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Molecular Structure, Conformational Preference and Vibrational Spectral Analysis of 2-, and 3- Furancarboselenaldehyde Using DFT

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Abstract

This study deals with the molecular structure, conformational stability, electronic properties, and spectral properties of 2-and 3-furancarboselenaldehyde. The absorption, wavelength and excitation energy in methanol, the ^1H and ^{13}C NMR chemical shifts in chloroform, and the vibrational wavenumber for the rotational isomers were investigated. The calculations are done using the B3YLP hybrid density functional with the 6-311++G basis set. The energy difference between *cis* and *trans* conformers shows that the *trans* conformers of 2- and 3-furancarboselenaldehyde are energetically favoured with energy differences of 0.64 and 1.39 kcal/mol, respectively. The reorganization energies of all molecules were calculated in order to study their electronic and charge transport properties. The Integral Equation Formalism in the Polarizable Continuum Model (IEF-PCM) was carried out by using nine different solvents (heptane, chloroform, tetrahydrofuran, dichloroethane, acetone, ethanol, methanol, dimethylsulfoxide, and water) to study the effect of solvation. The solvent effect affects the stability of 2-furancarboselenaldehyde by favouring the stability of *cis* conformer as the dielectric constant of the solvent increases. On the other hand, the stability of *trans* conformers of 3-furancarboselenaldehyde increases as the dielectric constant of the solvent increases. Simulated infrared and UV visible spectra of molecules, reorganization energy, and geometrical parameters were investigated. To the best of our knowledge, no experimental or theoretical studies have been done on 3-furancarboselenaldehyde. Furthermore, limited work has been done for 2- furancarboselenaldehyde.

Keywords: Conformer; DFT; Potential energy surface; Solvation; vibrational spectra; UV-spectra

1. Introduction

One of the essential double bonds in organic chemistry is the carbonyl compounds (aldehyde and ketones) produced by the 2nd-period elements in the periodic table. Recently, several theoretical studies have been carried out on the effect of the substitution of oxygen by selenium [1-5]. For instance, the influences of substitution on the molecular structures and vibrational spectra of selenoketone and selenaldyhde has been reported [1-3]. The rotational barrier and thermodynamic parameters of 2- furancarboselenaldehyde have been studied [4]. Xu and co-workers [5] have reported the biosynthesis of selenocyteine and demonstrated its protective role in the human body, including cancer prevention, heart disease, and aging. On the other hand, the substitution of oxygen by selenium produce less stable compounds, as reported herein [6].

2-Furancarboselenaldehyde (C_4H_3O-CSeH) is a furan derivative that contains (CSeH) group in *ortho* position to the oxygen atom of the furan ring. The rotational barrier and thermodynamic parameters of 2- furancarboselenaldehyde (2-FCSe) have been reported by Ramasami *et al.* [4]. In the gas and

solution phase, the rotation of (CSeH) group on the furan ring in 2-FCSe leads to two geometrical isomers for each molecule, whereby the oxygen and selenium can be either SeO-*cis* or SeO-*tran*s. The *trans* conformer was more stable in the gas phase, and moreover, the stability of the *cis* conformer increased as a result of the increased polarity of the solvent. It's worth mentioning that the work on 2-FCSe is limited to the above-indicated study. On the other hand, neither experimental nor theoretical studies have been reported for 3-FCSe.

The electronic mobility of organic molecules is an indicator of the conductivity of that molecule (high mobility means high charge transport from one molecule to another). Reorganization energy is the main factor that determines charge mobility, which is the energy loss when a charge carrier (electrons or holes) passes through a molecule. The smaller values for the reorganization energy of the semiconductor material imply higher electronic mobility [7,8]. On the other hand, the HOMO-LUMO gap indicates whether the material is an *n*- or *p*-type semiconductor [9]. The type and/or position of substituent also affects the reorganization energies and HOMO-LUMO gap and might potentially convert the material from *n* to *p*-type and vice versa [10-12].

In the present study, we looked at the molecular structures, conformational stability, internal rotation, reorganization energy, UV spectroscopy in methanol, ^{1}H and ^{13}C NMR chemical shifts in chloroform, and vibrational analysis of 2- and 3-furancarboselenaldehydes in the gas phase. Moreover, attention is also paid to the influence of different solvents on the stability and molecular structures of 2- and 3-furancarboselenaldehydes. The influences of solvents were studied using the integral equation formalism version of the polarized continuum model (IEF-PCM) [13–19]. We compared our 2-FCSe and 3-FCSe results to those of their analogous 2-and 3-formyl furans [20].

2. Computational methods

The Gaussian 09 program suit [21] was used to optimize the structures, predict the energies and vibrational wavenumbers for the systems in Fig (1). All calculations have been done using the most popular hybrid density, B3YLP [22-24]. Becke's 3 parameter exchange-correlation functional, which uses 3 parameters mixed in the exact Hartree-Fock exchange-correlation [22], and LYP is the Lee-Yang and Parr correlation functional [23]. We have used the 6-311++G (d, p) basis set. Frequency computation was carried out using the optimized

structure to provide a complete description of the molecular motions involved in the standard modes. The transition states of the two molecules were optimized at the same level of theory and are located by the presence of one imaginary frequency. The energy of the conformers was used to calculate the energy difference, ΔE (Equation 1).

$$\Delta E = \Delta E_{cis} - \Delta E_{trans} \tag{1}$$

The reorganization energies for λ^+ and λ^- transfer can be calculated from [25]

$$\lambda^+ = \left(E_0^+ - E_+^+\right) + \left(E_+^0 - E_0^0\right) \tag{2}$$

$$\lambda^- = \left(E_0^- - E_-^-\right) + \left(E_-^0 - E_0^0\right) \tag{3}$$

where, E_0^0, E_+^+, and E_-^- are the total energies of the neutral, cationic, and anionic species in their equilibrium structures, respectively. E_0^+ is the total energy of the cation in the neutral geometry E_+^0, is the total energy of the neutral system in the cation geometry, E_0^- is the total energy of the anion in the neutral geometry, and, E_-^0 is the total energy of the neutral species in the anion geometry.

