

# THEORETICAL STUDY ON THE ROTATION BARRIER AND ENERGY DIFFERENCE BETWEEN MALEALDEHYDE AND FUMARALDEHYDE AND THEIR ANALOGUES (Y = O, S, SE)

Lim Kie Zen, Hassan Hadi Abdallah\*, Chong Shu Xian and Wong Zhi Xiang

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia.

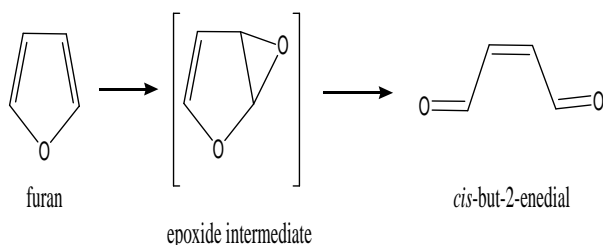
\* Corresponding author. Tel.: +60-4-6533598, Fax: +60-4-6574854, Email address: hwchems@usm.my

**ABSTRACT:** But-2-enedial consists of cis and trans isomers which are known as malealdehyde and fumaraldehyde, respectively. Density functional theory (DFT/B3LYP) and Møller-Plesset perturbation theory (MP2) are used for calculating the optimized structure for malealdehyde and fumaraldehyde conformers with sulphur and selenium analogues. The basis set 6-311++G(d,p) is applied for all calculations. Dipole moments, charges and vibrational frequencies were assigned and reported. The rotation barrier,  $B1$  between malealdehyde and fumaraldehyde was investigated in both gas and solution phase. Nine solvents were used in optimizing molecules in solution phase by using Integral Equation Formalism Polarization Continuum Model with DFT method. The energy difference,  $E$  of the cis and trans isomers were also calculated. Optimized malealdehyde, fumaraldehyde and transition state geometries have  $C_{2v}$ ,  $C_{2h}$  and  $C_1$  point group respectively. It was found that both conformers are more stable in solution phases than in gas phase. With the increase of dielectric constant of solvents, the stability of conformers increases. Based on the energy obtained, the fumaraldehyde conformer for all analogues are more stable compared to malealdehyde conformer. When Y atom is substituted with O, S and Se atom, the stability of both the compounds increases in the order of increasing atomic size.

Keywords: Malealdehyde, Fumaraldehyde, But-2-enedial, energy difference, rotational barrier, solvent effect

## 1.0 INTRODUCTION

But-2-enedial is one of the simplest unsaturated dialdehydes. It consists of two aldehyde groups connected by a double bond. The cis conformation, malealdehyde, can be found in food, smog, and cigarette smoke [1-4] and it can be produced from furan by different ways such as; 1) via microsomal enzyme by forming epoxy-intermediate as shown in Scheme 1 [5]. 2) The oxidation of furan by cytochrome P450 [6-8].



Scheme 1: Formation of malealdehyde via epoxy-intermediate.

Malealdehyde and furan have similar properties in binding covalently to the protein and DNA. Hence it is toxic and carcinogenic [9,10]. For fumaraldehyde, it is also toxic. It can be formed by oxidation of deoxyribose in DNA [2,11]. Due to the toxicity and carcinogenic activity of fumaraldehyde and malealdehyde, DFT method is used to study the stabilities, rotations and vibrational frequencies. To the best of our knowledge, we could not find any theoretical and experimental study for the rotational barrier of such compound and hence this study is conducted.

## 2.0 COMPUTATIONAL METHOD

Malealdehyde, fumaraldehyde and their sulfur and selenium analogues are generated by using ChemDraw, Chem3D and Gauss View [12]. Gauss View is used for visualizing the optimized structure and the assignment of vibrational frequencies. The transition state structure was modelled between the malealdehyde and fumaraldehyde with dihedral angle of  $90^\circ$ . Figure 1 shows the 2D structure and atoms numbering for malealdehyde and fumaraldehyde.

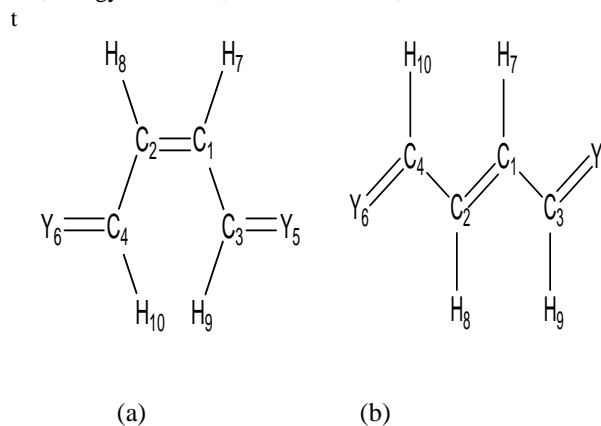


Figure 1: 2D structures and atoms numbering of (a) malealdehyde (cis) and (b) fumaraldehyde (trans), with the oxygen (Y=O), sulfur (Y=S) and selenium analogues (Y=Se).

Gaussian 03 suite [13] has been used to run all the computations under Linux Fedora operating system. B3LYP with 6-311++G(d,p) basis set is applied to all atoms without any restriction. The optimized structure is used as the input for the second order Møller-Plesset perturbation theory (MP2) calculations with the same basis set without any restriction. The absence of the imaginary frequency for the optimized structure of malealdehyde and fumaraldehyde demonstrated they are in their ground state of energy level. The solvent effect towards the conformers is explored. Nine solvents with dielectric constant varying from 2 to 80 have been explored using Self Consistent Reaction field (SCRF) [14]. The energy difference,  $E$  is calculated as the difference between the energy of cis and trans conformer. In addition to that, the rotational barrier,  $B1$  which is the difference between the the cis conformer energy value and transition state energy is calculated.

