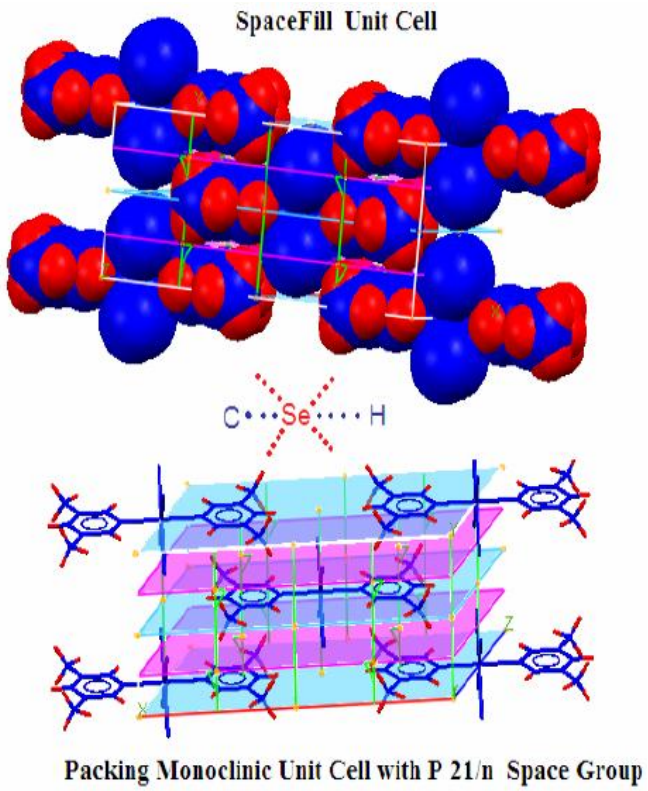


Figure 4 : Packing and spacefill unit cells of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone with different plans of symmetry showing selenium-ion as nucleation center.

the fully protonated structures are small and may be due to some uncorrected experimental error. The shape of the hydrogen-bond potential-energy well must change due to slight changes in the local environment as suggested by Wilson[43].

From TABLE 2 it was observed that there are more than one type of hydrogen bonding as clear in TABLE 1 namely N_2…H_1 =0.864(3) Å, Se_1….H_{1D} =0.873(4) Å, Se_1….H_1 =0.852(1)Å, N_{1D}…H_3 = 0.988(3) Å and Se….H_1 = 0.825(4) Å. These observations supplied from TABLE 2 confirm that selenium anion make as nucleation center through different possibilities of H-bond formation that enhance 3D-nucleation process of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

The four types of H-bonding as clear in Figure 3 two are intra-H-bond in the same molecule of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone which are Se…H….CN and Se….H….N while the others two inter-H-bond are Se…H…..N and Se….H….Se. These types are slightly short in contrast with normal H-bond compared with similar hydrogen bonds reported in[43] since O—H and H….O distances show no abnormalities compared with O—H….O hydrogen bonds of similar length Steiner and Saenger[44] reported that there is no evidence of disorder in the anisotropic displacement parameters of the protons. These distances reported in TABLE 2 lie in the region where the proton position has been found to be near the centre of the hydrogen bond.

TABLE 2 : Selected bond distances in the packing unit cell of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

Number	Atom1	Atom2	Type	Distance Å
1	Se1	C2	Single	2.4458(4)
2	H1	Se1	Single	0.8254(4)
3	C1	N1	Aromatic	1.364(5)
4	H1	C1	Single	0.949(5)
5	C2	C1	Aromatic	1.405(7)
6	H3	C3	Single	0.996(5)
7	H1	N1D	Single	0.988(3)
8	C3	C2	Single	1.519(5)
9	C4	C2	Aromatic	1.394(8)
10	H4	C4	Single	0.950(5)
11	C5	C4	Aromatic	1.407(5)
12	C6	C5	Single	1.513(7)
13	H1	N2	Single	0.864(3)
14	H6	C6	Single	0.960(3)
15	C5	N1	Aromatic	1.326(7)
16	H5	C5	Single	0.950(4)
17	C1B	Se1	Single	2.4458(4)
18	H1D	Se1	Single	0.8521(4)
19	C1F	Se1	Single	2.4458(4)
20	H3B	C3	Single	0.988(3)
21	H6B	C6	Single	0.960(3)
22	H1D	Se1	Single	0.873(4)
23	H1D	N1D	Aromatic	1.364(5)
24	H1D	C1D	Single	0.949(5)
25	C2D	C1D	Aromatic	1.405(7)

TABLE 3 shows some selected bonds torsion in the packing unit cell of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone which contains ten molecule. It is obviously that the torsion on the most cases are equilibrated that reflect the high stability inside unit cell. These equilibrated bonds such as C_1-N_1-Se_1-H_1 with positive 45.5(3) and C_1..N_1..Se_1..H_{1B} with negatively value -45.5(3) consider good model that reflects stability of lattice.

