

## Synthesis of V-shaped Schiff base ligand of type (N<sup>1</sup>E,N<sup>2</sup>E)-N<sup>1</sup>,N<sup>2</sup>-bis(pyridin-2-yl-methylene)-ethane-1,2-diamine, DFT/XRD/HAS analysis

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### Abstract

A new functionalized V-shaped Schiff base (N<sup>1</sup>E,N<sup>2</sup>E)-N<sup>1</sup>,N<sup>2</sup>-bis(pyridin-2-ylmethylene)ethane-1,2-diamine ligand was synthesized in good yield *via* condensation of picolinaldehyde with ethane-1,2-diamine in ethanol solution under open reflux condition. The prepared N4-SB was characterized by XRD single crystal then computed *via* Hirshfeld surface analysis (HSA). Moreover, the two-dimensional fingerprint (2D-FP) and structural DFT optimization processes were also performed. The DFT structural parameters like bonds and angles lengths were matching with their XRD experimental relatives.

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## 1. Introduction

Schiff bases SB's are considerably used in catalysis, industry and organic fields due to their preparative accessibility and structural properties [1-4]. As an important family of polydentate N-donor ligands, V-shaped considers being one of a very suitable chelate ligand, which is geometrically suitable for metal center coordination [5-7]. SB ligands with their N, N-donors possess properties like facile approach, stability, relative ancillary, tunable electronic and steric coordination modes with metal center make it with high-value compounds of interest to most scientists [8]. The imine  $\text{-N=C}$  group functions a serious SB's in the role of the pharmaceutical of SB's, which are comparable to indigenous biological molecules due to the presence of unsaturated azomethine in their backbone [9]. The SB transition metal ion complexes and the free SB ligand are normally to reveal antibacterial activities against several bacteria types like *E. Coli*, *S. Aureus*, and *B. Subtilis* [8-10]. On the other hand, many studies illustrated the anticancer, the antioxidant and antimicrobial biological activity of SB and their complexes [8-10]. Moreover, the SB's and their complexes are widely used as structural coordination typical models, catalytic, analytical and other industrial processes [11, 12]. Recently we prepared several chemical compounds including SB's ligands that were used in many practical applications [13-24]. As a continuation of this approach simple V-shaped N4-chelate SB has been prepared *via* the condensation of picolinaldehyde with ethane-1,2-diamine. The SB V-shaped structure was proved by the XRD-crystal structure and calculated by DFT and HSA. The DFT-angle and bond distances structural parameters were successfully matched to the XRD-experimental parameters.

## 2. Materials

### 2.1. Chemicals

All solvents and chemicals were available from Sigma-Aldrich and employed without any purification.

### 2.2. Computational Details

The 2D-FP and HAS were carried out using Crystal Explorer 3.1 [25], Gaussian 09W 32 bit software was served for all DFT operations in gaseous state at DFT/B3LYP/6-311G(d) [26]

### 2.3. Synthesis of the SB

Ethane-1,2-diamine (0.01 mol) was dissolved in 5 mL of ethanol, then added to stirring picolinaldehyde (0.01 mol) dissolved 10 mL of ethanol. The mixture was subjected to reflux for 4 h. The precipitate product was filtrated, washed with hexane and purified by crystallization from  $\text{H}_2\text{O}/\text{ETOH}$  to afford the desired crystal in a good yield.

### 2.4. XRD-analysis

The structure was solved with the SHELXT, the model was refined with version 2018/3 of SHELXL [27]. The crystal structure and refinement parameters data of the the desired SB are illustrated in Table 1.

**Table 1.** Refinement details of SB crystal structure.

Chemical formula	C <sub>14</sub> H <sub>14</sub> N <sub>4</sub>
<i>M<sub>r</sub></i>	238.29
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.347 (5), 5.9339 (12), 13.165 (2)
β (°)	122.266 (8)
<i>V</i> (Å <sup>3</sup> )	1278.0 (5)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm <sup>-1</sup> )	0.61
Crystal size (mm)	0.30 × 0.27 × 0.25
Diffractometer	Bruker X8 Proteum
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.837, 0.862
No. of measured, independent and observed reflections	1539, 933, 881
<i>R</i> <sub>int</sub>	0.015
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.582
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.043, 0.120, 1.05
No. of reflections	933
No. of parameters	82
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.10, -0.10

### 3. Results and Discussions

#### 3.1. XRD and DFT analysis

The final (N<sup>1</sup>E,N<sup>2</sup>E)-N<sup>1</sup>,N<sup>2</sup>-bis(pyridin-2-ylmethylene)ethane-1,2-diamine product was prepared via condensation of one mole of ethane-1,2-diamine with two mole of picolinaldehyde in ethanol under for 4 hours of reflux conditions as seen in Scheme 1.