### Appendix

Oxygen analogue			
Malealdehyde		Fumaraldehyde	
LUMO	HOMO	LUMO	HOMO
Sulphur analogue			
Malealdehyde		Fumaraldehyde	
LUMO	HOMO	LUMO	HOMO
Selenium analogue			
Malealdehyde		Fumaraldehyde	
LUMO	HOMO	LUMO	HOMO

Figure 2: LUMO and HOMO orbitals for malealdehyde and fumaraldehyde in O, S and Se analogues

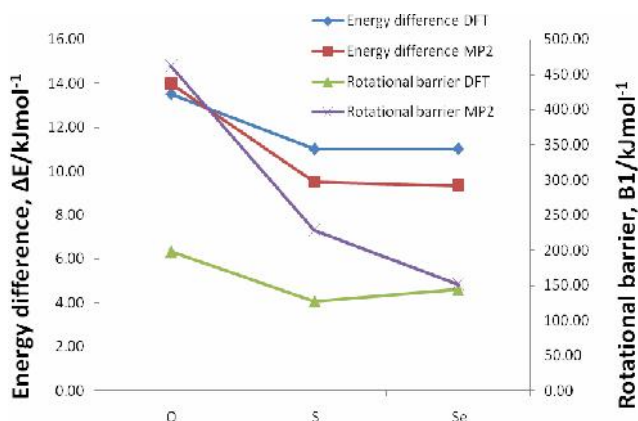


Figure 3: Graph of rotational barrier,  $B_1$  and energy difference,  $E$  against oxygen, sulfur and selenium analogues in gas phase with DFT and MP2 in gas phase

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Geometry optimization

The optimized structure of malealdehyde (cis) and fumaraldehyde (trans) has  $C_{2v}$  and  $C_{2h}$  point group respectively in the gas and different solution phases. Table 1 and 2 show the optimized structural parameters of malealdehyde and fumaraldehyde with their sulfur and selenium analogues by using DFT and MP2 methods. The bond length of the  $C=Y$  bond increases significantly when Y is substituted with S and Se atom at DFT and MP2 levels of calculations. All of the bond lengths and bond angles differ by a maximum of 0.15 Å and 6.0° in the gas phase. However, in solution phase, all bond lengths and bond angles differ by only a maximum of 0.01Å and 2.0° respectively.

Results show that malealdehyde and its analogues have a larger dipole moment compared to fumaraldehyde and its analogues, as expected from a cis structure. The electron withdrawing Y atoms in cis conformation withdraw electrons from the neighbouring atom to the same direction, promoting the overall dipole moment. On the other hand, the electron withdrawing Y atoms in trans conformation withdraw electrons in the opposite direction, reducing the effective dipole moment. The angle of Y5-C3-H9 and Y6-C4-H10 for malealdehyde and fumaraldehyde decreased gradually when Y atom is substituted with S and Se atom due to the decrease in repulsion between the Y atom and the corresponding H atom. It was also found that the Y5-C3-H9 and Y6-C4-H10 angles obtained in malealdehyde are smaller than fumaraldehyde.

#### 3.2 LUMO-HOMO energy band gap

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values have been tabulated in Table 3 and as shown in Figure 2. The energy gap is the energy difference between HOMO and LUMO. The energy band gap measures the excitability of the molecule; a smaller band gap results in electron being excited more easily. The fumaraldehyde conformer has a smaller energy band gap compared to malealdehyde. Thus, fumaraldehyde of O, S and Se analogues are more likely to be excited. For malealdehyde analogues, the energy band gap has a large increment when Y atom is substituted with S and Se atom. However, the energy band gap for

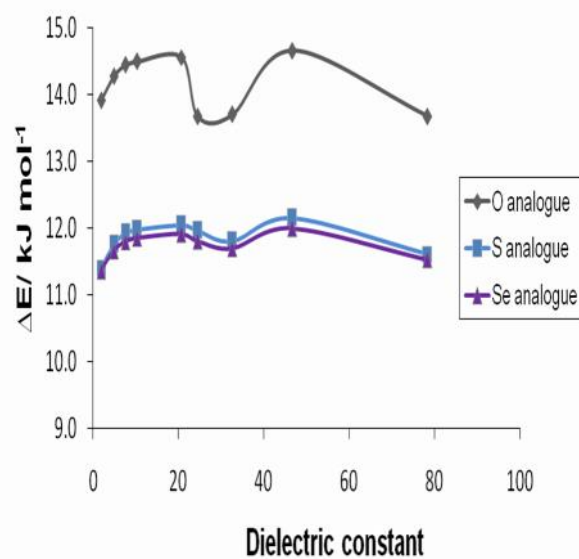


Figure 4: Graph of variation of the energy difference,  $\Delta E$  against dielectric constant of the solvents

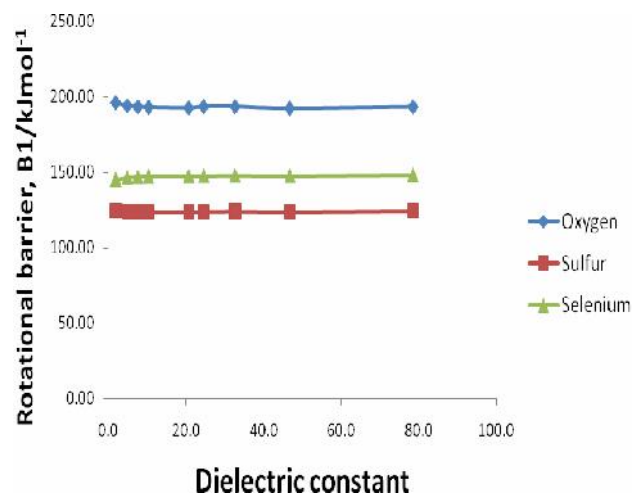


Figure 5: Graph of variation of rotation barrier,  $B_1$  against dielectric constant of the solvents

fumaraldehyde analogues experienced a sharp decline when Y atom is substituted with S and Se atom.

#### 3.3 Partial charges

Table 4 shows the partial charges (Mulliken charges) of all atoms of malealdehyde, fumaraldehyde and its transition state for O, S and Se analogues in the gas phase. These partial charges are useful to explain the electrostatic interactions for all the conformers. All of the Y atoms for fumaraldehyde for O, S and Se analogues are more electronegative than malealdehyde. It can be predicted that the electrostatic interaction between H and Y atom in fumaraldehyde is greater than malealdehyde conformer. The partial negative charge of Y atoms is observed decreased in the sequence of S, O and Se atom.