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TABLE 3 : Selected bonds torsion in the packing unit cell of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

Number	Atom1	Atom2	Atom3	Atom4	Torsion
1	C1	N1	Se1	H1	45.5(3)
2	C1	N1	Se1	H1B	-45.5(3)
3	C1	N1	Se1	H1D	-134.5(3)
4	C1	N1	Se1	H1F	134.5(3)
5	C1	N1	Se1	N1D	Undefined
6	C7	N1	Se1	H1	-134.5(4)
7	C7	N1	Se1	H1B	134.5(4)
8	C7	N1	Se1	H1D	45.5(4)
9	C7	N1	Se1	H1F	-45.5(4)
10	C7	N1	Se1	N1D	Undefined
11	H1	C1	N1	Se1	-0.0(6)
12	H1	C1	N1	C7	180.0(5)
13	C2	C1	N1	Se1	-180.0(4)
14	C2	C1	N1	C7	0.0(7)
15	C3	C2	C1	N1	-180.0(4)
16	C3	C2	C1	H1	0.0(7)
17	C4	C2	C1	N1	-0.0(7)
18	C4	C2	C1	H1	-180.0(5)
19	H2	C3	C2	C1	-0.0(6)
20	H2	C3	C2	C4	-180.0(4)
21	H3	C3	C2	C1	-120.2(5)
22	H3	C3	C2	C4	59.8(6)
23	H3B	C3	C2	C1	120.2(5)
24	H3B	C3	C2	C4	-59.8(6)
25	H4	C4	C2	C1	-180.0(5)
26	H4	C4	C2	C3	-0.0(8)
27	C5	C4	C2	C1	0.0(7)
28	C5	C4	C2	C3	180.0(4)
29	C6	C5	C4	C2	180.0(4)
30	C6	C5	C4	H4	-0.0(8)

TABLE 4 : Selected bond angles in the packing unit cell of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

Number	Atom1	Atom2	Atom3	Angle ^123
1	H1	Se1	N1	90.5(1)
2	H1	Se1	H1B	91.08(1)
3	H1	Se1	H1D	180.00(1)
4	H1	Se1	H1F	88.92(1)
5	H1	Se1	N1D	89.5(1)
6	N1	Se1	H1B	90.5(1)
7	N1	Se1	H1D	89.5(1)
8	N1	Se1	H1F	89.5(1)
9	N1	Se1	N1D	180.0(1)
10	H1B	Se1	C1D	88.92(1)
11	H1B	Se1	C1F	180.00(1)
12	H1B	Se1	N1D	89.5(1)
13	H1D	Se1	C1F	91.08(1)
14	H1D	Se1	N1D	90.5(1)
15	H1F	Se1	N1D	90.5(1)
16	Se1	N1	C1	119.4(3)
17	Se1	N1	C7	121.6(3)
18	C1	N1	C7	118.9(4)
19	N1	C1	H1	119.2(5)
20	N1	C1	C2	121.6(4)
21	H1	C1	C2	119.1(5)
22	C1	C2	C3	118.1(4)
23	C1	C2	C4	117.7(4)
24	C3	C2	C4	124.1(4)
25	H1	C3	H3	109.4(4)
26	H1	C3	C2	110.0(4)
27	H1	C3	H3B	109.4(4)
28	H5	C3	C2	109.4(4)
29	H5	C3	H3B	109.2(4)
30	C2	C3	H3B	109.4(4)

TABLE 4 explains some selected bonds angles in the packing unit cell of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone. One can indicate that no violation in most of bond angles as clear in TABLE 4 which confirms the torsion data in TABLE 3. The angles with selenium center as ($H_1Se_1N_1$^) = 90.5(1)° are good example for representing stability of this compound **(I)** (4,6-dimethyl-3-cyanopyridine-(2H)-selenone) that enhanced by H-bond as proved in structure analysis in the present investigations.

