

## Synthesis, Structural Characterization and EF-QTAIM Study of a New Schiff Base Ligand, Pyridine 3-Carbaldehyde Thiosemicarbazone (as a Molecular Wire)

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(Received 13 March 2020, Accepted 6 June 2020)

A new Schiff base ligand, pyridine 3-carbaldehyde thiosemicarbazone (1), was synthesized and structurally characterized. Its synthesis involves a Schiff base condensation of thiosemicarbazide and pyridine 3-carbaldehyde. The new compound was determined through elemental analyses, FT-IR spectroscopy, and single-crystal X-ray crystallography. Compound 1 has a monoclinic crystallographic arrangement with a P21/n space group. It can be introduced as a tridentate NNS donor ligand for the synthesis of several complexes with new structures. With several H-bondings, the structure showed the three-dimensional structures. In addition, the electronic properties of pyridine 3-carbaldehyde thiosemicarbazone were studied, in atomic-scale, using density functional theory (DFT) and quantum theory of atoms in molecules (QTAIM). Also, the external electric field (EF) effects on electronic/vibrational properties of this chemical compound (as molecular wire) were studied using QTAIM at the atomic scale (EF-QTAIM). Moreover, analysis of the current-voltage (I-V) curve results showed that this molecule can be used as a stable molecular wire.

**Keywords:** Crystal structure, Schiff base ligand, Thiosemicarbazone, H-bonding, QTAIM

### INTRODUCTION

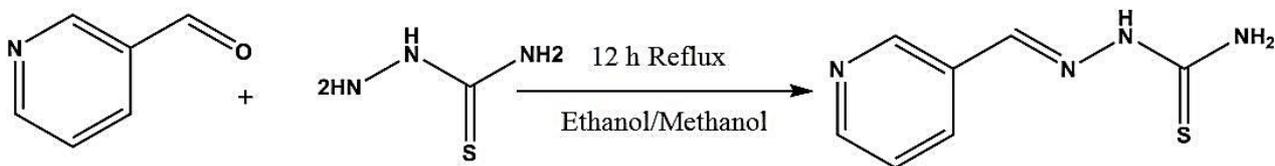
The design and synthesis of new organic ligands with donor sites are essential in coordination chemistry [1-3]. A Schiff base ligand plays many essential roles in coordination chemistry and formation of coordination compounds. A Schiff base is formed from a condensation reaction between an amine and an aldehyde molecule through the formation of imine (C=N) bond. The amine and aldehyde compounds used for the formation of Schiff base ligands have a significant effect on the behavior of these compounds. Position of donor atoms in Schiff base ligand also has a significant effect on the formation of coordination compounds [4-6].

The Schiff base ligands and their coordination compounds potentially have bioactive applications, and

antimicrobial, antibacterial, antifungal, and anticancer activities [7-9]. The Schiff base coordination compounds have contributed widely to the coordination chemistry of chelate systems. The Schiff bases involving in the pyridine ring have received considerable attention in the literature [10,11]. The semicarbazones usually behave as chelating ligands, which are versatile in both neutral and anionic forms [12]. Metal complexes of thiosemicarbazones and semicarbazones have gained special attention due to their importance in medicine and biological system [13,14]. Furthermore, the metal complexes of thiosemicarbazones have demonstrated antimicrobial, anticancer, and antiviral activities [15,16].

In this work, we report the synthesis of a new Schiff base ligand, pyridine 3-carbaldehyde thiosemicarbazone. The new compound was characterized by FT-IR, CHN and single-crystal X-ray analyses. In addition, the local/atomic electronic properties of molecular systems, shown in

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Scheme 1. The Schiff base ligand of pyridine 3-carbaldehyde thiosemicarbazone (1)

Scheme 1, are studied, using the quantum theory of atoms-in-molecules (QTAIM)[17-19]. The QTAIM describes an open quantum system in terms of the topology of the electron density,  $\rho(r)$ , to determine its chemical behavior and reactivity via partitioning the molecular space into atomic basins ( $\Omega$ ) which allows partitioning of overall electronic properties into additive atomic contributions in one consistent theoretical framework. Based on the QTAIM, the local kinetic energy ( $K(r)$ ), potential/virial energy ( $v(r)$ ) and thus total electronic energies ( $E$ ) can be obtained by summing the corresponding quantities of all  $N_{\Omega}$  atomic basins ( $\Omega$ ) of the molecule as,

$$K = \sum_{\Omega} K(\Omega) \quad ; \quad V = \sum_{\Omega} V(\Omega) \quad (1)$$

and thus  $E = \sum_{\Omega} E(\Omega)$ . Also, the Schrödinger form of the electronic kinetic energy is given in terms of the electronic wavefunction as

$$K(\Omega) = \frac{-\hbar^2}{4m} N \int_{\Omega} d\tau' [\psi \nabla^2 \psi^* + \psi^* \nabla^2 \psi] d\tau' \quad (2)$$

where  $\int_{d\tau'}$  denotes integration over the spin coordinates of all electrons and the spatial coordinates of all electrons but one. Also, based on the atomic Virial theorem, the total atomic electronic energy,  $E(\Omega)$ , is sum of the kinetic and potential/virial energies,  $K(\Omega)$  and  $V(\Omega)$ , as