#### 3.4 Vibrational parameters for but-2-enedial cis and trans conformers in gas phase

Table 5 shows all of the vibrational parameters for but-2-enedial malealdehyde and fumaraldehyde conformers with

Table 1: Optimized structural parameters of malealdehyde and fumaraldehyde with their sulfur and selenium analogues obtained using DFT/B3LYP/6-311++G(d,p)

	Malealdehyde			Transition State			Fumaraldehyde		
	Bond length (Å)								
	Y=O	Y=S	Y=Se	Y=O	Y=S	Y=Se	Y=O	Y=S	Y=Se
r(C1-C2)	1.346	1.364	1.374	1.454	1.473	1.488	1.341	1.360	1.369
r(C1-C3)	1.479	1.441	1.427	1.441	1.370	1.336	1.477	1.439	1.425
r(C1-H7)	1.087	1.086	1.086	1.091	1.090	1.089	1.087	1.086	1.086
r(C2-C4)	1.479	1.441	1.427	1.441	1.370	1.336	1.477	1.439	1.425
r(C2-H8)	1.087	1.086	1.086	1.091	1.090	1.089	1.087	1.086	1.086
r(C3-O5)	1.211	1.639	1.788	1.229	1.705	1.903	1.209	1.638	1.788
r(C3-H9)	1.105	1.089	1.086	1.105	1.089	1.089	1.109	1.092	1.089
r(C4-O6)	1.211	1.639	1.788	1.229	1.705	1.903	1.209	1.638	1.788
r(C4-H10)	1.105	1.089	1.086	1.105	1.089	1.089	1.109	1.092	1.089
	Angle (°)								
C1-C2-C4	126.4	126.4	126.4	124.5	123.9	122.8	122.0	122.5	122.7
C1-C2-H8	119.8	118.2	117.7	119.7	117.8	117.1	121.6	120.3	119.8
C1-C3-Y5	121.9	123.9	123.9	122.5	123.2	126.9	123.5	124.8	124.6
C1-C3-H9	117.8	117.5	118.3	116.9	118.5	121.0	115.3	115.7	116.7
C2-C1-H7	119.8	118.2	117.7	119.7	117.8	117.1	121.6	120.3	119.8
C2-C1-C3	126.4	126.4	126.4	124.5	123.9	122.8	122.0	122.5	122.7
C2-C4-Y6	121.9	123.9	123.9	122.5	123.2	126.9	123.5	124.8	124.6
C2-C4-H10	117.8	117.5	118.3	116.9	118.5	121.0	115.3	115.7	116.7
C3-C1-H7	113.8	115.4	115.9	115.8	118.3	120.1	116.4	117.2	117.5
C4-C2-H8	113.8	115.4	115.9	115.8	118.3	120.1	116.4	117.2	117.5
Y5-C3-H9	120.4	118.6	117.8	120.7	118.3	112.1	121.2	119.5	118.7
Y6-C4-H10	120.4	118.6	117.8	120.7	118.3	112.1	121.2	119.5	118.7
	Rotational constant (GHz)								
A	15.884	15.201	14.382	20.558	19.641	18.146	32.297	28.679	27.071
B	1.594	0.705	0.276	1.382	0.637	0.245	1.334	0.624	0.250
C	1.449	0.674	0.270	1.356	0.632	0.245	1.281	0.610	0.247
	Dipole moment (Debye)								
	0.816	0.908	0.940	1.056	0.711	0.052	0.144	0.233	0.289

its O, S and Se analogues. The number of various degrees of freedom for polyatomic nonlinear molecules is calculated as  $3n - 6$ . Thus, there are 24 vibrational frequencies for malealdehyde and fumaraldehyde. For malealdehyde ( $C_{2v}$ ), there are 20 IR active and 24 raman active frequencies. On the other hand, fumaraldehyde ( $C_{2h}$ ), has 12 IR active and 12 raman active frequencies. The vibrational frequencies of symmetrical  $CH=Y$  stretching lies in the range of  $3200 - 3000 \text{ cm}^{-1}$  and  $3150 - 2950 \text{ cm}^{-1}$ . Also, the vibrational frequencies of symmetrical  $C=C$  stretching for malealdehyde and fumaraldehyde lies in the range of  $1700 - 1550 \text{ cm}^{-1}$  in O, S and Se analogues. Malealdehyde conformer displays higher vibrational frequencies than the trans conformer. This is due to the fact that higher dipole moment has higher absorption frequency.[15,16]

Figure 3 shows rotational barrier,  $B_1$  and energy difference,  $E$  for O, S and Se analogues by using DFT and MP2 level of calculations. The energy difference,  $E$ ,

is the difference between malealdehyde and fumaraldehyde energies, while the rotational barrier,  $B_1$ , is the energy difference of the transition state and the malealdehyde. The results show that the energy difference,

$E$  is greater than the rotational barrier energy,  $B_1$ , by using DFT level of calculation, while MP2 method of calculation did not show such systematic difference. However, the energy difference decreases with the following sequence of  $S < Se < O$  for DFT and MP2 methods respectively. Also, the effect of substituting the O atom with S and Se atom leads to a decline in the rotational barrier energy  $B_1$ , by MP2 method, but did not show a systematically change in DFT level of calculation.

### 3.5 Rotational barrier, $B_1$ , energy difference, $E$ and other thermodynamic parameters (gas phase)

Table 6 shows the sum of electronic and zero-point energies of malealdehyde, fumaraldehyde and transition state with their sulphur and selenium analogues in gas phase. Optimized structure were obtained by B3LYP/6-

Table 2: Optimized structural parameters of the malealdehyde and fumaraldehyde with their sulfur and selenium analogues obtained using MP2/6-311++G(d,p)

	Malealdehyde			Transition State			Fumaraldehyde		
	Bond length (Å)								
	Y=O	Y=S	Y=Se	Y=O	Y=S	Y=Se	Y=O	Y=S	Y=Se
r(C1-C2)	1.355	1.368	1.377	1.577	1.528	1.522	1.350	1.364	1.373
r(C1-C3)	1.481	1.450	1.438	1.328	1.327	1.326	1.479	1.448	1.436
r(C1-H7)	1.088	1.089	1.089	1.088	1.091	1.092	1.089	1.090	1.090
r(C2-C4)	1.481	1.450	1.438	1.328	1.327	1.326	1.479	1.448	1.436
r(C2-H8)	1.088	1.089	1.089	1.088	1.091	1.092	1.089	1.090	1.090
r(C3-O5)	1.221	1.632	1.783	1.355	1.775	1.935	1.219	1.631	1.782
r(C3-H9)	1.104	1.092	1.090	1.095	1.091	1.090	1.109	1.095	1.093
r(C4-O6)	1.221	1.632	1.783	1.355	1.775	1.935	1.219	1.631	1.782
r(C4-H10)	1.104	1.092	1.090	1.095	1.091	1.090	1.109	1.095	1.093
Angle (°)									
C1-C2-C4	126.0	125.9	125.8	123.8	123.2	123.2	121.4	122.3	122.2
C1-C2-H8	119.7	118.3	118.0	115.8	116.3	116.0	121.5	120.3	119.9
C1-C3-Y5	121.5	123.1	123.2	119.6	121.3	121.4	123.3	124.1	124.1
C1-C3-H9	118.0	117.7	118.6	122.7	121.4	122.1	115.3	115.8	116.8
C2-C1-H7	119.7	118.3	118.0	115.8	116.3	116.0	121.5	120.3	119.9
C2-C1-C3	126.0	125.9	125.8	123.8	123.2	123.2	121.4	122.3	122.2
C2-C4-Y6	121.5	123.1	123.2	119.6	121.3	121.4	123.3	124.1	124.1
C2-C4-H10	118.0	117.7	118.6	122.7	121.4	122.1	115.3	115.8	116.8
C3-C1-H7	114.3	115.7	116.2	120.4	120.5	120.8	117.0	117.4	117.9
C4-C2-H8	114.3	115.7	116.2	120.4	120.5	120.8	117.0	117.4	117.9
Y5-C3-H9	120.5	119.2	118.2	117.5	117.2	116.5	121.4	120.1	119.1
Y6-C4-H10	120.5	119.2	118.2	117.5	117.2	116.5	121.4	120.1	119.1
Rotational constant (GHz)									
A	15.722	15.042	14.034	18.313	21.632	18.955	31.951	28.142	26.568
B	1.587	0.708	0.277	1.430	0.617	0.247	1.327	0.625	0.250
C	1.442	0.676	0.272	1.358	0.615	0.246	1.274	0.612	0.247
Dipole moment (Debye)									
	0.699	0.779	0.861	1.242	0.563	0.820	0.143	0.230	0.285