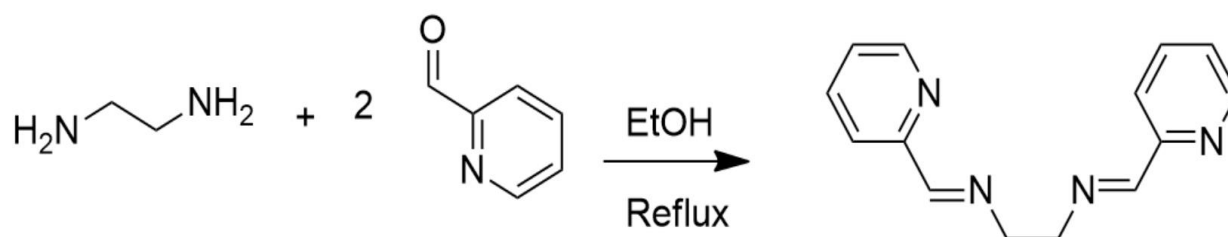
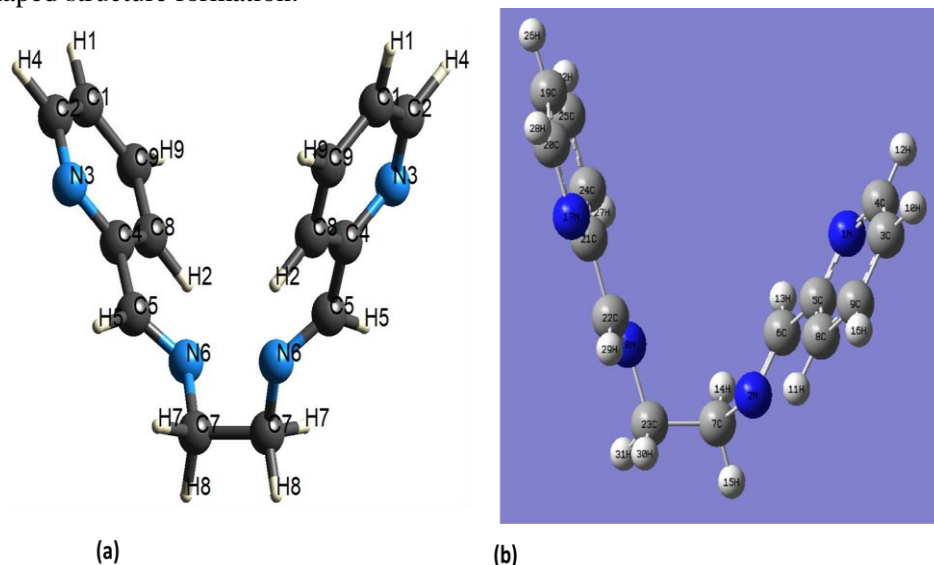
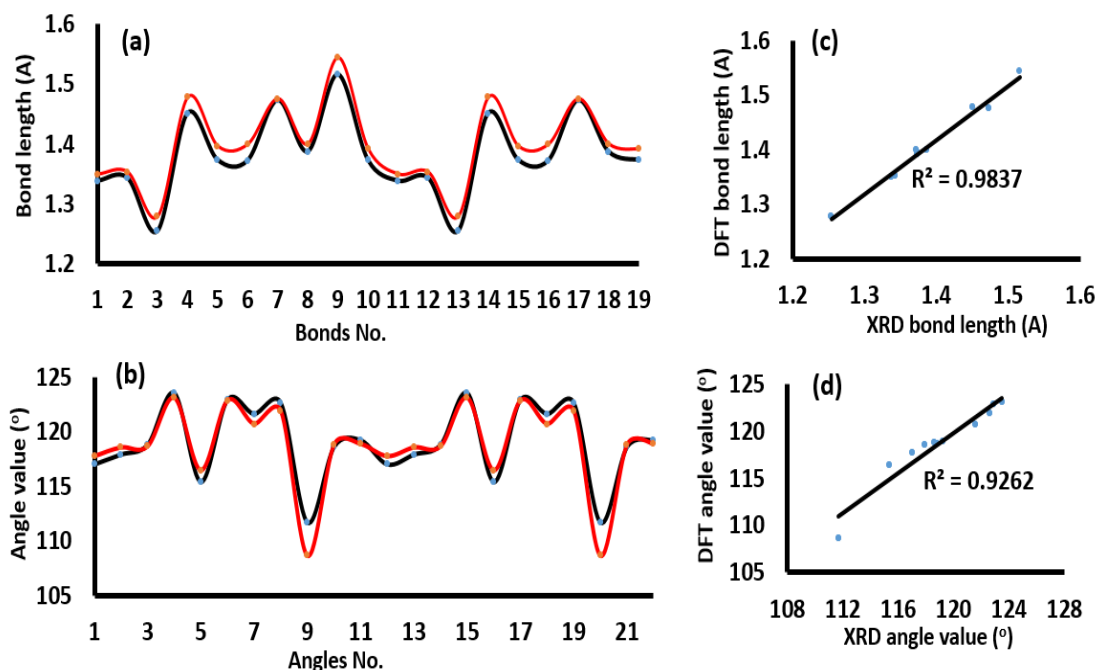
**Scheme 1.** Synthesis of desired V-shaped SB ligand.