Solvation effects on conformational preference were investigated using solvents with different polarities. The dielectric constants (ε) of 1.92, 4.90, 7.58, 10.36, 20.70, 24.55, 32.63, 46.70, and 78.39 were used as the values for heptane, chloroform, tetrahydrofuran (THF), dichloroethane, acetone, ethanol, methanol, dimethylsulfoxide (DMSO), and water, respectively. To model the solvent effect, the integral equation formalism (IEF) version [13-19] of the polarized quantum model (PCM) of the SCRF was used [14, 18, 19]. The molecular cavity was constructed using the universal force field (UFF), whereby the cavity takes the shape of interlocking spheres centered on each solute atom with radii equal to the van der Waals radii of an atom scaled by a factor of 1.1. In the SCRF calculations, the energy of solvation, (ΔE_{sol}), was calculated as the difference between the energy of the molecule in the continuum $E_{(PCM)}$ and the energy of the molecule in the gas phase, $E_{(gas\ phase)}$.

$$\Delta E_{sol} = E_{(PCM)} - E_{(gas\ phase)} \tag{4}$$

The VEDA 4 program was used to characterize the normal vibrational modes based on potential energy distribution (PED) [26] as previously described [27]. The wavenumber and intensity obtained from the computation were used to simulate infrared spectra.
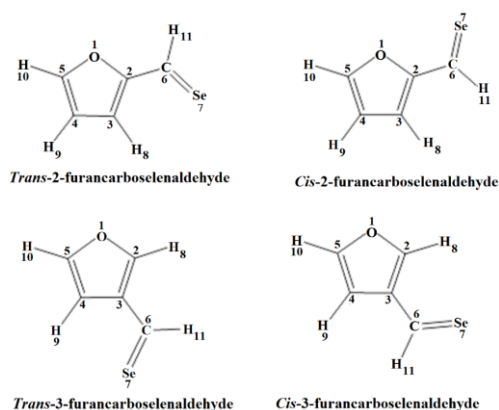
Fig. 1. Atom numbering for *trans* and *cis* conformers of 2-FCSe and 3-FCSe

3. Results and discussion

Table 1 summarizes the total energy of *cis*, *trans,* and transition states in the gas phase of 2-FCSe and 3-FCSe. The relative energy ΔE ($E_{cis\_}$ E_{trans}) and rotational barrier are given in kcal/mol. The *trans* conformers are more stable than the *cis* conformers by 0.64 and 1.39 kcal/mol for 2-FCSe and 3-FCSe, respectively. The stability of the *trans* conformer of the 2-FCSe is in agreement with the previous theoretical study [4]. A similar trend was reported for the oxygen analogue (2-formylfuran), where the trans conformers of 2-formylfuran and 3-formylfuran are energetically favoured with energy differences of 0.85 and 0.92 kcal/mol, respectively [20]. Thus, comparing our results with formyl furan implies that the substitution of the formyl group (COH) in formyl furan with (CSeH) does not affect conformational preference in either 2- or 3-formyl furans [20].

The internal rotation of the (CSeH) group around the C-C single bond leads to the *cis* and *trans* conformers. The dihedral angle angles ϕ (C_3C_2─C_6Se_7), in 2-FCSe and $\phi(C_4C_3$─$C_6Se_7)$ in 3-FCSe were varied from $\phi = 0^o$ (OSe-*cis* position where the ring oxygen and selenium atoms were *cis* to one another) to $\phi = 180^o$ (OSe-*trans* position where the ring oxygen and selenium atoms were *trans* to one another) in steps of 15°. Full geometry optimization was carried out at the transition state, which was characterized by one imaginary frequency. Figure 2 represents the potential energy surface as a function of the dihedral angle (ϕ) of the two molecules. The transition states occur at the dihedral angles of 89.9º and 89.1º for 2-FCSe and for 3-FCSe, respectively. The internal rotation of 2-FCSe is higher than that of 3-FCSe, due to the conjugation of the furan ring double bonds and a lone pair of electrons on oxygen atoms with the C=Se bond. This allows the delocalization of electrons as depicted in

the resonance structures of the studied molecules (Figure 3). This leads to four resonance structures in 2-FCSe compared to three resonance structures in 3-FCSe.

Table 1:
Computed total energies (Hartree), relative energy (kcal/mol), rotational barriers (kcal / mol) and relative stabilization energy of conformers.

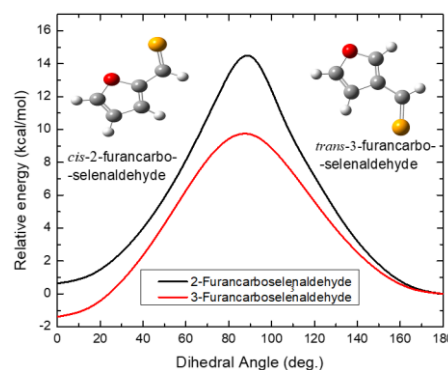| Parameters		2-FCSe	3-FCSe
Total Energy of Cis		-2669.74163	-2669.73522
Total Energy of Trans		-2669.74460	-2669.73744
Transition state Energy		-2669.71960	-2669.71974
Relative energy,	ΔE	0.64	1.39
Cis-trans	barrier	13.82	9.71
Trans-cis	barrier	15.69	11.11

Fig. 2. Computed internal rotational potential energy profiles for 2-FCSe and 3-FCSe.
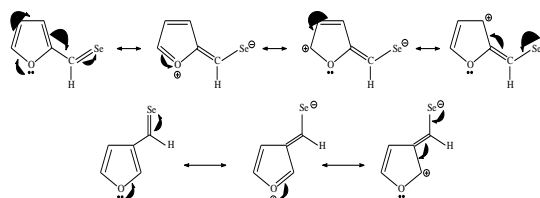

Fig.3. Conjugation in 2-FCSe and 3-FCSe

The IEF-PCM was used to understand the influence of solvent on the stability of the conformer modelled at the B3LYP/6-311++G (d, p) level of theory. The computed relative energy ΔE (E_{cis}-E_{trans}) of 2-FCSe and 3-FCSe in gas and solution phases are reported in Table 2. As evident in Table 2, the *trans*-2-FCSe is more stable in the gas and in the medium of low dielectric constant (heptane), but the *cis* conformer becomes more stable in the medium of high dielectric constant and the stability of the *cis*-2-FCSe increases as the dielectric constant of the solvent increases. This is in agreement with the previous theoretical study [4]. However, for 3-FCSe, the *trans* conformer remains the most stable conformer in all the solvents, and its stability increases with the increase in the dielectric constant of the solvents. Thus, the

conformational preference of the more stable conformer of 3-FCSe is independent of the solvent medium, but the stability increases with an increase in the dielectric constant of the solvent. Figure 4 (*a*) shows the variation of relative energy with the dielectric constant. The dipole moments of 2-FCSe and 3-FCSe are reported in Table 2. The dipole moment of the *cis* isomers is higher than that of *trans* isomers, and the dipole moment of both *cis* and *trans* isomers increases with the increase in dielectric constant of the solvents. The dipole moment of the solute plays an essential role in polarization because of the pure electrostatic nature of the interaction between solvent and solute. In the PCM, the higher dipole moment of the *cis* conformer shows high charge distribution and causes polarization of the solvent, which in turn polarizes the solute. Fig. 4 (*b*) shows the variation in the dipole moment as a function of the dielectric constant of solvents.