$$E(\Omega) = K(\Omega) + v(\Omega) \quad (3)$$

In this work, geometry optimization and calculation of the

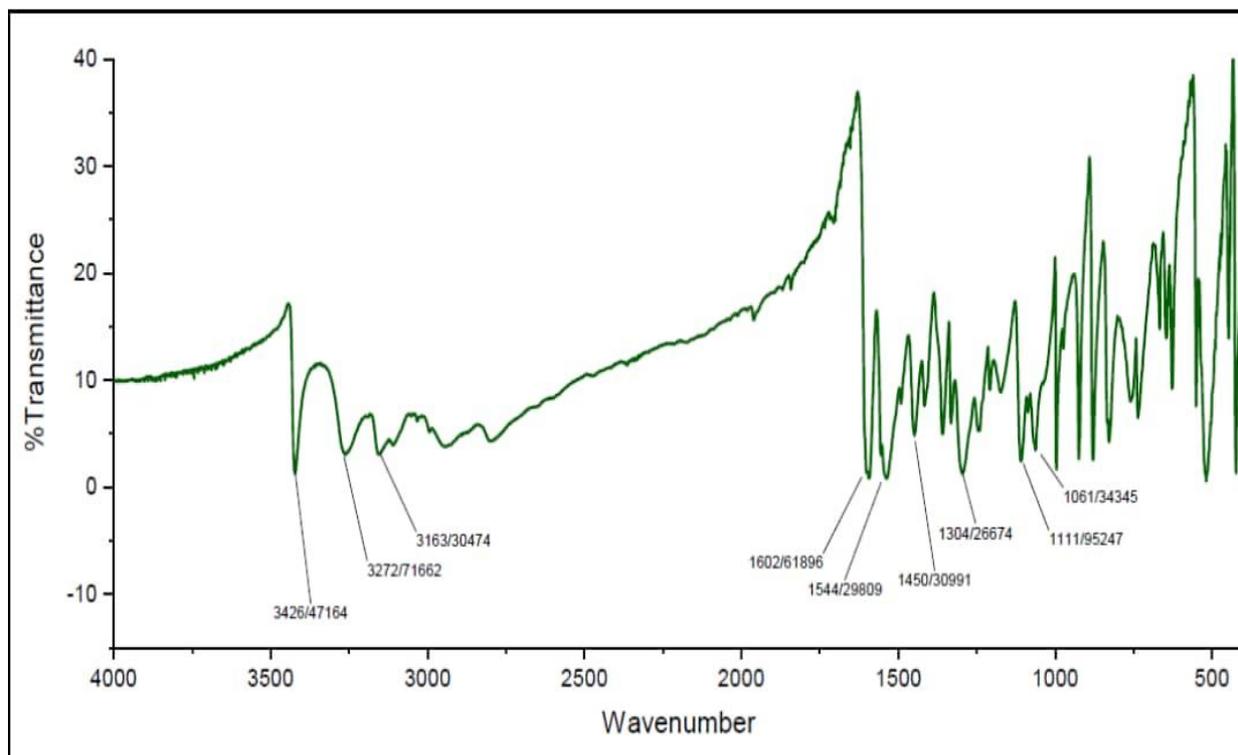
structural and electronic wave functions of pyridine 3-carbaldehyde thiosemicarbazone have been carried out at the DFT-UB3LYP/6-311G\* level of theory, using 09 program [20]. Also, the QTAIM analysis was carried out using Bader's AIMPACK program package [21].

## EXPERIMENTAL

From Sigma-Aldrich (Seoul, South Korea), the chemicals were acquired and utilized as received with no additional purifying. The specimens' elemental evaluations were performed utilizing a VarioMicroanalyzer. Utilizing KBr disks within 4000-400  $\text{cm}^{-1}$ , recording infrared spectra was performed on a Bruker Vector 22 FT-IR spectrometer. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Using epoxy adhesive, a crystal of the compound was mounted over glass fiber. The data were collected utilizing an X-ray diffractometer through graphite-monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and acting at 30 mA and 50 kV over the  $2\theta$  range of 7.34-52.00°. The FT-IR spectra were recorded on a Shimadzu system FT-IR 160 spectrophotometer using KBr pellets.

### Synthesis of Pyridine 3-Carbaldehyde Thiosemicarbazone (1)

Thiosemicarbazide (10 mmol) was dissolved in 30 ml methanol under reflux condition, and pyridine 3-carbaldehyde (10 mmol) was dissolved in 30 ml ethanol and added dropwise to the solution within 10 min. The mixture was refluxed on 69 °C for 12 h to give a solution with a yellow precipitate. The precipitate was filtered, washed with



**Fig. 1.** The FT-IR spectrum of 1.

methanol, dried in oven 50 °C for 4 h and used without further purification. (Yield: 88%), [m. p.: 163 °C]. 0.1 g of the precipitate dissolved in 10 ml hot methanol, the solution was cooled and allowed to crystallize at room temperature. After keeping the solution in the air for 3 days, by slow evaporation of the solvent, white crystals formed at the bottom of the vessel. The resulting crystals were collected by filtration and dried at room temperature. Anal. Calcd. for  $C_8H_{12}N_4OS$ : C, 45.27; H, 5.70; N, 26.39. Found: C, 45.00; H, 6.00; N, 27.00. Characteristic FT-IR data (KBr,  $cm^{-1}$ ): 519, 627, 996, 1063, 1109, 1448, 1359, 1593, 3262, 3422.

### Crystallographic Analysis

The single-crystal X-ray analysis showed that the compound is crystallized in a monoclinic structure with a space group of  $P2_1/n$ . The unit cell parameters are:  $a = 11.6078$  (11),  $b = 6.9473$  (5),  $c = 13.7974$  (13),  $\alpha = 90$ ,  $\beta = 112.129$  (3),  $\gamma = 90$ . The volume of unit cell is 1030.70

(16)  $\text{\AA}^3$  (Table S1).

## RESULTS AND DISCUSSION

The FT-IR of 1 is shown in Fig. 1. Two medium bands at 3422 and 3262  $cm^{-1}$  for the  $NH_2$  and N-H stretching, and a sharp band at 1109 related to N-N bond are observed. Furthermore, the strong band obtained at 1602  $cm^{-1}$  clearly indicates the presence of an imine functionality resulting from the condensation of thiosemicarbazide with pyridine 3-carboxaldehyde

The bands at 2846 and 2955  $cm^{-1}$  correspond to the C-H bond of aldehyde. The strong bands at 1448  $cm^{-1}$  and 1395-1593  $cm^{-1}$  are related to aliphatic C-N bonds and aromatic C=C bonds, respectively. The low energy pyridine ring in-plane and out-of-plane vibrations are observed at 627 and 519  $cm^{-1}$ . The O-H vibration of methanol solvent is not observed in FT-IR, that might be due to the intermolecular