Fig. 1 illustrates the XRD and DFT-structure analysis of the desired SB ligand, which was crystallized in Monoclinic, space group  $C2/c$  with the following lattice parameters:  $c = 13.165 \text{ \AA}$ ,  $b = 5.9339 (12) \text{ \AA}$ ,  $a = 19.347 (5) \text{ \AA}$ , and  $\beta = 122.266 (8)^\circ$ . The selected bond angle and bond length of DFT outcomes and experimental XRD are listed in Table 2. The geometry of both C=N double bond groups is confirmed as the E-isomer. The XRD and DFT outcomes have also proved the V-shaped structure formation.



**Fig.1.** (a) 3D-ORTEP diagram, and (b) DFT structures of SB.

The XRD structural analysis parameters were compared to the 3D arrangement of DFT-optimized relatives (Fig. 2a and Fig. 2b). A high level of agreement between DFT and XRD results were recorded, since the graphical correlations of values of bond lengths and bond angles gave  $R^2 = 0.9837$  and  $0.9262$ , respectively, Fig. 2c and Fig. 2d.. Such seen reflected the simulated and experimental outcomes of bond length values are better compared to the angels values.



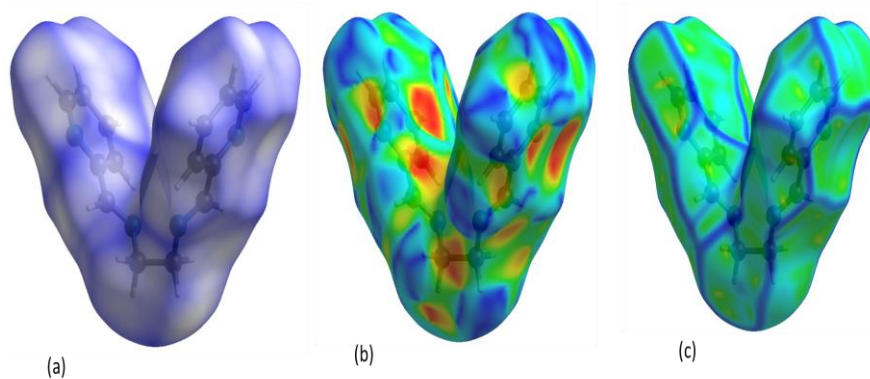
**Fig. 2.** (a) DFT/XRD histogram of bond lengths, (b) DFT/XRD histogram bond angles, (c) DFT/XRD-graphical correlation for bond lengths and (d) bond angles.