Table 3: LUMO, HOMO and energy band gap for malealdehyde and fumaraldehyde with their sulfur and selenium analogues

	Oxygen analogue		Sulfur analogue		Selenium analogue	
	Cis	Trans	Cis	Trans	Cis	Trans
LUMO (a.u.)	-0.12867	-0.12982	-0.01981	-0.15488	-0.03521	-0.16082
HOMO (a.u.)	-0.28719	-0.28786	-0.35663	-0.24691	-0.33338	-0.23502
Energy band gap/ kJ mol <sup>-1</sup>	416.19	414.93	884.32	241.62	782.85	194.81

311++G(d,p) and MP2/6-311++G(d,p) methods. Furthermore, the energy difference between the malealdehyde and fumaraldehyde ( $E = E_{\text{malealdehyde}} - E_{\text{fumaraldehyde}}$ ), the rotation barrier energy between malealdehyde and transition state conformers ( $B1 = TS - E_{\text{malealdehyde}}$ ) and some thermodynamic parameters ( $H$ ,  $G$ , and  $S$ ) were reported.

The results for DFT calculations,  $B1$  value did not show a systematic change as  $Y = O$  is replaced by  $S$  and  $Se$  atom.

However, MP2 method showed a decreased in  $B1$  value. By using DFT,  $E$  and  $G$  values are decreased systematically as  $Y = O$  is replaced by  $S$  and  $Se$  atom. Fumaraldehyde and its analogues show a lower energy values compared to malealdehyde conformer. This demonstrates that the fumaraldehyde analogues are m

Table 4: Charges in  $e$  on the atoms of the optimized malealdehyde, fumaraldehyde and transition state with their sulphur and selenium analogues.

	Cis rotamer			Transition state			Trans rotamer		
	Y=O	Y=S	Y=Se	Y=O	Y=S	Y=Se	Y=O	Y=S	Y=Se
B3LYP/6-311++G(d,p)									
C1	0.053	-0.094	0.091	0.073	-0.029	0.024	0.072	-0.077	0.145
C2	0.053	-0.094	0.091	0.073	-0.029	0.024	0.072	-0.077	0.145
C3	-0.164	0.174	-0.421	-0.200	-0.105	-0.418	-0.150	0.178	-0.459
C4	-0.164	0.174	-0.421	-0.200	-0.105	-0.418	-0.150	0.178	-0.459
Y5	-0.226	-0.462	-0.044	-0.228	-0.307	0.025	-0.233	-0.467	-0.052
Y6	-0.226	-0.462	-0.044	-0.228	-0.307	0.025	-0.233	-0.467	-0.052
H7	0.231	0.197	0.230	0.232	0.210	0.186	0.199	0.123	0.181
H8	0.231	0.197	0.230	0.232	0.210	0.186	0.199	0.123	0.181
H9	0.106	0.185	0.145	0.122	0.230	0.183	0.112	0.243	0.185
H10	0.106	0.185	0.145	0.122	0.230	0.183	0.112	0.243	0.185
MP2/6-311++G(d,p)									
C1	0.034	-0.156	-0.017	0.182	-0.035	0.064	0.068	-0.139	0.053
C2	0.034	-0.156	-0.017	0.182	-0.035	0.064	0.068	-0.139	0.053
C3	-0.227	0.208	-0.337	-0.500	-0.098	-0.470	-0.219	0.213	-0.385
C4	-0.227	0.208	-0.337	-0.500	-0.098	-0.470	-0.219	0.213	-0.385
Y5	-0.188	-0.474	-0.072	-0.083	-0.396	-0.053	-0.197	-0.474	-0.081
Y6	-0.188	-0.474	-0.072	-0.083	-0.396	-0.053	-0.197	-0.474	-0.081
H7	0.253	0.219	0.251	0.245	0.259	0.241	0.220	0.145	0.204
H8	0.253	0.219	0.251	0.245	0.259	0.241	0.220	0.145	0.204
H9	0.127	0.204	0.174	0.156	0.269	0.218	0.128	0.255	0.209
H10	0.127	0.204	0.174	0.156	0.269	0.218	0.128	0.255	0.209

In summary, we can conclude that, (i) the fumaraldehyde and its analogues are more stable and more energetically preferable, (ii) the rotational barrier energy ( $B1$ ) is much larger than the energy difference ( $E$ ); (iii) the rotational barrier energy,  $B1$  increases in the sequence of S, O, Se analogue

### 3.6 Rotational barrier, $B1$ , energy difference, $E$ and other thermodynamic parameters (solution phase phase)

Table 7 shows the dielectric constant of nine different solvents while Figure 4 and 5 show the graph of energy difference,  $\Delta E$  and rotational barrier,  $B1$  under solvent's dielectric constant varied from 2 to 80. Table 8 shows the calculated rotational barrier and other thermodynamic parameters ( $E$ ,  $H$  and  $G$ ) malealdehyde and fumaraldehyde with its O, S and Se analogues in solution phase. Malealdehyde and fumaraldehyde are most stable in solution phase than in gas phase with the increment of dielectric constant of solvent. In solution phase, the energy difference decreases according to the sequence of  $Se < S < O$ , whereas the rotational barrier decreases according to sequence  $S < Se < O$ . For both rotational barrier and energy difference, oxygen analogue obtained the highest value. The energy differences for sulfur and selenium analogues are very close but show a bigger difference to

oxygen analogue. The rotation barrier,  $B1$  is much higher than the energy difference,  $E$ . High value of rotation barrier,  $B1$  indicates the rotation hindrance for conformer conversion.

ore stable than the malealdehyde conformers.