SE-microscopy measurements

Figure 5a-b show the SEM-micrographs for pure 4,6-dimethyl-3-cyanopyridine-(2H)-selenone applied on the ground powders that prepared in ethanolic solution.

The average grain size was calculated and found in between 1.13 and 2.91μm.

The EDX examinations was performed on random spots in the same sample confirmed and are consistent with our XRD analysis for monoclinic phase with $P2_1/n$ space group, such that the differences in the molar ratios EDX are fitted with molecular formula of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

From Figure 5a-b it is so difficult to observe inhomogeneitiy within the micrograph due to that the

powders used are very fine and the particle size estimated is too small.

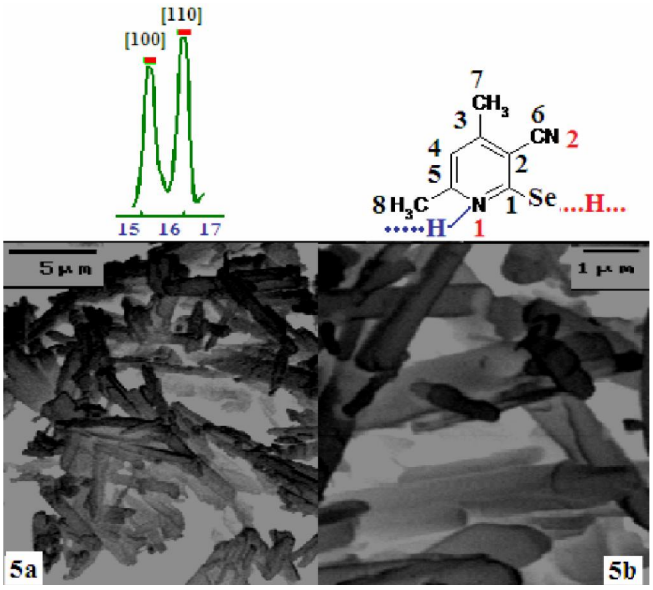

Figure 5a,b : SE-micrograph captured for 4,6-dimethyl-3-cyanopyridine-(2H)-selenone with two different magnification factors (5_a) 5 µm and (5_b) 1 µm.

The grain size for 4,6-dimethyl-3-cyanopyridine-(2H)-selenone monoclinic -phase was calculated according to:

Scherrer's formula[45],

$B = 0.87 \lambda / D \cos \theta$ (1)

where D is the crystalline grain size in nm, θ, half of the diffraction angle in degree, λ is the wavelength of X-ray source (Cu-K∝) in nm, and B, degree of widening of diffraction peak which is equal to the difference of full width at half maximum (FWHM) of the peak at the same diffraction angle between the measured sample and standard one. From SEM-maping, the estimated average grain size was found to be (1.13 and 2.91µm) which is relatively large in comparison with that calculated applying Scherrer's formula for pure 4,6-dimethyl-3-cyanopyridine-(2H)-selenone monoclinic -phase (D ~ 0.89 µm). This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology. Similar behavior was reported by[46,47].

These results estimated from Scherrer's calculations are consistent with those deduced from structure visualization of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone in the current study in which selenium ion make as nucleation center through different possibilities of H-bond formation that enhance and reinforce 3D-nucleation process of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone and consequently lead to corresponding decrease in the grain size estimated of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone.

CONCLUSIONS

The conclusive remarks inside this article can be summarized in the following points;

1- Compound (I) 4,6-dimethyl-3-cyanopyridine-(2H)-selenone is mainly belongs to monoclinic crystal structure with *P21/n* space group as confirmed in crystallographic data.

2- XRD- powder diffraction could used as quantitative tool for estimating different phases for small nucleus of organic compounds.

3- There are four types of H-bonding two are intra-H-bond in the same molecule of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone which are Se…H….CN and Se….H….N while the others two inter-H-bond are Se…H…..N and Se….H….Se, these four types of hydrogen bonding are responsible for forming 3D-framnet of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone as solid array material.

4- The visualized investigations exhibited good fitting with experimental data.

5- The average grain size was calculated and found in between 1.13 and 2.91µm which is relatively high in contrast with that calculated throughly applying Scherrer's formula for pure 4,6-dimethyl-3-cyanopyridine-(2H)-selenone monoclinic -phase (D ~ 0.89 µm).

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