**Table 2.** XRD/DFT selected angles and bond lengths.

Bond no.	Bond (Å)	Exp. XRD	DFT/B3LYP	Angles No.	Angles (°)	Exp. XRD	DFT/B3LYP
1	N3 C2	1.338(2)	1.349	1	C2 N3 C4	117.0(1)	117.75
2	N3 C4	1.343(2)	1.3524	2	C5 N6 C7	117.9(1)	118.55
3	N6 C5	1.254(2)	1.2784	3	C2 C1 C9	118.8(2)	118.65
4	N6 C7	1.451(2)	1.4781	4	N3 C2 C1	123.5(2)	123.09
5	C1 C2	1.373(3)	1.3956	5	N3 C4 C5	115.4(1)	116.45
6	C1 C9	1.372(3)	1.3995	6	N3 C4 C8	122.9(1)	122.85
7	C4 C5	1.473(2)	1.4752	7	C5 C4 C8	121.6(1)	120.7
8	C4 C8	1.387(3)	1.3997	8	N6 C5 C4	122.6(1)	121.88
9	C7 C7	1.516(2)	1.5443	9	N6 C7 C7	111.7(1)	108.64
10	C8 C9	1.373(2)	1.391	10	C4 C8 C9	118.6(1)	118.81
11	N3 C2	1.338(2)	1.349	11	C1 C9 C8	119.2(2)	118.86
12	N3 C4	1.343(2)	1.3524	12	C2 N3 C4	117.0(1)	117.75
13	N6 C5	1.254(2)	1.2784	13	C5 N6 C7	117.9(1)	118.55
14	N6 C7	1.451(2)	1.4781	14	C2 C1 C9	118.8(2)	118.65
15	C1 C2	1.373(3)	1.3956	15	N3 C2 C1	123.5(2)	123.09
16	C1 C9	1.372(3)	1.3995	16	N3 C4 C5	115.4(1)	116.45
17	C4 C5	1.473(2)	1.4752	17	N3 C4 C8	122.9(1)	122.85
18	C4 C8	1.387(3)	1.3997	18	C5 C4 C8	121.6(1)	120.7
19	C8 C9	1.373(2)	1.391	19	N6 C5 C4	122.6(1)	121.88