### 4.0 CONCLUSION

DFT and MP2 are the two types of methods of calculation which can be used to study the rotational barrier, thermodynamic parameters, and others information such as the charges and vibration frequencies for but-2-enedial malealdehyde and fumaraldehyde conformers. The LUMO-HOMO energy band gap for fumaraldehyde is lower than malealdehyde. Thus, the fumaraldehyde is expected to be more likely to be excited. There are 24 vibrational frequencies for malealdehyde and fumaraldehyde according to the number of various degrees of freedom for polyatomic nonlinear molecules is calculated as  $3n - 6$ . The malealdehyde has higher vibrational frequencies than fumaraldehyde. The energy difference for both compounds in gas phase decreased with the sequence of  $S < Se < O$ . Meanwhile, it decreased with the sequence of  $Se < S < O$  in solution phase.

Table 5(a): Vibrational parameters for malealdehyde (Y=O) conformer

Frequency	IR	Raman	Depolarisation	Depolarisation	Symmetry	Assignment
3172.4	2.5	131.2	0.14	0.24	A <sub>1</sub>	symmetrical
3155.3	0.5	47.1	0.75	0.86	B <sub>2</sub>	assymmetrical
2964.7	97.3	125.6	0.27	0.42	A <sub>1</sub>	symmetrical
2931.3	9.0	11.0	0.75	0.86	B <sub>2</sub>	assymmetrical
1762.3	5.3	276.2	0.30	0.46	A <sub>1</sub>	symmetrical
1757.1	480.4	29.9	0.75	0.86	B <sub>2</sub>	assymmetrical
1664.0	7.6	106.6	0.19	0.31	A <sub>1</sub>	symmetrical
1431.1	0.7	5.0	0.75	0.86	B <sub>2</sub>	CH rocking
1428.5	1.0	27.7	0.36	0.53	A <sub>1</sub>	CH
1361.7	4.9	0.8	0.75	0.86	B <sub>2</sub>	CH rocking
1241.1	6.6	65.4	0.45	0.62	A <sub>1</sub>	CH scissoring
1131.3	75.9	4.2	0.75	0.86	B <sub>2</sub>	C-C bending
1042.3	0.0	2.5	0.75	0.86	A <sub>2</sub>	CH twisting
1020.7	0.0	0.9	0.75	0.86	A <sub>2</sub>	CH
1019.3	3.8	4.6	0.75	0.86	B <sub>1</sub>	CH
985.9	41.1	9.8	0.69	0.82	A <sub>1</sub>	CH scissoring
760.7	40.3	0.0	0.75	0.86	B <sub>1</sub>	CH wagging
695.9	0.1	0.8	0.75	0.86	B <sub>2</sub>	C-C bending
451.8	13.7	5.7	0.17	0.29	A <sub>1</sub>	C-C
389.0	12.1	0.1	0.75	0.86	B <sub>2</sub>	CH
317.8	0.0	6.3	0.75	0.86	A <sub>2</sub>	CH
181.6	13.4	1.8	0.26	0.41	A <sub>1</sub>	C-C
135.9	0.0	0.6	0.75	0.86	A <sub>2</sub>	C=O twisting
91.3	24.9	1.8	0.75	0.86	B <sub>1</sub>	C=O wagging

Table 5(b): Vibrational parameters for fumaraldehyde (Y=O) conformer

Frequency	IR	Raman	Depolarisation	Depolarisation	Symmetry	Assignment
3158.5 (3201.7)	4.1 (0.0)	0.0	0.00	0.00	B <sub>u</sub>	assymmetrical CH stretching
3157.1 (3201.6)	0.0 (2.3)	132.1	0.25	0.40	A <sub>g</sub>	symmetrical CH stretching
2912.4 (2976.8)	0.0 (0.0)	224.3	0.31	0.47	A <sub>g</sub>	symmetrical CH (carbonyl) stretching
2910.1 (2974.7)	153.1	0.0	0.00	0.00	B <sub>u</sub>	assymmetrical CH (carbonyl)
1769.0 (1733.0)	536.9	0.0	0.00	0.00	B <sub>u</sub>	assymmetrical C=O stretching
1767.6 (1729.0)	0.0 (0.0)	374.3	0.36	0.53	A <sub>g</sub>	assymmetrical C=O stretching
1675.4 (1661.6)	0.0 (0.0)	173.3	0.29	0.45	B <sub>u</sub>	C=C stretching
1419.0 (1433.3)	2.3 (3.0)	0.0	0.00	0.00	A <sub>g</sub>	CH (carbonyl) rocking
1397.0 (1412.6)	0.0 (0.0)	13.3	0.31	0.47	A <sub>g</sub>	CH (carbonyl) scissoring
1303.0 (1304.0)	0.0 (0.0)	12.7	0.14	0.24	A <sub>g</sub>	CH scissoring
1239.0 (1237.5)	7.0 (6.7)	0.0	0.00	0.00	B <sub>u</sub>	CH rocking
1153.5 (1173.4)	0.0 (0.0)	77.3	0.50	0.66	A <sub>g</sub>	C-C bending
1066.0 (1094.8)	171.8	0.0	0.00	0.00	B <sub>u</sub>	C-H (carbonyl) bending
1031.1 (1015.8)	0.0 (16.7)	11.2	0.75	0.86	B <sub>g</sub>	CH (carbonyl) twisting
1022.4 (1013.4)	27.7 (0.0)	0.0	0.00	0.00	A <sub>u</sub>	CH bending
1018.8 (1004.9)	23.6 (38.3)	0.0	0.00	0.00	A <sub>u</sub>	C=O wagging
821.2 (794.2)	0.0 (0.0)	3.0	0.75	0.86	B <sub>g</sub>	CH bending
642.7 (641.4)	28.2 (20.5)	0.0	0.00	0.00	B <sub>u</sub>	CH scissoring
433.0 (431.7)	0.0 (0.0)	2.4	0.42	0.59	A <sub>g</sub>	CH bending
409.1 (407.8)	0.0(0.0)	5.7	0.14	0.24	A <sub>g</sub>	CH scissoring
281.9 (272.3)	10.3 (10.7)	0.0	0.00	0.00	A <sub>u</sub>	CH (carbonyl) wagging
186.9 (174.8)	0.0 (0.0)	0.7	0.75	0.86	B <sub>g</sub>	CH twisting
152.0 (150.3)	23.0 (20.9)	0.0	0.00	0.00	B <sub>u</sub>	CH (carbonyl) rocking
85.1 (79.9)	19.7 (17.2)	0.0	0.00	0.00	A <sub>u</sub>	C=O wagging