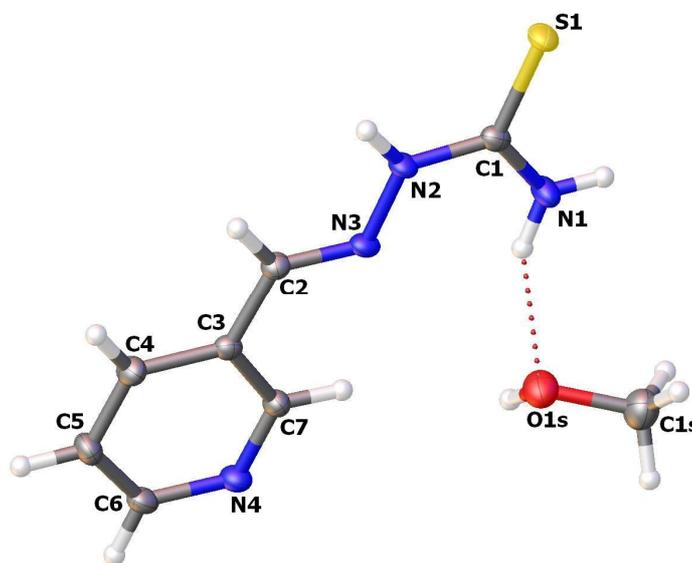


Fig. 2. The structure of ligand from X-ray crystallography.

H-bonding interactions. The origin of broad signals between 1700-3500  $\text{cm}^{-1}$  may be indicative of this effect.

The structure of 1 is shown in Fig. 2. The synthesized ligand crystallizes in a monoclinic system with space group of  $P2_1/n$ . Single X-ray crystal analysis reveals that 1 consists of a Schiff base molecule and one methanol molecule. The structural formula of the compound can be summarized as  $[L] \cdot (\text{CH}_3\text{OH})$ . As seen in Fig. 1 and according to FT-IR data, the ligand is not deprotonated and is in its regular form.

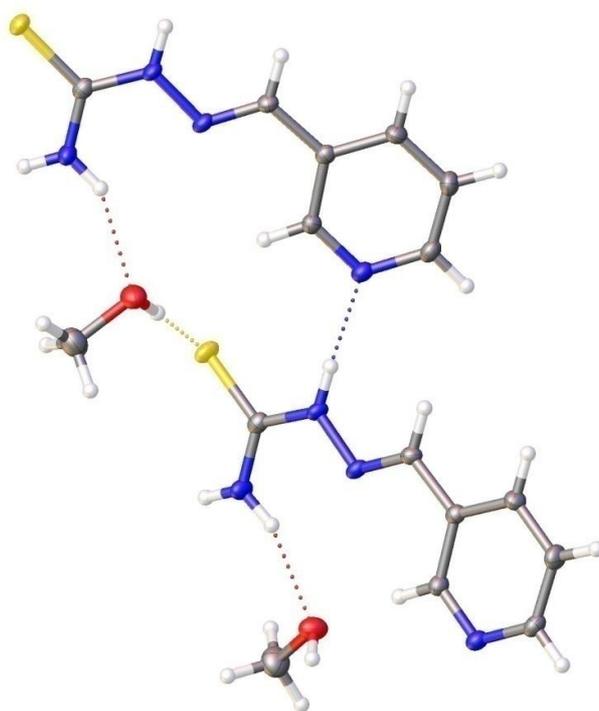
The X-ray crystallography showed that the shortest bond distances of the pyridine ring are N4-C7 (1.3353(18) Å) and N4-C6 (1.3431(19) Å). The bond distances of C-C or C=C of pyridine ring are between 1.375(2) Å and 1.388(2) Å. The bond distances and angles are summarized in Table 2. The bond length of C2=N3 (1.2774(19) Å) in 1 is in consistent with the bond distance of C=N in similar ligands [22]. Although the molecule contains an aromatic cycle, there is no pi-pi stacking interaction in the structure of 1. The packing of the molecules in three-dimensional structures is due to the several hydrogen bondings illustrated in Figs. 3-5. Hydrogen bonds are summarized in

Table 3.

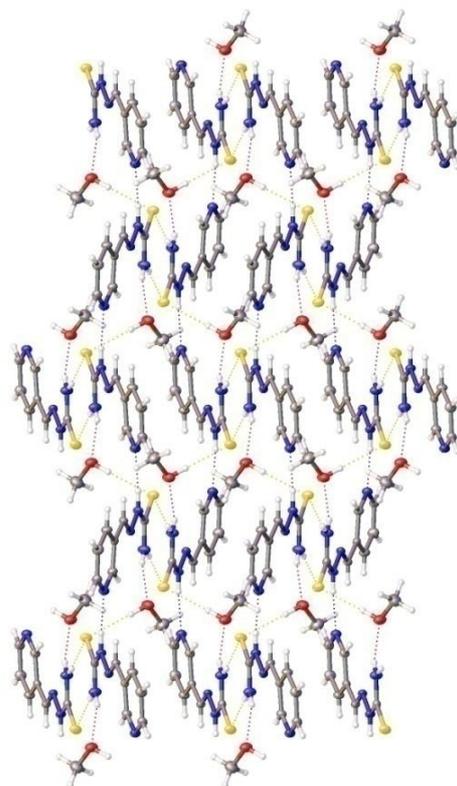
## QTAIM STUDY RESULTS: QUANTUM CHEMISTRY METHODOLOGY

In this work, electronic characteristics (at atomic scale) of the chemical compound under study, Scheme 1, are performed using quantum theory of atoms in molecules (QTAIM). The geometry optimization and calculation of the structural and electronic properties of the target compound have been carried out at DFT-UB3LYP/6-311G\* level of theory, [23], using G09/QTAIM programs [20,21].