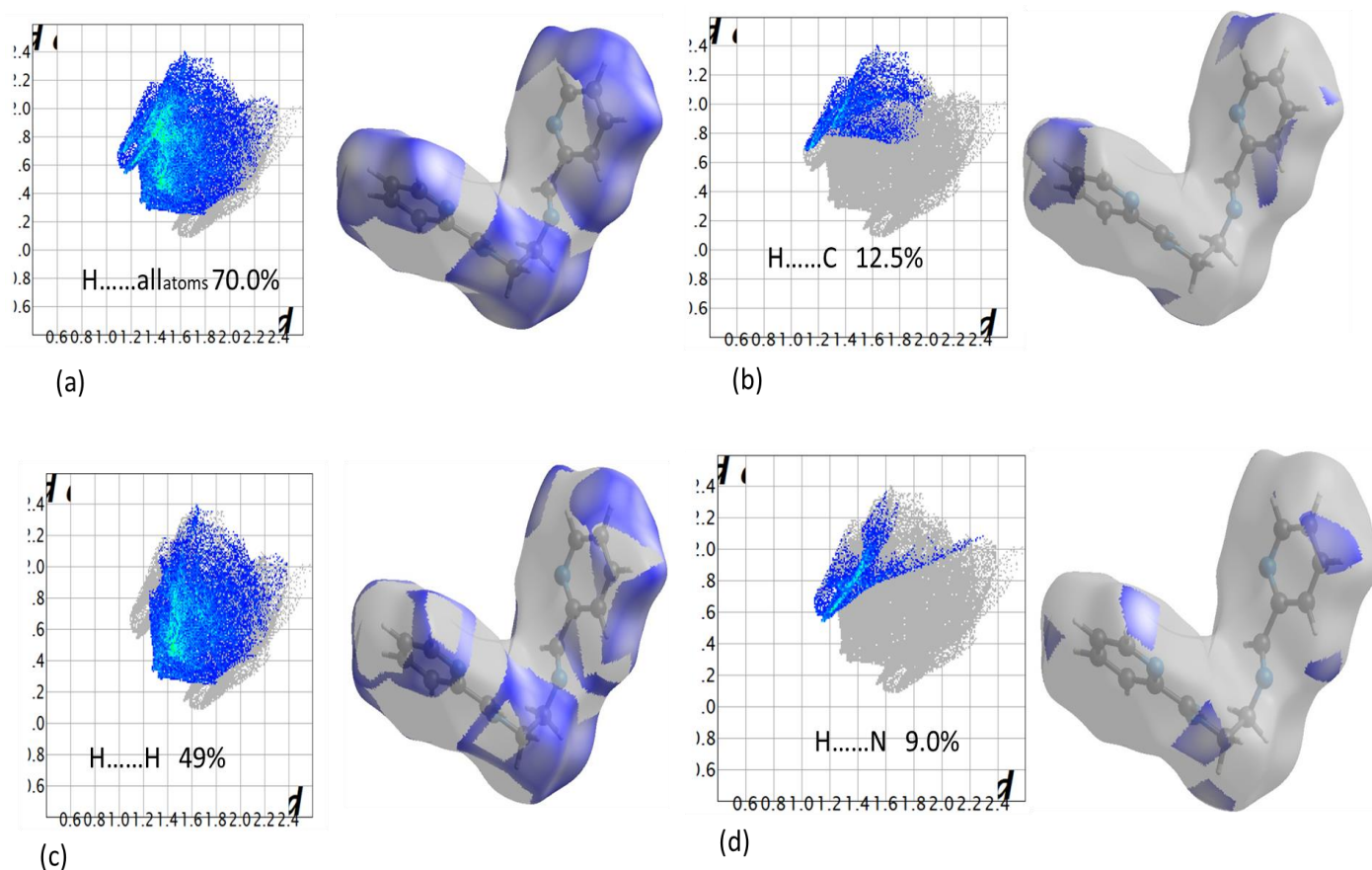
### 3.2. HSA investigation

The HSA analysis was carried out using CIF file of the solved crystal. The analysis supported the formation of V-shaped of the desired SB N4-ligand, since no red-spots on the structure surface at the  $d_{\text{norm}}$  of the molecule, therefore no interactions were cited in the lattice of the crystal [28-30], such results are matched well with XRD-experimental collected data (Fig. 3). The shape index (Fig. 3b) showed the presence of broad red color, which reflects the electronic abundance around the aromatic ring and 4-nitrogen atoms.

**Fig. 3.** (a) Mapped  $d_{\text{norm}}$ , (b) shape index (c-d) and (c)

### 3.3. 2D-FP investigations

The 2D-FP computational analysis confirmed the existence of intermolecular interactions in the subordinate:  $\text{H}\cdots\text{H} > \text{C}\cdots\text{H} > \text{N}\cdots\text{H}$  only, as illustrated in Fig. 4a-d. The percentage of atom-to-atom fingerprint interactions revealed the  $\text{H}\cdots\text{H}$  bonds with 49% ratio consider to be the major contributor, the  $\text{C}\cdots\text{H}$  with 12.5%, meanwhile the  $\text{N}\cdots\text{H}$  with 9% consider to be the minor contributor.



**Fig. 4.** 2D-FP atom-to-atom ratios and interactions contributions.

## 4. Conclusions

The V-shaped N4-SB novel ligand was synthesized in good yield *via* condensation of picolinaldehyde with ethane-1,2-diamine in ethanol solution under reflux condition. The N4-SB V-shaped structure was proved by XRD-crystal diffraction, 2D-FP, and HSA analysis. The optimization result of the DFT structure was matched well with the XRD experimental result. The DFT bonds and angles structural parameters lengths were matching very good with the experimental XRD results.

## REFERENCES

- [1] I. Warad, A. A. Khan, M. Azam, S. I. Al-Resayes, and S. F. Haddad. *J. Molec. Struct.*, 1062 (2014): 167-173.
- [2] I. Warad, M. Abdoh, N. Shivalingegowda, N. K. Lokanath, R. Salghi, M. Al-Nuri, S. Radi, B. Hammouti, *J. Molec. Struct.*, 1099 (2015): 323-329.
- [3] M. Azam, I. Warad, S. I. Al-Resayes, N. Alzaqri, M. R. Khan, R. Pallepogu, S. Dwivedi, J. Musarrat, and M. Shakir. *J. Mol. Struct.*, 1047 (2013): 48-54.
- [4] I. Warad, M. Azam, U. Karama, S. Al-Resayes, A. Aouissi, and B. Hammouti. *J. Mol. Struct.*, 1002 (2011): 107-112.
- [5] N. Li, L. Chen, F. Lian, F. Jiang, and M. Hong, *Inorg. Chim. Acta*, 363 (2010): 3291–3301
- [6] H. Wu, J. Yuan, Y. Zhang, F. Shi, G. Pan, J. Kong, and X. Fan *Inorg. Chim. Acta*, 404 (2013): 13–22
- [7] R. M. Ramadan, A. K. Abu Al-Nasr, and A. F.H. Noureldeen. *Spectrochim. Acta A*, 132 (2014): 417–422.