The values of solvation energies show that in all solvents, the *cis* conformer of 2-FCSe is more soluble within the PCM compared to the *trans* conformer, whereas the *trans* conformer of 3-FCSe is more soluble than the *cis* conformer. Solvation energies are reported in Table 2. Figure 5 shows the variation of the solvation energy with the dielectric constant of the solvent.

3.1 Reorganization (λ^{+}, λ^{-}) and HOMO-LUMO energies

Table 3 shows the values of the internal reorganization energies for the *hole* (λ^{+}) and *electron* (λ^{-}) transfers, HOMO, LUMO energies, and HOMO-LUMO energy gap of *cis* and *trans* isomers of 2-FCSe and 3-FCSe. The reorganization energy is one of the major parameters that determines the charge transfer rates (charge transport). It gives information about the changes in the total energies when the structures are changed from those of the neutral system to those of the charged ones. From Table 3, it is seen that a large value of λ^{+} is in the furan molecule compared to other substituted systems, where 2-*cis*-FCSe and 3-*trans*-FCSe show the largest value of λ^{-} than furan and other substituted molecules. A large value means a large change upon oxidation and reduction, while the small values of the reorganization energy of organic molecules indicate higher electronic mobility (high charge transport from one molecule to another).

The HOMO energies are associated with the electron-donating ability of the molecule of interest. Therefore, higher values of E_{HOMO} indicate an enhanced ability to donate electrons to the unoccupied molecular orbital of a receptor material. Therefore, a molecule with a higher E_{HOMO} can be considered a good electron carrier. Whereas, on the contrary, the value of E_{LUMO} is related to the ability of

the molecule to accept electrons. Accordingly, a molecule with a lower value of E_{LUMO} implies a greater ability to accept electrons, and it can then act as a *hole* carrier. Lower values of the HOMO-LUMO gap suggest lower kinetic stability and higher conductivity [9]. Inspection of Table 3 reveals that furan has the lowest value for the HOMO-LUMO gap compared to the other molecules. The value of the HOMO-LUMO energy gap for furan falls below the range of organic semiconductors, 1.4 - 4.2 eV [28]. The introduction of the –CSeH group increases the energy gap and the ΔE HOMO-LUMO becomes within the range of organic semiconductors, which means it improves the carrier mobility of 2-FCSe and 3-FCSe materials. The values of HOMO-LUMP gaps in 3-FCSe are relatively higher than those in 2-FCSe, a result that is consistent with the values of λ. From the HOMO-LUMO point of view, furan can be considered as an *n*-type semiconductor material compared to 2-FCSe and 3-FCSe.
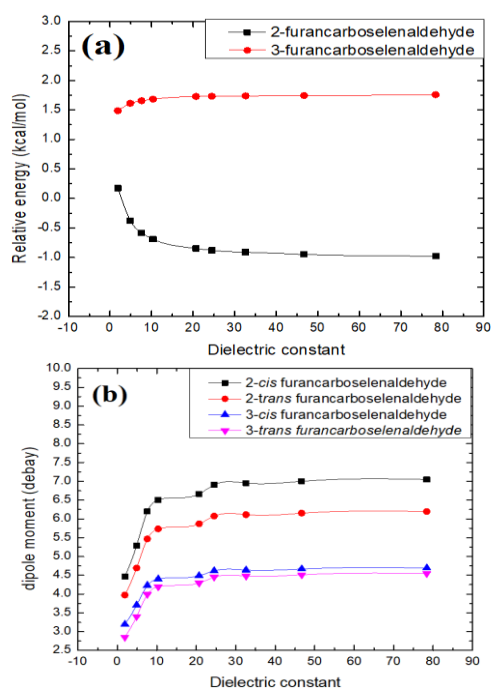

Fig. 4. *(a)* Variation of relative energies with the dielectric constant of the solvents *(b)* variation in the dipole moment as a function of a dielectric constant of solvents.

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Table 2:

Computed relative energy (ΔE) (in kcal∕mol), dipole moment μ (in Debye), and solvation energy (ΔEsol)
of 2-FCSe and 2-FCSe in the gas phase and different solvents.

Phase	ε	2- FCSe						3- FCSe				
		ΔE	ΔE_sol		μ			ΔE	ΔE_sol			
			cis	trans	cis	trans			Cis	trans	cis	trans
Gas	-	0.640	-	-	4.47	3.97		1.394	-	-	3.1	2.85
Heptane	1.92	0.176	-1.86	-1.40	5.29	4.69		1.487	-1.35	-1.44	3.7	3.40
Chloroform	4.81	-0.377	-3.80	-2.78	6.20	5.47		1.613	-2.65	-2.87	4.2	3.99
THF	7.52	-0.584	-4.44	-3.22	6.50	5.73		1.657	-3.07	-3.33	4.4	4.19
Dichloroethane	9.68	-0.690	-4.77	-3.44	6.66	5.87		1.682	-3.28	-3.56	4.4	4. 30
Acetone	21.01	-0.847	-5.26	-3.77	6.90	6.07		1.726	-3.58	-3.91	4.6	4.45
Ethanol	24.60	-0.879	-5.35	-3.83	6.95	6.11		1.732	-3.63	-3.97	4.6	4.48
Methanol	32. 60	-0.910	-5.45	-3.90	7.00	6.15		1.738	-3.69	-4.03	4.6	4.51
DMSO	46.70	-0.948	-5.55	-3.96	7.05	6.20		1.744	-3.75	-4.10	4.6	4.54
Water	78. 39	-0.979	-5.58	-4.02	7.10	6.24		1.757	-3.81	-4.17	4.7	4.57

Table 3:
Reorganization (λ+, λ-), HOMO, LUMO energies, HOMO-LUMO energy gap (in eV) of cis and trans
isomers of 2-FCSe and 3-FCSe calculated at the B3LYP/6-311++G** level of theory