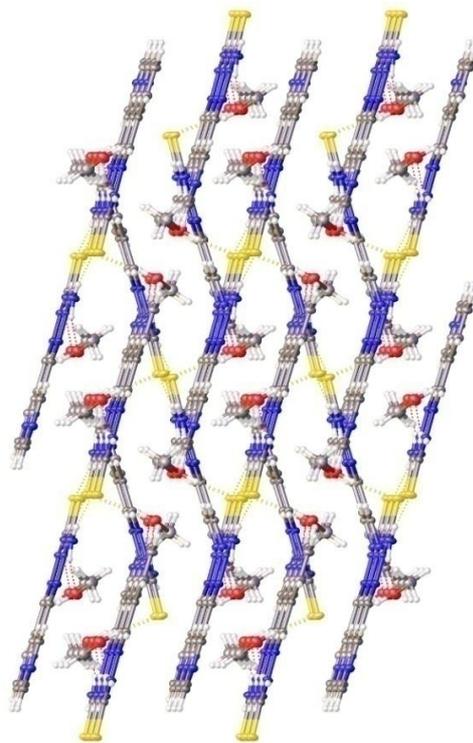
Also, based on the QTAIM analysis, the compound under study is divided into four intra-molecular sections: left ( $S_L$ ), right ( $S_R$ ), up ( $S_U$ ) and down ( $S_D$ ) defined in terms of the sub-sections,  $S_I$  to  $S_{IV}$ , via  $S_L \equiv S_{II} \oplus S_{IV}$ ,  $S_U \equiv S_I \oplus S_{III}$  and  $S_D \equiv S_{III} \oplus S_{IV}$  (Fig. 6), where  $A_{\text{Molecule}} = \sum_{\Omega} A(\Omega)$  and  $S_i \equiv \sum_{I \in S_i} N_{S_i}(\Omega)$ . For example, within QTAIM, the electronic kinetic energy of each section  $S_i$  is given by:  $\langle K(S_i) \rangle_{\Omega} \equiv K(S_i) = \sum_{\Omega \in S_i} K(\Omega)$ .



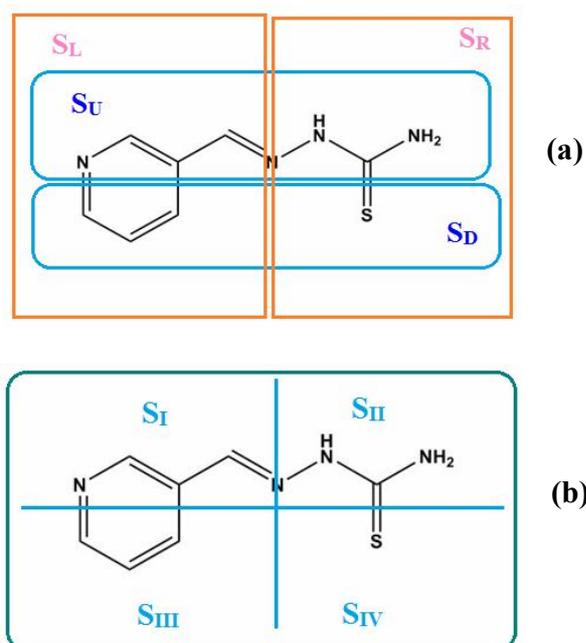
**Fig. 3.** H-bonding interactions in 1.



**Fig. 4.** Expansion of ligand with intermolecular H-bonding interactions in two dimensions.



**Fig. 5.** Expansion of ligand with intermolecular H-bonding interactions in three dimensions.



**Fig. 6.** The intermolecular sections (a), and the sub-sections (b) of the chemical compound under study.

**Table 2.** Selected Bond Distances (Å) and Bond Angles (°) of 1

		C(2)-H(2)	0.953(18)
S(1)-C(1)	1.7056(15)	C(3)-C(4)	1.388(2)
N(1)-C(1)	1.320(2)	C(3)-C(7)	1.391(2)
N(1)-H(1NA)	0.88(2)	C(4)-C(5)	1.386(2)
N(1)-H(1NB)	0.83(2)	C(4)-H(4)	0.929(19)
N(2)-C(1)	1.3448(19)	C(5)-C(6)	1.375(2)
N(2)-N(3)	1.3763(16)	C(5)-H(5)	0.968(19)
N(2)-H(2N)	0.90(2)	C(6)-H(6)	0.951(18)
N(3)-C(2)	1.2774(19)	C(7)-H(7)	0.936(18)
N(4)-C(7)	1.3353(18)	O(1S)-C(1S)	1.418(2)
N(4)-C(6)	1.3431(19)	O(1S)-H(1SO)	0.89(2)
C(2)-C(3)	1.4662(19)	C(1S)-H(1SA)	0.98
C(1S)-H(1SB)	0.98	C(5)-C(4)-C(3)	118.95(14)
C(1S)-H(1SC)	0.98	C(5)-C(4)-H(4)	120.5(11)
C(1)-N(1)-H(1NA)	121.1(13)	C(3)-C(4)-H(4)	120.5(11)
C(1)-N(1)-H(1NB)	19.4(14)	C(6)-C(5)-C(4)	118.99(14)
H(1NA)-N(1)-H(1NB)	118.8(18)	C(6)-C(5)-H(5)	120.4(12)
C(1)-N(2)-N(3)	118.33(12)	C(4)-C(5)-H(5)	120.6(12)
C(1)-N(2)-H(2N)	121.0(12)	N(4)-C(6)-C(5)	123.20(14)
N(3)-N(2)-H(2N)	120.6(12)	N(4)-C(6)-H(6)	116.8(10)
C(2)-N(3)-N(2)	116.02(13)	C(5)-C(6)-H(6)	120.0(11)
C(7)-N(4)-C(6)	117.25(13)	N(4)-C(7)-C(3)	123.81(14)
N(1)-C(1)-N(2)	118.43(14)	N(4)-C(7)-H(7)	116.0(11)
N(1)-C(1)-S(1)	122.60(12)	C(3)-C(7)-H(7)	120.2(11)
N(2)-C(1)-S(1)	118.98(11)	C(1S)-O(1S)-H(1SO)	106.9(14)
N(3)-C(2)-C(3)	119.72(14)	O(1S)-C(1S)-H(1SA)	109.6
N(3)-C(2)-H(2)	122.7(10)	O(1S)-C(1S)-H(1SB)	109.6
C(3)-C(2)-H(2)	117.5(10)	H(1SA)-C(1S)-H(1SB)	109.6
C(4)-C(3)-C(7)	117.79(13)	O(1S)-C(1S)-H(1SC)	109.6
C(4)-C(3)-C(2)	120.54(13)	H(1SA)-C(1S)-H(1SC)	109.6
C(7)-C(3)-C(2)	121.65(13)	H(1SB)-C(1S)-H(1SC)	109.6