- [8] B.S. Creaven, B. Duff, D.A. Egan, K. Kavanagh, G. Rosair, V.R. Thangella, M. Walsh, *Inorg. Chim. Acta*, 363 (2010): 4048-4058.
- [9] A. Golcu, M. Tumer, H. Demirelli, R.A. Wheatley, *Inorg. Chim. Acta*, 358 (2005): 1785-1797.
- [10] G. Ceyhana, C. Celik, S. Urus, I. Demirtas, M. Elmastas, M. Tumer, *Spectrochim. Acta A*, 81 (2011): 184-198.
- [11] S. A. Beyramabadi, M. Saadat-Far, A. Faraji-Shovey, M. Javan-Khoshkholgh, and A. Morsali, *J. Molec. Struct.*, 1208 (2020): 127898-127905.
- [12] V. Nagalakshmi, M. Sathya, M. Premkumar, D. Kaleeswaran, G. Venkatachalam, and K. Balasubramani, *J. Organomet. Chem.* 914 (2020): 121220-121230.
- [13] S. Tighadouini, S. Radi, M. Bacquet, J.P. Dacquin, Y.N. Mabkhot, I. Warad, and M. Zaghrioui. *Sep. Sci. Technol.* 50 (2015): 710-717.
- [14] I. Warad. *Molecules* 15, (2010): 4652-4669.
- [15] I. Warad, M. R. H. Siddiqui, S. Al-Resayes, A. Al-Warthan, and R. Mahfouz, *Transit. Metal Chem*, 34, (2009):347-352.
- [16] I. Warad, Z. Al-Othman, S. Al-Resayes, S. S. Al-Deyab, and E. Kenawy. *Molecules* 15 (2010): 1028-1040.
- [17] M. E. Belghiti, Y. Karzazi, S. Tighadouini, A. Dafali, C. Jama, I. Warad, B. Hammouti, and S. Radi. *J Mater Environ Sci* 7 (2016): 956-967.
- [18] I. Warad, A. A. F. Eftaiha, M. A. Al-Nuri, A. I. Husein, M. Assal, A. Abu-Obaid, N. Al-Zaqri, T. B. Hadda, and B. Hammouti. *J. Mater. Environ. Sci.*, 4 (2013): 542-557.
- [19] A. Mansri, B. Bouras, B. Hammouti, I. Warad, and A. Chetouani. *Res. Chem. Intermediates*, 39 (2013): 1753-1765.
- [20] M. Suleiman, M. Al-Masri, A. A. Ali, D. Aref, A. Hussein, I. Saadeddin, and I. Warad, *J Mater Environ Sci.* 6, (2015): 513-518.
- [21] I. Warad, F. Eftaiha, M. Al-Nuri, I. Husein, M. Assal, A. Abu-Obaid, N. Al-Zaqri, B. Hadda and B. Hammouti, *J Mater Environ Sci.*, 4, (2013): 542-557.
- [22] A. Chetouani, K. Medjahed, S. Al-Deyab, I. Warad, and A. Mansri, *J Mater Environ Sci.*, 7 (2012): 6025-6043.
- [23] M. Belghiti, Y. Karzazi, S. Tighadouini, A. Dafal, C. Jama, I. Warad and B. Hammouti, and S. Radi, *J Mater Environ Sci.*, 7 (2016): 956-967.
- [24] M. Rbaa, F. Benhiba, B. Obot, H. Oudda, I. Warad, B. Lakhri, and A. Zarrouk, *J. Molec. Liq.* 276 (2019): 120-133.
- [25] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, D. Jayatilaka, and M. A. Spackman, Crystal explorer 2.1. University of Western Australia, Perth (2007).
- [26] M.J. Frisch, G.W. Trucks, et. al. Gaussian 09, Gaussian Inc., Wallingford CT, 2009.
- [27] G. M. Sheldrick, *Acta Cryst.*, A64 (2008): 112-114.
- [28] I. Warad, O. Bsharat, S. Tabti, A. Djedouani, M. Al-Nuri, N. Al-Zaqri, K. Kumara, N.K. Lokanath, S. Amereih, and Ib. M. Abu-Reidah *J. Mol. Struct.*, 1185 (2019): 290-299.
- [29] M. R. Aouad, M. Messali, N. Rezki, N. Al-Zaqri, and I. Warad, *J. Molec. Liq.*, 264 (2018): 621-630
- [30] M. R. Aouad, M. Messali, N. Rezki, M. A. Said, D. Lentz, L. Zubaydi, and I. Warad, *J. Molec. Struct.*, 1180 (2019): 455-461.