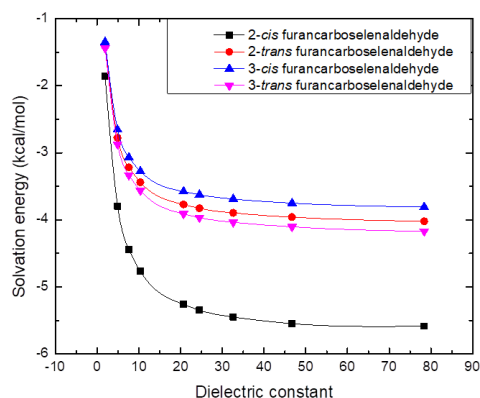| Molecule	λ^+	λ^-	HOMO	LUMO	ΔE_{gab}
Furan	1.699	0.644	-6.531	-0.168	0.363
Cis-2-FCSe	0.150	1.448	-5.774	-3.015	2.759
Trans-2-FCSe	0.173	0.217	-5.907	-3.087	2.820
Cis-3-FCSe	0.191	0.285	-5.941	-2.984	2.957
Trans-3-FCSe	0.186	1. 351	-5.923	-2.900	3.023

Fig. 5. Variation of solvation energy with a dielectric constant of the solvent

3.2. Vibrational Spectral Analysis

Both 2-FCSe and 3-FCSe are composed of 11 atoms, and as such, calculations of vibrational wavenumbers gave twenty-seven IR and Raman active fundamental vibrations that belong to

irreducible representations of the C_s point group. Tables 4 and 5 show the vibrational frequency, intensity, and Raman activities of *cis* and *trans*-2-FCSe.

The results of the *cis* and *trans* of 3-FCSe are depicted in Tables 6 and 7. The assignments of the calculated vibrational modes proposed on the basis of potential energy distribution (PED) using the VEDA 4 program [26] are provided in the last columns of Tables 4-7. As previously described [27], the PED calculation necessitates the creation of 3N–6 linearly independent coordinates that represent vibrational motions (stretching, bending, and torsion) in the molecule. As evident from the tables, the first high vibrational frequencies ($v_1 - v_4$) are attributed to the C-H stretching modes of the molecules. These vibrations are calculated to be in the range of 3111 – 3287 cm^{-1}, and are mainly CH stretching modes with a contribution of around 68%–100% to PED. The v_4 vibrational modes of both *cis* and *trans* conformers of 2-FCSe and 3-FCSe are found to be pure CH vibrational modes with a 100% contribution to PED. The animation option of the *Gauss View* [29] was

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used to confirm the vibrational assignments obtained from the VEDA 4 program.

To differentiate between the isomers, we used the strong band of CC-stretching of the furan ring, which appeared at around (1480-1550) cm⁻¹. These bands appeared at 1490 cm⁻¹ and 1478 cm⁻¹ in the IR spectra of *cis* and *trans* 2-FCSe, respectively. In 3-FCSe, it appears at 1533 cm⁻¹ and 1539 cm⁻¹ for the *cis* and *trans* isomers, respectively. By comparing the spectra of FCSe and formyl furan [20], it is observed that the C=Se stretching mode of FCSe appears at a lower wavenumber compared to that of the C=O stretching mode of formyl furan.

The vibrational wavenumbers and the corresponding intensity calculations are used to simulate the vibrational IR spectra of the molecules using a pure Lorentizian band shape with a bandwidth of full width and half maximum (FWHM) of 10 cm⁻¹. Figure 6 (*a*) and (*b*) show the calculated IR spectra of the *cis* and *trans* conformers of the 2-FCSe and 3-FCSe, respectively.

The IR spectra of two isomers are dominated by the high intensity of the (C = Se) group stretching frequency. This band is calculated to be at 861 and 870 cm⁻¹ (for the *cis* and *trans*-IR spectra of 2-FCSe),

and at 868 and 867 cm⁻¹ for the *cis* and *trans* of 3-FCSe, respectively.

3.3   UV spectra analysis

The TD-DFT method was used to calculate the electronic absorption spectra of the studied molecules in the methanol solvent. Table 8 shows the calculated absorption wavelength (λ), oscillator strength (f), and excitation energy (ε).

Figure 7 (*a*) - (*d*) show the calculated UV spectra of *cis* and *trans* conformers of the 2-FCSe and 3-FCSe, respectively. The absorption maximum values for the two conformers of the two molecules are calculated to be around 650 nm, but this transition is not probable because the oscillator strengths for this transition are 0.00. Thus, the most probable transitions are at 356, 366, 365, and 336 nm for the *cis*-2-FCSe, *trans*-2-FCSe, *cis*-3-FCSe, and *trans*-3-FCSe, respectively. The proposed assignments of major orbital contributions for all the transitions in the molecules are provided in the last column of Table 8.

Table 4:
Calculated vibrational parameters of *cis*-2-FCSe computed at B3LYP/6-311++G(d,p) level of theory.

No	Frequencies (cm⁻¹)	IR intensity (Km mol⁻¹)	Raman Activity	Assignment (PED ≥ 10%)
v_1	3274	0.24	191.32	vCH(76)
v_2	3254	0.41	96.19	vCH(81)
v_3	3243	1.75	104.11	vCH(94)
v_4	3124	5.91	84.78	vCH(100)
v_5	1581	68.54	191.92	vCC(32) + δHCC(12)
v_6	1490	130.44	539.02	vCC(30) + δHCO(20)
v_7	1429	32.11	132.03	δCCO(21) + vCC(10) + δHCC(25)
v_8	1337	43.87	22.71	vCC(11) + vCO(10) + δHCSe(12) + δHCC(16)
v_9	1300	3.47	9.95	vOC(14) + vCC(10) + δHCSe(42)
v_{10}	1214	8.42	17.53	δHCC(18) + δHCSe(19) + δCCO(10) + vCC(20)
v_{11}	1184	0.42	16.96	vOC(40) + vCC(32) + δHCO(34)
v_{12}	1112	21.76	10.22	vOC(28) + δHCC(12) + vCC(15)
v_{13}	1045	54.69	29.28	δHCC(36)
v_{14}	963	13.10	0.76	vSeC(14) + vCC(15) + vOC(35)
v_{15}	903	2.28	6.84	δCCO(53) + vOC(17)
v_{16}	902	1.42	2.47	τHCCC(29) + τHCOC(12)
v_{17}	870	22.81	0.72	τHCCC(22) + τHCOC(14)
v_{18}	861	97.00	116.45	vSeC(51)
v_{19}	820	3.93	1.10	τHCCC(44) + τHCOC(19)
v_{20}	774	67.08	2.12	τHCOC(36) + τHCCC(46)
v_{21}	696	6.23	3.23	δSeCC(21) + δCCO(18)
v_{22}	666	0.09	2.57	τCCOC(49)
v_{23}	596	13.37	0.10	τCCOC(74) + τHCOC(11)
v_{24}	342	1.07	17.58	δSeCC(11) + vCC(11) + v eC(26) + δCCO(29)
v_{25}	296	4.27	0.95	τCCOC(29)

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ν_{26}	139	0.69	4.75	δCCO(39) + δSeCC(56)
ν_{27}	103	0.52	0.92	τSeCCC(84)

Table 5:

Calculated vibrational parameters of trans-2-FCSe computed at B3LYP/6-311++G(d,p) level of theory.