Table 5(c): Vibrational parameters for malealdehyde (Y=S) conformer

Frequency	IR	Raman	Depolarisation	Depolarisation	Symmetry	Assignment
3175.2 (3203.2)	2.6 (2.8)	97.5	0.17	0.30	A <sub>1</sub>	symmetrical CH stretching
3159.3 (3185.4)	0.7 (1.7)	20.5	0.75	0.86	B <sub>2</sub>	assymmetrical CH stretching
3122.1 (3157.7)	4.2 (5.0)	76.6	0.18	0.30	A <sub>1</sub>	symmetrical CH (carbonyl) stretching
3103.5 (3137.7)	5.1 (3.4)	19.1	0.75	0.86	B <sub>2</sub>	assymmetrical CH (carbonyl)
1590.2 (1600.0)	6.0 (6.1)	2119.3	0.29	0.45	A <sub>1</sub>	C=C stretching
1466.5 (1467.3)	83.7 (26.8)	47.3	0.75	0.86	B <sub>2</sub>	CH rocking
1345.5 (1353.3)	9.6 (9.7)	11.7	0.56	0.72	A <sub>1</sub>	CH (carbonyl) scissoring
1321.7 (1328.6)	25.7 (5.0)	1.4	0.75	0.86	B <sub>2</sub>	CH (carbonyl) rocking
1263.2 (1264.0)	2.2 (1.2)	490.2	0.36	0.53	A <sub>1</sub>	CH scissoring
1186.5 (1197.3)	98.4 (31.4)	32.4	0.75	0.86	B <sub>2</sub>	CH rocking
1125.7 (1152.4)	12.8 (12.9)	1105.8	0.33	0.50	A <sub>1</sub>	symmetrical C=S stretching
1049.5 (1082.9)	65.2 (0.2)	6.1	0.75	0.86	B <sub>2</sub>	assymmetrical C=S stretching
1034.5 (963.8)	0.0 (0.0)	1.6	0.75	0.86	A <sub>2</sub>	CH twisting
950.5 (958.2)	0.3 (0.0)	25.3	0.07	0.13	A <sub>1</sub>	CH scissoring
906.1 (859.0)	0.0 (18.0)	5.9	0.75	0.86	A <sub>2</sub>	CH (carbonyl) twisting
893.5 (825.9)	6.6 (0.0)	3.2	0.75	0.86	B <sub>1</sub>	CH (carbonyl) wagging
822.9 (779.5)	61.1 (58.9)	0.6	0.75	0.86	B <sub>1</sub>	CH bending
614.6 (614.5)	0.6 (2.2)	0.4	0.75	0.86	B <sub>2</sub>	C=C bending
335.9 (337.1)	14.8 (8.7)	0.2	0.75	0.86	B <sub>2</sub>	CH rocking
325.8 (305.3)	0.0 (0.2)	5.4	0.75	0.86	A <sub>2</sub>	CH twisting
304.2 (262.3)	0.5 (0.0)	30.3	0.26	0.42	A <sub>1</sub>	C=O bending
140.4 (135.5)	0.0 (2.7)	2.4	0.75	0.86	A <sub>2</sub>	CH (carbonyl) twisting
133.3 (68.0)	4.0 (0.0)	10.3	0.39	0.56	A <sub>1</sub>	CH (carbonyl) scissoring
77.8 (59.1)	4.5 (2.9)	1.5	0.75	0.86	B <sub>1</sub>	C=S wagging

Table 5(d): Vibrational parameters for fumaraldehyde (Y=S) conformer

Frequency	IR	Raman	Depolarisation	Depolarisatio	Symmetry	Assignment
3164.1 (3190.8)	4.2 (6.7)	0.0	0.48	0.00	B <sub>u</sub>	assymmetrical CH stretching
3158.8 (3187.6)	0.0 (0.0)	84.2	0.30	0.46	A <sub>g</sub>	symmetrical CH stretching
3086.8 (3117.1)	0.0 (0.0)	145.0	0.31	0.47	A <sub>g</sub>	symmetrical CH (carbonyl) stretching
3085.6 (3116.2)	16.2 (16.4)	0.0	0.26	0.41	B <sub>u</sub>	assymmetrical CH (carbonyl)
1605.7 (1611.2)	0.0 (0.0)	2724.1	0.33	0.49	A <sub>g</sub>	C=C stretching
1426.7 (1440.7)	154.8 57.3)	0.0	0.00	0.00	B <sub>u</sub>	assymmetrical C=S stretching
1337.3 (1345.0)	0.0 (0.0)	67.1	0.25	0.40	A <sub>g</sub>	CH (carbonyl) scissoring
1306.8 (1306.8)	0.0 (0.0)	4.5	0.27	0.42	A <sub>g</sub>	CH scissoring
1233.7 (1237.3)	26.0 (18.9)	0.0	0.00	0.00	B <sub>u</sub>	CH rocking
1204.1 (1222.6)	160.6 (55.4)	0.0	0.00	0.00	B <sub>u</sub>	CH (carbonyl) rocking
1176.5 (1186.3)	0.0 (0.0)	1366.8	0.36	0.53	A <sub>g</sub>	C-C stretching
1054.8 (1090.4)	0.0 (0.0)	697.8	0.28	0.44	A <sub>g</sub>	C=S stretching
1015.6 (1008.7)	53.2 (5.1)	0.0	0.00	0.00	A <sub>u</sub>	CH wagging
979.2 (986.7)	18.6 (62.6)	0.0	0.00	0.00	B <sub>u</sub>	CH bending
941.1 (857.1)	0.0 (0.0)	11.3	0.75	0.86	B <sub>g</sub>	CH twisting
893.7 (852.1)	26.1 (27.0)	0.0	0.00	0.00	A <sub>u</sub>	CH (carbonyl) wagging
850.5 (804.8)	0.0 (0.0)	1.0	0.75	0.86	B <sub>g</sub>	CH twisting
514.7 (516.8)	12.5 (2.1)	0.0	0.00	0.00	B <sub>u</sub>	CH (carbonyl) wagging
395.6 (394.4)	0.0 (0.0)	10.1	0.15	0.26	A <sub>g</sub>	CH twisting
295.4 (282.8)	2.7 (0.0)	0.0	0.00	0.00	A <sub>u</sub>	CH rocking
281.8 (255.2)	0.0 (2.4)	21.0	0.35	0.52	A <sub>g</sub>	CH scissoring