**Table 3.** H-bonds for [ $\text{\AA}$  and  $^\circ$ ]

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1NA)...O(1S)	0.88(2)	2.13(2)	2.9388(18)	152.4(17)
N(1)-H(1NB)...S(1)#1	0.83(2)	2.62(2)	3.4368(15)	167.9(18)
N(2)-H(2N)...N(4)#2	0.90(2)	1.99(2)	2.8899(18)	174.6(18)

Symmetry transformations used to generate equivalent atoms:

#1  $-x, -y+1, -z+1$  #2  $x-1/2, -y+3/2, z-1/2$ **Table 4.** The Values of the Electronic Sectional  $\rho(S_i)$ ,  $K(S_i)$  and  $\nu(S_i)$ , Introduced in Eqs. (1)-(3), for Intra-molecular Sections ( $S_i$ ), of Pyridine 3-Carbaldehydethiosemicarbazone Molecular System, are Calculated Using QTAIM Theory (*all in a.u.*)

$S_i$	$\rho(S_i)$	$K(S_i)$	$\nu(S_i)$
$S_I$	31.50	221.00	-445.00
$S_{II}$	20.50	147.50	-297.00
$S_{III}$	16.50	112.5	-226.75
$S_{IV}$	15.935	397.50	-800.50

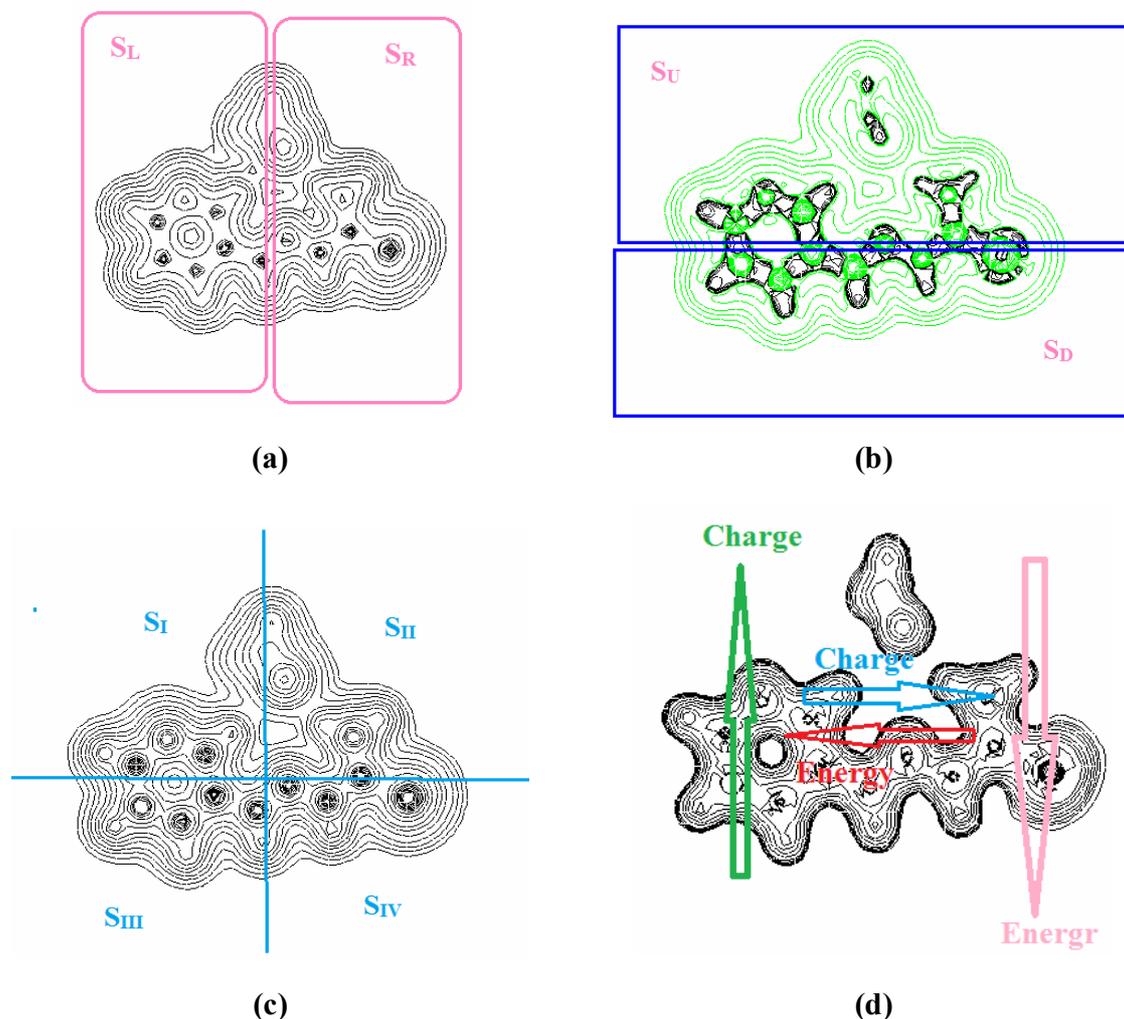
In addition, starting from the electronic wave functions of the optimized structures, the atomic basins are determined using a density gradient method. Also, based on the QTAIM analysis, the average values of some electronic properties, such as atomic electron density and energy, are calculated. Samples of these results are reported in Table 4 and shown in Fig. 7. Moreover, density of states (DOS) spectrum (and virtual/occupied orbitals) of pyridine 3-carbaldehyde thiosemicarbazone is shown in Fig. 8. Also, the external electric field (EF) effects on electronic/vibrational properties of this chemical compound (as a molecular wire) are studied using QTAIM at atomic scale (EF-QTAIM). A part of results is plotted in Figs. 8-10.

Analysis of EF-QTAIM calculation results shows that pyridine 3-carbaldehyde thiosemicarbazone can be

categorized into donor (*n-type*) and acceptor (*p-type*) intra-molecular sections, as an as intra-molecular semiconductor-like system.