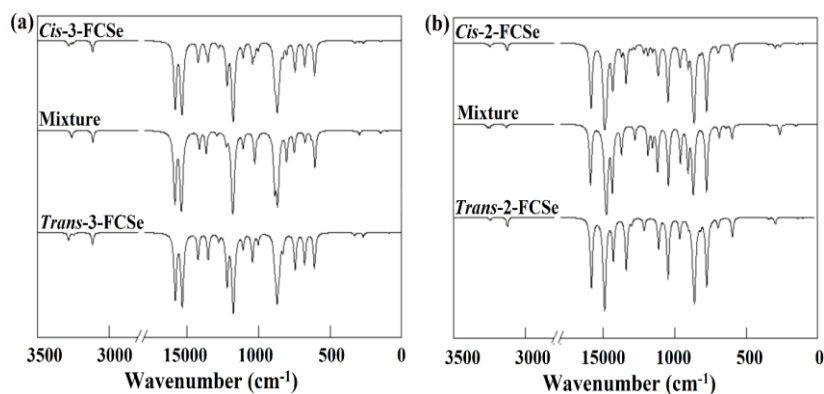| No	Frequencies (cm^{-1})	IR intensity (Km mol^{-1})	Raman Activity	Assignment (PED ≥ 10%)
ν_1	3272	0.21	217.83	νCH(67)
ν_2	3261	1.79	31.84	νCH(78)
ν_3	3247	1.91	96.99	νCH(70)
ν_4	3131	2.17	87.84	νCH(100)
ν_5	1586	53.10	106.94	νCC(36) + δHCC(11)
ν_6	1478	179.63	579.60	νCC(31) + δHCO(22)
ν_7	1434	61.65	259.99	δCCO(27) + δCCO(19)
ν_8	1370	20.24	12.56	νCC(18) + δHCSe(35) + δCCO(11)
ν_9	1276	9.66	3.29	δHCC(30) + HCSe(12) + δHCO(21)
ν_{10}	1184	20.83	25.44	νOC(42) + νCC(11) + δHCO(29)
ν_{11}	1154	13.16	5.26	νOC(11) + ν CC(23) + δHCSe(33)
ν_{12}	1117	37.03	12.72	νOC(30) + δHCC(12) + δ CCO(11) + ν CC(17)
ν_{13}	1042	54.31	47.42	δHCC(34) + δ CCO(13)
ν_{14}	904	35.85	18.27	δCOC(23) + δ CCO(45)
ν_{15}	912	1.19	2.29	τHCCC(42)
ν_{16}	958	28.02	3.37	νOC(46)
ν_{17}	870	53.05	123.69	νSeC(43)
ν_{18}	862	24.42	1.24	τHCCC(29) + τHCOC(13) + τSeCCC(19)
ν_{19}	848	0.96	1.47	τHCCC(31) + τHCOC(21)
ν_{20}	774	63.81	3.18	τHCOC(45) + τHCCC (40)
ν_{21}	686	8.32	6.69	δSeCC(22) + δ COC(27) + δCCO (12) + νCC(11)
ν_{22}	639	1.80	0.40	τCCOC(46) + τHCCC (13)
ν_{23}	596	9.75	0.28	τCCOC(13) + τHCOC (12)
ν_{24}	328	1.06	13.80	δSeCC(22) + νSeC(28) + δCCO(41)
ν_{25}	263	6.91	3.30	τCCOC(34) + τSeCCC(15)
ν_{26}	151	1.01	3.58	δ CCO(34) + δSeCC (56)
ν_{27}	114	0.01	0.44	τSeCCC(54)

Fig. 6. Simulated IR spectra of (a) 3-FCSe and (b) 2-FCSe

Table 6:
Calculated vibrational parameters of *cis*-3- FCSe computed at B3LYP/6-311++G(d,p) level of theory.

No	Frequencies (cm^{-1})	IR intensity (Km mol^{-1})	Raman Activity	Assignment (PED $\geq$ 10%)
v_1	3287	1.45	155.57	vCH(68)
v_2	3281	4.00	45.08	vCH(74)
v_3	3247	1.39	72.15	vCH(71)
v_4	3115	8.43	89.14	vCH(100)
v_5	1582	80.12	100.29	vCC(27) + δHCC(11)
v_6	1533	101.77	249.72	vCC(12) + δHCO(14)
v_7	1423	19.87	14.11	δHCSe(27) + δCCO(14)+ vCC(14)
v_8	1352	20.52	94.83	vCC(17) + vCO(12) + δHCO(10)
v_9	1279	5.36	3.42	vCO(10)+ δHCO(39) + δHCSe(22)
v_{10}	1220	51.49	18.05	vCO(10)+ δHCSe (22) + δHCO(19)
v_{11}	1175	130.99	52.65	vCO(28)+ δHCC(14)+ δCCO(17) + δHCSe(10)
v_{12}	1107	10.24	2.62	vCO(18) + δ HCC(25)+ δHCO(27) + vCC(16)
v_{13}	1041	22.42	11.01	vCO(65)
v_{14}	1002	7.08	8.52	δHCC(21) + δCCO(39) + δCOC(10)
v_{15}	888	11.16	11.61	δCCO(16) + δCOC(49) + vSeC(13)
v_{16}	877	17.83	0.46	τHCCC(42)+ τHCOC(12)
v_{17}	868	77.39	69.16	vSeC(51)
v_{18}	855	23.34	4.24	τHCCC(44) + τHCOC(18)
v_{19}	828	10.95	0.21	τHCCC(12) + τHCOC(63)+ τCCOC(15)
v_{20}	743	30.61	0.10	τHCOC(10) + τHCCC(29)
v_{21}	677	25.45	3.80	δSeCC(24) + δCCC (15)
v_{22}	612	0.46	2.22	τCCOC(15) + τHCOC(11)
v_{23}	608	29.45	0.01	τCCOC(50) + τHCOC(19)
v_{24}	326	2.16	10.26	δCCC(28) + δSeCC(13) + vSeC(23) + δ CCO(17)
v_{25}	267	2.62	2.90	τCCOC(15)
v_{26}	147	0.19	3.12	δCCC(44) + δSeCC(52)
v_{27}	89	0.26	0.30	τSeCCC(89)