197.6 (140.3)	0.0 (0.0)	0.1	0.75	0.86	B <sub>g</sub>	CH twisting
116.1 (116.0)	7.4 (5.5)	0.0	0.00	0.00	B <sub>u</sub>	CH (carbonyl) rocking
65.4 (54.0)	4.2 (2.6)	0.0	0.00	0.00	A <sub>u</sub>	C=S wagging

Table 5(e): Vibrational parameters for malealdehyde (Y=Se) conformer

Frequency	IR	Raman	Depolarisation	Depolarisation	Symmetry	Assignment
3174.5 (3199.3)	1.9 (1.9)	73.1	0.19	0.31	A <sub>1</sub>	symmetrical CH stretching
3159.1 (3182.2)	1.0 (3.1)	11.6	0.75	0.86	B <sub>2</sub>	assymmetrical CH stretching
3151.9 (3177.1)	0.3 (0.6)	85.7	0.16	0.28	A <sub>1</sub>	symmetrical CH (carbonyl) stretching
3135.4 (3159.6)	1.9 (1.2)	16.2	0.75	0.86	B <sub>2</sub>	assymmetrical CH (carbonyl) stretching
1551.2 (1553.2)	5.5 (6.7)	3274.8	0.30	0.46	A <sub>1</sub>	C=C stretching
1470.6 (1462.3)	61.2 (8.3)	43.0	0.75	0.86	B <sub>2</sub>	assymmetrical C=Se stretching
1302.2 (1301.9)	8.5 (10.7)	231.1	0.40	0.57	A <sub>1</sub>	CH (carbonyl) scissoring
1290.1 (1287.3)	18.6 (0.8)	1.2	0.75	0.86	B <sub>2</sub>	CH (carbonyl) wagging
1262.2 (1256.6)	7.9 (5.1)	865.6	0.35	0.51	A <sub>1</sub>	CH scissoring
1205.2 (1203.1)	60.5 (9.4)	26.6	0.75	0.86	B <sub>2</sub>	CH rocking
1074.1 (1075.7)	4.3 (5.8)	1037.0	0.35	0.52	A <sub>1</sub>	C-C bending
1034.8 (951.5)	0.0 (0.0)	1.4	0.75	0.86	A <sub>2</sub>	CH twisting
911.8 (940.8)	48.9 (2.3)	8.7	0.75	0.86	B <sub>2</sub>	C-C bending
878.8 (860.9)	0.0 (4.3)	1.3	0.75	0.86	A <sub>2</sub>	CH (carbonyl) twisting
863.6 (825.3)	1.0 (11.3)	1.5	0.75	0.86	B <sub>1</sub>	CH wagging
844.3 (797.9)	74.5	2.6	0.75	0.86	B <sub>1</sub>	CH (carbonyl) wagging
839.2 (789.0)	5.4 (0.0)	325.3	0.25	0.40	A <sub>1</sub>	C=C scissoring
537.7 (541.0)	1.4 (7.1)	1.1	0.75	0.86	B <sub>2</sub>	C-C scissoring
318.1 (304.7)	0.0 (6.6)	5.8	0.75	0.86	A <sub>2</sub>	CH twisting
301.3 (268.2)	14.2 (0.0)	0.3	0.75	0.86	B <sub>2</sub>	C=Se twisting
203.5 (206.7)	0.3 (0.1)	30.3	0.26	0.41	A <sub>1</sub>	C=C bending
139.9 (108.8)	0.0 (0.0)	0.0	0.75	0.86	A <sub>2</sub>	CH (carbonyl) twisting
100.7 (103.1)	1.7 (1.2)	14.1	0.39	0.56	A <sub>1</sub>	C=C bending
70.5 (57.4)	1.6 (1.0)	2.2	0.75	0.86	B <sub>1</sub>	CH (carbonyl) wagging

Table 5(f): Vibrational parameters for fumaraldehyde (Y=Se) conformer

Frequency	IR	Raman	Depolarisation	Depolarisation (U)	Symmetry	Assignment
3164.2	3.2 (7.3)	0.0	0.00	0.00	B <sub>u</sub>	assymmetrical CH stretching
3157.1	0.0 (0.0)	64.8	0.30	0.46	A <sub>g</sub>	symmetrical CH stretching
3122.5	0.0 (0.0)	129.3	0.28	0.44	A <sub>g</sub>	symmetrical CH (carbonyl) stretching
3121.0	4.4 (5.0)	0.0	0.27	0.43	B <sub>u</sub>	assymmetrical CH (carbonyl)
1571.5	0.0 (0.0)	3947.7	0.33	0.50	A <sub>g</sub>	C=C stretching
1409.7	119.8	0.0	0.00	0.00	B <sub>u</sub>	assymmetrical C=Se stretching
1311.5	0.0 (0.0)	76.5	0.21	0.34	A <sub>g</sub>	CH bending
1281.6	0.0 (0.0)	26.6	0.39	0.56	A <sub>g</sub>	C=C stretching
1237.1	69.4	0.0	0.42	0.59	B <sub>u</sub>	CH rocking
1199.9	48.8	0.0	0.38	0.55	B <sub>u</sub>	C-C stretching
1184.0	0.0 (0.0)	1755.1	0.36	0.53	A <sub>g</sub>	C-C stretching
1014.8 (986.3)	54.3	0.0	0.00	0.00	A <sub>u</sub>	CH wagging
932.6 (921.3)	0.0 (0.0)	6.0	0.75	0.86	B <sub>g</sub>	CH twisting
896.2 (853.0)	0.0 (16.9)	1054.2	0.29	0.44	A <sub>g</sub>	C=C scissoring
860.2 (847.9)	34.3 (0.0)	0.0	0.00	0.00	A <sub>u</sub>	CH (carbonyl) wagging
852.3 (825.9)	0.0 (39.0)	2.5	0.75	0.86	B <sub>g</sub>	CH (carbonyl) twisting
823.4 (820.1)	22.2 (0.0)	0.0	0.00	0.00	B <sub>u</sub>	C=C scissoring