In addition, the external field effect on the gap between the highest occupied and the lowest unoccupied molecular orbitals, HOMO-LUMO gap (HLG), have been calculated; these results are not reported for brevity. Based on the results, the HLG gap values almost decreased by increasing the field strength. Also, the DOS spectra, Fig.8, show that the orbital's energy gap ( $E_{HOMO} - E_{LUMO}$ ) of these molecular systems is relatively small. For example, at  $EF = 0$ , the value of the HLG is nearly  $HLG \approx -0.150\text{au}$ .

On the other hand, the molecular electric conductance ( $G$ ) can be obtained by



**Fig. 7.** The QAIM-based electronic contour maps of local  $\rho(r)$  (a), local  $\nabla^2\rho(r)$  (b), local  $v(r)$  (c), and local  $K(r)$  (d), introduced in Eqs. (1)-(3), for pyridine 3-carbaldehyde thiosemicarbazone.

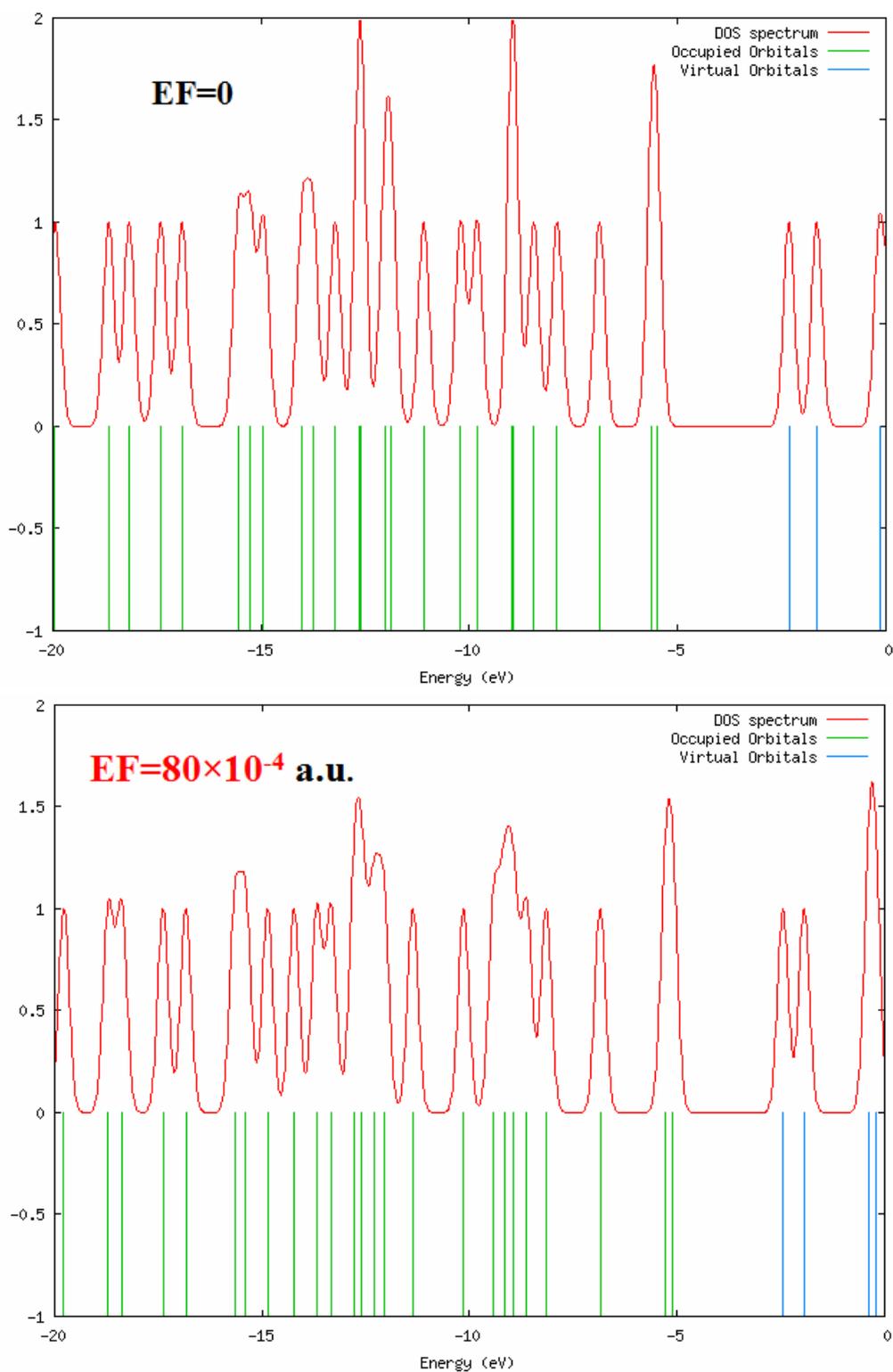
$$G \equiv \frac{1}{R} = \left( \frac{2e^2\tau_{elec}(\varepsilon)}{h} \right) \quad (4)$$

where  $\tau_{elec}(\varepsilon)$  is defined as  $\tau_{elec}(\varepsilon) \approx \exp(-\beta l)$ ,  $l$  is the molecular length and  $\beta$  is the tunneling decay coefficient [24]. Also,  $\Phi$  is related to HIG ( $E_{HOMO} - E_{LUMO}$ ) [24-25]. Based on Landaur formula, Eq. (4), the I-V characteristic curve and the electronic spatial extent (ESE) of this molecular wire are calculated and plotted in Fig. 11. This figure shows that the current increases (almost-linear) with