3.4 Nuclear Magnetic Resonance (NMR) analysis

The ^{1}H and ^{13}C NMR spectroscopy is a very important and powerful analytical tool used to the identification and characterized organic compounds. In the present work, the optimized structural parameters of both conformers of 2-FCSe and 3-FCSe were used to calculated the ^{1}H and ^{13}C chemical shifts in chloroform solvent medium using the default GIAO of the Gaussian 09. The calculated chemical shifts values (in ppm) for the *cis* and *trans* conformers of the studied molecules are presented in Table 9. Generally, the ^{13}C NMR chemical shifts for the aromatic ring are greater than the 100-ppm shift. The ^{13}C NMR chemical shift values of the furan ring are reported to be between 123.7 and 182.2 ppm with

C2 and C5 having higher values due to the electronegative of the furan oxygen atom. For all the molecules the exocyclic C6 has the highest chemical value due to the influence of the CSeH attached to the carbon atom. The C6 chemical shift values for the 2-FCSe are higher than those of 3-FCSe due to the differences in the conjugation between the furan ring double bonds and lone pair of electrons on oxygen atoms with C=Se bond at positions 2 for 2-FCSe and position 3 for 3-FCSe (see Figure 3). The proton chemical shift values for all the molecules are downfield, typical of an aromatic system. These values are in the range of 6.6 – 8.0 ppm. The CSeH proton chemical shift values are calculated to be around 11.5 ppm for the 2-FCSe and 12.1 ppm for the

3-FCSe conformers. These high proton chemical shift values are due to the electron-withdrawing effect of the CSe group.

Table 7:
Calculated vibrational parameters of *trans* -3-FCSe computed at B3LYP/6-311++G (d, p) level of theory.

No	Frequencies (cm^{-1})	IR intensity $(Km\ mol^{-1})$	Raman Activity	Assignment (PED ≥ 10%)
v_1	3287	0.10	148.17	vCH(83)
v_2	3266	1.57	76.57	vCH(97)
v_3	3259	3.51	35.25	vCH(83)
v_4	3114	7.90	85.58	vCH(100)
v_5	1584	95.61	173.95	vCC(25)+ δ HCC(10)
v_6	1539	133.88	206.13	vCC(13)+ δ HCO(13)
v_7	1413	12.58	32.76	vCC(17) + δCCO(20)+δHCSe(13)
v_8	1366	16.34	81.09	vCC(30) + v CO(14) + δ HCO(18) +δHCSe(15)
v_9	1292	2.63	12.37	δHCO(38) +δ HCC(10)+δ HCSe(29)
v_{10}	1226	7.79	36.89	vCC(15) + δ HCSe(26)
v_{11}	1178	157.12	39.94	vOC(46) + δ HCC(15)
v_{12}	1107	11.03	2.69	vOC(17) + δHCC(23) + δHCO(30) + vCC(15)
v_{13}	1025	25.84	5.84	vOC(66)
v_{14}	999	2.16	9.85	δHCC(25) + δ CCO(39)
v_{15}	890	3.12	0.88	τHCOC(22)+ τHCCC(47)+ τCCOC(10)
v_{16}	884	58.16	4.21	δCOC(66)
v_{17}	867	63.23	81.97	vSeC(54)
v_{18}	866	38.02	4.29	τHCCC(47) + τHCOC(10) + τSeCCC(24)
v_{19}	803	23.57	2.55	τHCCC(18) + τHCOC(40) + τCCOC(20)
v_{20}	750	15.42	0.31	τHCOC(47)+ τHCCC(19)
v_{21}	673	7.46	2.23	δSeCC(22)
v_{22}	630	3.49	1.42	τCCOC(64)
v_{23}	604	30.18	1.36	τCCOC(60) + τHCOC(17)
v_{24}	329	0.72	13.88	δCCC(39) + δSeCC(14) + vCC(12)+ vSeC(24)
v_{25}	293	2.70	0.84	τCCOC(15) + τSeCCC(20)
v_{26}	145	1.72	2.85	δ CCC(39) + δSeCC(51)
v_{27}	102	0.45	0.18	τSeCCC(51)

Table 8:
Calculated absorption wavelength(λ),Oscillator strength(*f*), excitation energy (ε) of 2-FCSe and 3-FCSe

| λ (nm)	ε (ev)	*f*	Assignment*
		Cis-2-FCSe	
660. 32	1.88	0.0000	H→L(100)
356.10	3.48	0.5930	H→L+1(100)
259.97	4.77	0.0480	H→L+3(3), H→L+4(92), H→L+5(4)
		Trans-2-FCSe	
656.07	1.89	0.0000	H→L(100)
366.07	3. 39	0.5714	H→L+1(100)
246.79	4.68	0.0141	H→L+3(2), H→L+4(94), H→L+5(3)
		Cis-3-FCSe	
648.10	1.91	0.0000	H→L(100)
364.81	3.40	0.1773	H→L+1(9) , H→L+2 (91)
303.52	4.08	0.2449	H→L+3 (89), H→L+4 (9)
		Trans-3-FCSe	
615.81	2.01	0.0000	H→L(100)
335.75	3.69	0.2888	H→L+1 (19), H→L+2(91)
300.98	4.12	0.2573	H→L+3(79), H→L+4 (19)