445.6 (451.8)	11.3 (0.2)	0.0	0.00	0.00	0.00	B <sub>u</sub>	C-C bending
367.6 (367.7)	0.0 (0.0)	18.5	0.20	0.33		A <sub>g</sub>	C-C scissoring
292.5 (265.9)	1.3 (1.3)	0.0	0.00	0.00		A <sub>u</sub>	CH (carbonyl) wagging
194.2 (181.1)	0.0 (0.0)	2.6	0.75	0.86		B <sub>g</sub>	CH twisting
179.3 (167.7)	0.0 (0.0)	29.1	0.32	0.49		A <sub>g</sub>	C=Se bending
96.3 (94.9)	3.9 (3.1)	0.0	0.00	0.00		B <sub>u</sub>	C-C rocking
58.2 (47.3)	1.8 (1.2)	0.0	0.00	0.00		A <sub>u</sub>	C=Se wagging

Table 6: Energies of the cis, trans and transition state, rotational barrier, energy difference, and other thermodynamic parameters of the malealdehyde and fumaraldehyde with their sulphur and selenium analogues

Y	Cis (Hartrees)	Trans (Hartrees)	Transition State (Hartrees)	B1 kJ mol <sup>-1</sup>	E kJ mol <sup>-1</sup>	H kJ mol <sup>-1</sup>	G kJ mol <sup>-1</sup>	S J mol <sup>-1</sup> K <sup>-1</sup>
B3LYP/6-311++G(d,p)								
O	-305.3237435 (0.070834)	-305.3288866 (0.070650)	-305.2482736 (0.066158)	198.1463347	13.5032078	15.1780140	14.7395556	-0.001471
S	-951.2517667 (0.067088)	-951.2559557 (0.066949)	-951.2035420 (0.064285)	126.6138064	10.9983760	12.5603908	12.2374543	-0.001083
Se	-4957.9146982 (0.065659)	-4957.9188922 (0.065550)	-4957.8598562 (0.063795)	143.9877097	11.0114247	12.4553708	12.0536693	-0.001347
MP2/6-311++G(d,p)								
O	-304.49982503 (0.070928)	-304.50514897 (0.070897)	-304.49982503 (0.070928)	462.1506263	13.9780031	15.1438825	14.3667346	-0.002607
S	-949.65926716 (0.066745)	-949.66288951 (0.066798)	-949.57121162 (0.066971)	228.4043529	9.5104790	10.5597600	8.9660816	-0.005345
Se	-	-4954.16679482 (0.065328)	-4954.10553216 (0.064829)	151.5093726	9.3357257	9.9716480	9.3625321	-0.002043

- Values in bracket are the zero point energy

Table 7: The dielectric constant of the solvents

Solvent	Dielectric Constant
Heptane	1.92
Chloroform	4.90
Tetrahydrofuran	7.58
Dichloroethane	10.36

The rotational barriers for both compounds in gas and solution phase decrease according to the sequence of Se < S < O with DFT method of calculation. Both of the conformers are more stable in solution phase. Based on the energy obtained, the fumaraldehyde analogues for all analogues are more stable compared to malealdehyde analogues. When O atom is substituted with S and Se atom, the stability of the compounds increases.

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Acetone	20.70
Ethanol	24.55
Methanol	32.63
Dimethylsulfoxide	46.70
Water	78.39

Table 8: Energies of the malealdehyde, fumaraldehyde and transition state, rotational barrier, energy difference, and other thermodynamic parameters of the but-2-enedial and its sulphur and selenium analogues in different solvents

Solvent	Trans (Hartrees)	Cis (Hartrees)	Transition State (Hartrees)	B1 kJ mol <sup>-1</sup>	E kJ mol <sup>-1</sup>	H kJ mol <sup>-1</sup>	G kJ mol <sup>-1</sup>
B3LYP/6-311++G(d,p)							
Oxygen Analogue							
Heptane	-305.3347186	-305.3294178	-305.2547324	196.09	13.92	15.78	15.29
Chloroform	-305.3407517	-305.3353140	-305.2613883	194.09	14.28	16.31	15.71
Tetrahydrofuran	-305.3425277	-305.3370250	-305.2633376	193.47	14.45	16.51	15.91
Dichloroethane	-305.3434772	-305.3379530	-305.2643773	193.17	14.50	16.60	15.98
Acetone	-305.3448647	-305.3393177	-305.2658965	192.77	14.56	16.68	16.02
Ethanol	-305.3451048	-305.3398961	-305.2661533	193.61	13.68	15.66	15.13
Methanol	-305.3454535	-305.3402323	-305.2664995	193.59	13.71	15.67	15.26
Dimethylsulfoxide	-305.3456808	-305.3400961	-305.2667885	192.47	14.66	16.79	16.15
Water	-305.3460551	-305.3408455	-305.2671769	193.42	13.68	15.72	15.45
Sulphur Analogue							
Heptane	-951.2595071	-951.2551645	-951.2078301	124.28	11.40	13.22	12.86
Chloroform	-951.2633698	-951.2588918	-951.2116851	123.94	11.76	13.81	13.43
Tetrahydrofuran	-951.2645387	-951.2599970	-951.2128314	123.83	11.92	14.05	13.67
Dichloroethane	-951.2651705	-951.2606060	-951.2134467	123.82	11.98	14.14	13.77
Acetone	-951.2661000	-951.2615114	-951.2143474	123.83	12.05	14.25	13.89
Ethanol	-951.2662560	-951.2617008	-951.2144999	123.93	11.96	14.17	13.81
Methanol	-951.2664730	-951.2619749	-951.2147111	124.09	11.81	14.01	13.67
Dimethylsulfoxide	-951.2666532	-951.2620242	-951.2148796	123.78	12.15	14.39	14.04
Water	-951.2668996	-951.2624773	-951.2150921	124.41	11.61	13.81	13.52
Selenium Analogue							
Heptane	-	-	-	145.10	11.36	13.06	12.60
Chloroform	-	-	-	146.40	11.66	13.60	13.18
Tetrahydrofuran	-	-	-	146.77	11.80	13.82	13.40
Dichloroethane	-	-	-	146.98	11.85	13.90	13.49
Acetone	-	-	-	147.32	11.91	14.01	13.63
Ethanol	-	-	-	147.47	11.80	13.91	13.51
Methanol	-	-	-	147.65	11.69	13.80	13.42
Dimethylsulfoxide	-	-	-	147.49	12.00	14.13	13.75
Water	-	-	-	147.99	11.53	13.63	13.34

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