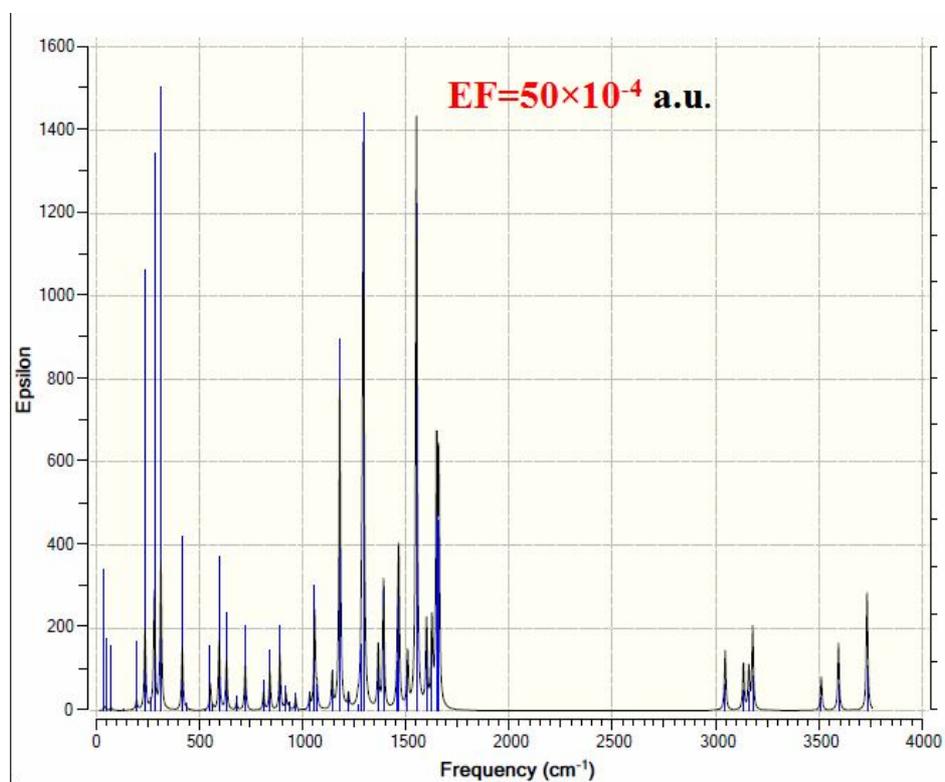
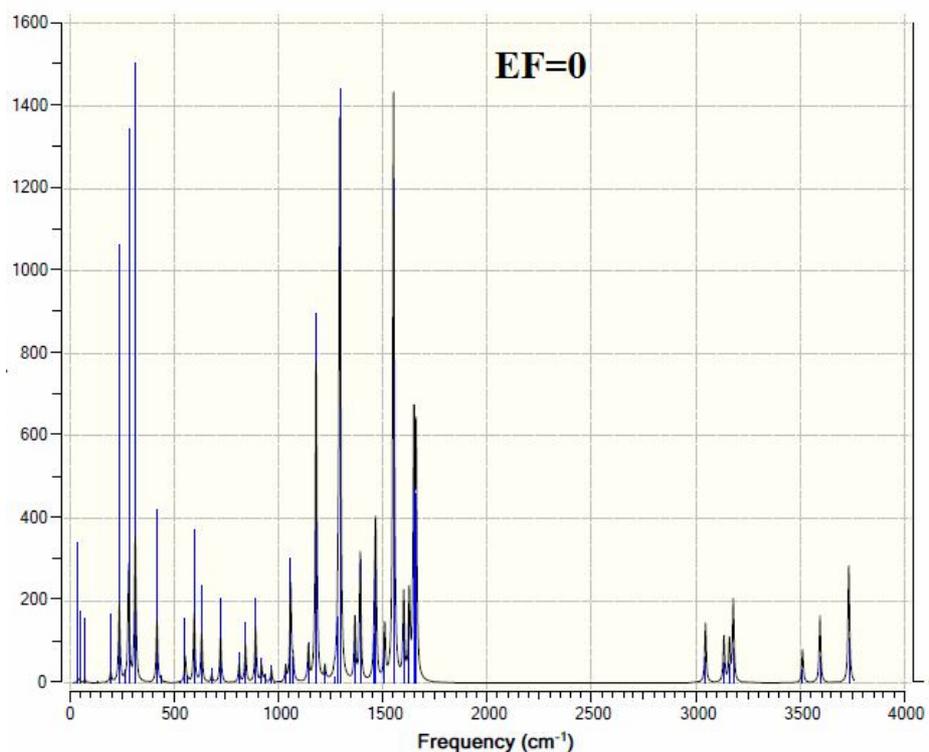
increasing the bias voltage. It can also be predicted that the intra-molecular charge/energy transfer efficiency (and thus intra-molecular semiconductor efficiency) of this chemical compound is acceptable. Therefore, it can be used in nanoelectronic circuits (as a stable molecular wire).

## CONCLUSIONS

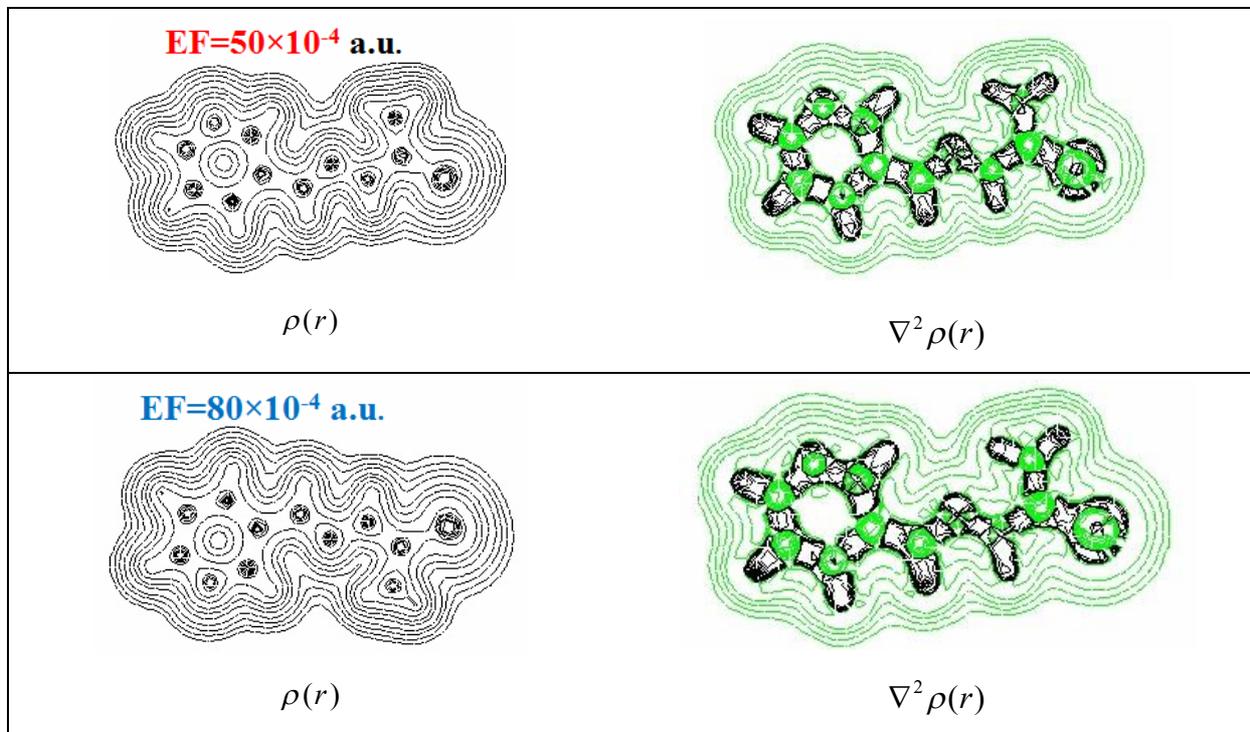
The novel Schiff base ligand of thiosemicarbazone 3-pyridinecarbaldehyde was synthesized and characterized by