* H = HOMO and L = LUMO

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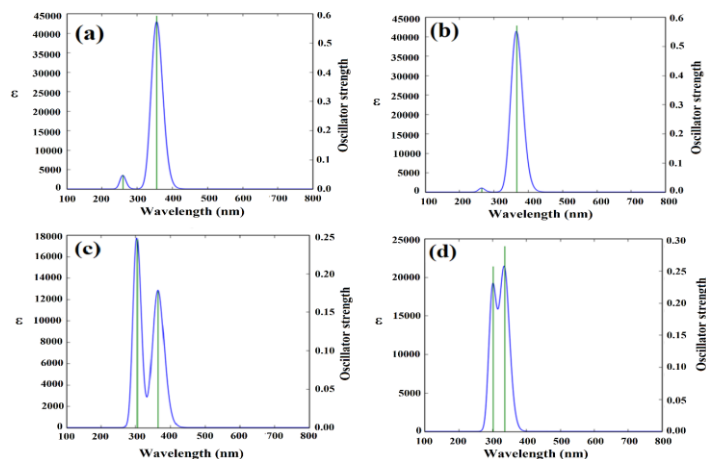
Fig. 7. Simulated UV spectra of (a) cis-2-FCSe, (b) Trans-2-FCSe, (c) cis-3-FCSe and (d) Trans-3-FCSe computed at B3LYP/6-311++G (d, p)

Table 9: Calculated ^{13}C and ^{1}H NMR chemical shifts (ppm) for *cis* and *trans* conformers of 2-FCSe and 3-FCSe

Atom*	Cis-2-FCSe	Trans-2-FCSe	Cis-3-FCSe	Trans-3-FCSe
C_2	180.8	182.2	161.7	168.1
C_3	140.8	135.2	155.7	157.3
C_4	131.2	131.9	127.7	123.7
C_5	171.4	169.3	162.1	163.0
C_6	248.5	251.7	273.3	267.9
H_8	6.9	8.0	8.6	7.8
H_9	6.8	6.6	6.6	7.3
H_{10}	7.9	7.9	7.6	7.4
H_{11}	11.5	11.6	12.1	12.1

* The atom numbering is given in Figure 1

3.5 Geometry Parameters

Some of the structural parameters obtained from the geometry optimizations of *cis* and *trans* conformers are presented in Table 10. The optimization was carried out without any constraints using the B3LYP/6-311++G (d,p) method. As evident from Table 10, the structural parameters of the molecules are very similar irrespective of the conformer and the position of the CHSe group on the formyl ring. This shows that the position of the CHSe group (*ortho* or *meta* position in the furan ring) has no significant effect on the structural parameters of 2-FCSe and 3-FCSe. Similarly, the C=Se bond length was calculated to be 1.79 Å for 2-FCSe and 1.78 Å for 3-FCSe. These values, are slightly longer than the corresponding C=O bond length of formyl furan. The exocyclic C_n-C_6 bond lengths for the two molecules are to be around 1.42 Å for 2-FCSe and 1.43 Å for 3-FCSe. These values which are less than the typical carbon-carbon single bond length value (1.54 Å) support the proposed conjugation (Figure 3) due to the delocalization of the lone pair of electrons on the furan oxygen atom.

Table 10:
Optimized geometric parameters of 2-FCSe and 3-FCSe computed at the B3LYP using 6-311++G(d,p) basis set in the gas phase

Geometric parameters	2-FCSe		3-FCSe	
	Cis	Trans	Cis	Trans

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$O_1 - C_2$	1.37	1.39	1.34	1.34
$C_2 - C_3$	1.38	1.38	1.38	1.38
$C_3 - C_4$	1.42	1.41	1.45	1.45
$C_4 - C_5$	1.37	1.37	1.35	1.35
$C_5 - O_1$	1.35	1.35	1.37	1.38
$C_n - C_6$	$1.42(C_2)$	$1.42(C_2)$	$1.44(C_3)$	$1.43(C_3)$
$C_6 = Se_7$	1.79	1.79	1.78	1.78
$C_n - H_8$	1.08	1.08	1.08	1.08
$C_4 - H_9$	1.08	1.08	1.08	1.08
$C_5 - H_{10}$	1.08	1.08	1.08	1.08
$C_6 - H_{11}$	1.09	1.09	1.09	1.09
Bond Angle ($°$)				
$O_1 C_2 C_3$	108.8	108.6	110.7	110.9
$C_2 C_3 C_4$	107.0	107.0	105.1	105.3
$C_3 C_4 C_5$	105.7	106.1	106.5	106.3
$C_4 C_5 O_1$	111.2	110.1	110.1	110.6
$C_5 O_1 C_2$	107.4	107.3	107.5	107.0
$C_3 C_6 Se_7$	115.9	116.2	115.6	115.4
$C_3 C_6 H_{11}$	113.1	114.3	114.6	115.1
$C_6 C_3 C_2$	130.4	134.8	128.4	124.9
$C_6 C_3 C_4$	$132.9(C_2)$	$132.9(C_2)$	$134.3 (C_3)$	$134.1(C_3)$
$H_{11} C_6 Se_7$	118.7	118.9	117.4	117.9
$C_2 C_3 H_8$	125.4	124.8	132.30	132.2
$C_3 C_4 H_9$	127.9	127.6	126.8	126.2
$C_4 C_5 H_{10}$	108.75	108.6	110.7	110.9
$O_1 C_5 H_{10}$	107.00	107.0	105.1	105.3
Dipole Moment (Debye)	4.47	3.97	3.19	2.85
Rotational constant (GHz)				
A	7.47	7.63	7.49	7.59
B	0.83	0.79	0.78	0.78
C	0.75	0.72	0.71	0.71

* The atom numbering is given in Figure 1

4. Conclusion

The molecular structure, conformational stability, reorganization energy, and vibrational wavenumber for the *trans* and *cis* conformers of 2-FCSe and 3-FCSe using the Gaussian 09 package have been conducted. The potential energy curves in the gas phase are obtained for the rotational dihedral angles ϕ ($C_3 C_2 - C_6 Se_7$) in 2-FCSe and ϕ ($C_4 C_3 - C_6 Se_7$) in 3-FCSe. From the computation, the *trans* conformers are energetically favored by 0.64 and 1.39 kcal/mol for 2-FCSe and 3-FCSe, respectively. The *trans-cis* rotational barriers are calculated to be 15.69 and 11.11 kcal/mol for 2-FCSe and 3-FCSe respectively. Calculated reorganization energies show lower electronic mobility (value of λ^+) in the furan molecule compared to other substituted systems. The *cis*-2-FCSe and *trans*-3-FCSe have lower electronic mobility (value of λ^-) than the other conformers and furan. The solvent effects are investigated using nine different values of dielectric constants, using the IEF-PCM model. The effect of the solvent is large enough to reverse the stability of 2-FCSe. The optimized geometrical parameters, UV spectra (in methanol solvent), ^1H and ^{13}C NMR chemical shifts (in chloroform solvent), and computed vibrational wavenumbers at the B3LYP/6-311++G (d, p) are reported. There result herein will be of interest to the organic and heterocyclic chemists that have the desired for the synthesis of the new selenium based heterocyclic compounds.

5. Conflicts of interest

There are no conflicts to declare.

6. References:

[1] Ramasami P., A theoretical gas phase study of the molecular structures and vibrational spectra of novel penta-1, 4-diyne-3-thioketone and penta-1,4-diyne-3-selenoketone, *J. Mol. Struct.* (Theochem) **767**,19-22 (2006).

[2] Ramasami P., Novel 1,5-difluoropenta-1,4-diyn-3-one, its sulfur and selenium analogues: MP2 and DFT gas phase study of their molecular structures and vibrational spectra, *J. Mol. Struct.* (Theochem) **775**, 87-92(2006).

[3] Kaur D., Kaur R.P., and Kaur R., Theoretical study of C-H bond dissociation energies of HC(=X)R {X = O, S, Se; R = H, CH_3, Cl, NH_2}, *J. Mol Struct.(Theochem)*, **803**, 95-101(2006)

[4] Ashisha H., and Ramasami P., Rotational barrier and thermodynamical parameters of furfural,

thiofurfural, and selenofurfural in the gas and solution phases: theoretical study based on density functional theory method, *Mol. Phys.* **106**, 175-185(2008),

[5] Xu X. M., Carlson B. A., Mix H., Zhang Y., Saria K., and Glass R. S., Biosynthesis of Selenocysteine on Its tRNA in Eukaryotes, *PLoS Biol.* **5** (1), 96-105(2007).

[6] Back T.J., Barton D.H.R, Britlen-Kelly M.R., and Guziec F.S., Olefin Synthesis by Two-fold Extrusion Processes. Part 3. 1 Synthesis and Properties of Hindered Selenoketones (Sefones), *J. chem. soc.perkin Trans.***1**, 2079-2089(1976).

[7] Cornil J., Brédas J.L., Zaumseil J., Sirringhaus H., Ambipolar Transport in Organic Conjugated Materials, *Adv. Mater.* **19**, 1791-1799(2007).

[8] Brédas J.L., Beljonne D., Coropceanu V., and Cornil J., Charge-Transfer and Energy-Transfer Processes in π-Conjugated Oligomers and Polymers: A Molecular Picture, *Chem. Rev.* **104**, 4971-5004(2004).

[9] Unlu H., A thermodynamic model for determining pressure and temperature effects on the band gap energies and other properties of some semiconductors, *Solid-State Electron.* **35**, 1343-1352(1992).

[10] Oshi R., Abdalla S., and Springborg M.,Study of the Influence of Functionalization on the Reorganization Energy of Naphthalene using DFT. , *Comput. Theor. Chem.***1099**,209-215(2017).

[11] Oshi R., Abdalla S., and Springborg M., Theoretical study on functionalized anthracene and tetraceneas starting species to produce promising semiconductor materials", Computational and Theoretical Chemistry, *Comput. Theor. Chem.***1128**, 60-69(2018).

[12] Oshi R., Abdalla S., and Springborg M., The impact of functionalization of organic semiconductors by electron donating groups on the reorganization energy, *Eur. Phys. J. D***73**, 124-132(2019).

[13] Tomasi J., Mennucci B., and Cammi R., Quantum Mechanical Continuum Solvation Models, *Chem. Rev.* **105**, 2999-3093(2005).

[14] Tomasi J., and Persico M., Molecular Interactions in Solution, *Chem. Rev.* **94**, 2027-2094(1994).

[15] Cances E., Mennucci B., and Tomasi J., A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics, *J. Chem. Phy.***107**, 3032-3041(1997).

[16] Mennucci B., Canc`es E., and Tomasi J., Evaluation of Solvent Effects in Isotropic and Anisotropic Dielectrics and in Ionic Solutions with a Unified Integral Equation Method: Theoretical Bases, Computational Implementation, and Numerical Applications, *J. Phys. Chem. B.* 101, 10506-10517(1997).

[17] Miertuˆs S., Scrocco E., and Tomasi J., Electrostatic Interaction of a Solute with a Continuum a Direct Utilization of ab Initio Molecular Potentials for the prevision of solvent Effect, *Chem. Phys.* **55**, 117-129(1981).

[18] Cammi R., Tomasi J., Remarks on the Use of the Apparent Surface Charges (ASC) Methods in Solvation Problems: Iterative versus Matrix-Inversion Procedures and the Renormalization of the Apparent Charges, *Chem J. Comput. Chem.* **16**, 1449-1458(1995).

[19] Canc`es E., and Mennucci B., New applications of integral equations methods for solvation continuum models: ionic solutions and liquid crystals, *J. Math. Chem.* **23**, 309-326 (1998).

[20] Umar Y., and Tijani J., Density functional theory study of the rotational barriers, conformational preference, and vibrational spectra of 2-formylfuran and 3-formylfuran, *J. Stru. Chem*, **56**, 1305-1312(2015).

[21] Frisch M.J. *et al* Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT. (2009)

[22]Becke A. D., Density functional thermochemistry-III. The role of exact exchange, *J. Chem. Phys.* **98**, 5648-5652 (1993).

[23] Lee C., Yang W., and Parr R.G., Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev.* B **37**, 785-788(1988).

[24] Sousa S. F., Fernandes P.A, Ramos M. J., General Performance of Density Functionals, *J. Phys. Chem.* A**111**, 10439-10452(2007).

[25] Stark M. S., Epoxidation of Alkenes by Peroxyl Radicals in the Gas Phase: Structure−Activity Relationships, *J. Phys. Chem. A***101**, 8296-8301(1997).

[26] Jamroz M. H., Vibrational Energy Distribution Analysis: VEDA 4 Program" Warsa (2004).

[27] Abdalla S., Umar Y., Mokhtar I., Conformational and Vibrational Analysis of 2-, 3- and 4-Pyridinecarbonyl Chloride Using DFT, *Zeitschrift für Physikalische Chemie* **230** (5-7), 867-882 (2016).

[28] Chen Z, He Z., Xu Y., and Yu W., (2017) Density functional theory calculations of charge transport properties of 'plate-like' coronene topological structures, *J. Chem. Sci.***129** (9): 1341-1347.

[29] Dennington II R., Kieth T.*,* and Millam J., *et al*, *Gauss View*, Version 5.0.8, Semichem, Inc., Shawnee Mission, KS (2008).