**Fig. 8.** External field effect on the DOS spectrum of pyridine 3-carbaldehyde thiosemicarbazone.



**Fig. 9.** External field effect on vibrational frequencies of pyridine 3-carbaldehyde thiosemicarbazone.



**Fig. 10.** External field effect on local  $\rho(r)$  and  $\nabla^2\rho(r)$  of pyridine 3-carbaldehyde thiosemicarbazone, calculated using EF-QTAIM.

CHN analysis, FT-IR, and single-crystal X-ray crystallography. The structure of ligand obtained by crystallography showed the compound crystallized in a monoclinic structure with a space group of  $P2_1/n$ . Several H-bondings were observed between methanol solvent and ligand. With labile interactions, the ligand showed a three-dimensional structure.

Finally, when an EF is applied on a single molecule, Figs. 7-11, the charge and energy are transferred between its different intramolecular sections, resulting in a change in the distribution of electronic (vibrational) energies. Also, EF effect on local electronic contour maps show that a single field-effect molecular system can be categorized in *n*-type-like (donor-like) and *p*-type-like (acceptor-like) sections, and the charge and energy exchange between these intramolecular sections (as intramolecular semiconductor-like device) are due to the external field. Thus, based on the

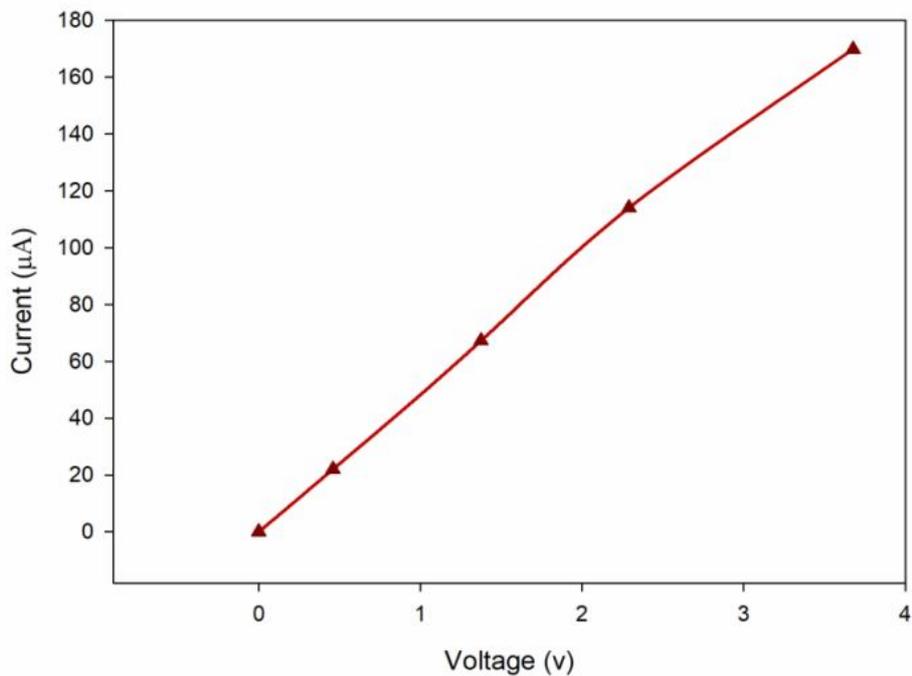
EF-QTAIM study results, it can be predicted that pyridine 3-carbaldehyde thiosemicarbazone compound can be used as an intramolecular semiconductor-like (or as an intramolecular wire-like) device in nanoelectronic systems.

### Supplementary Substance

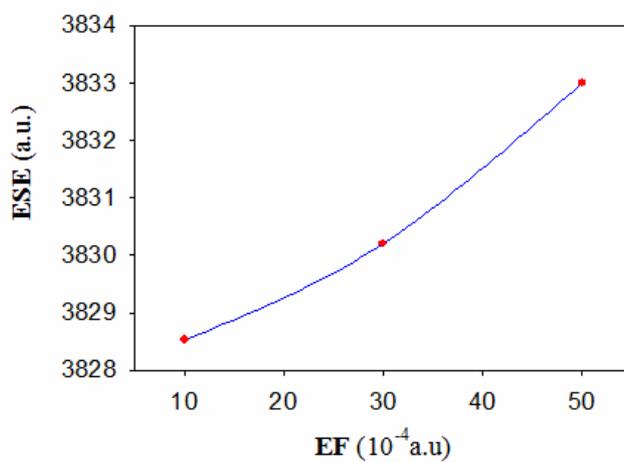
Here, the reported crystallographic information for the structures was provided by the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1986495. Duplicates of the information can be attained using the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: [de-posit@ccdc.cam.ac.uk](mailto:de-posit@ccdc.cam.ac.uk), Fax: +44-1223-336033).

### ACKNOWLEDGEMENTS

We acknowledge Sayyed Jamaledin Asadabadi University and the University of Qom for support of this work.



(a)



(b)

**Fig. 11.** The I-V characteristic curve (a) and electronic spatial extent (b) at various electric field intensities of the molecular wire studied in this work.

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