

## Theoretical study of the thermal properties of mono hydroxyl iso-indene molecule.

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### Abstract

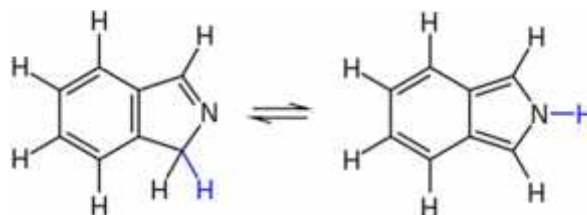
The study focuses on some aspects of the treatment of the optimized geometry and the thermal properties problems of an organic material (mono hydroxyl iso - indene). By replacing a hydrogen atom in the iso-indene by subgroups (OH) and (N and S) atoms through fixing one subgroup and changing the other in various positions in the two rings. A computational calculation also provides a powerful tool for estimating thermal properties. Moreover, the calculated thermal properties included the internal thermal energy, enthalpy, Gibbs free energy, specific heat and entropy. These properties were calculated using Gaussian 09 package of program. Generally, it has been found that the interior thermal energy decreasing, but specified heat and entropy for molecules increase with the addition of substituent OH and (N & S) subgroups compared to the original molecule, this indicates that energy depends on the number of atoms in a molecule. All calculations were carried out by employing according to theory of density function(DFT) at three parameter with the Lee-Yang-Parr functional (B3 LYP) level with 6-31g\*\* basis sets.

**Key words:** DFT, iso-inden molecule, internal thermal energy, enthalpy, Gibbs free energy, specific heat and entropy.

### 1- Introduction

Synthesis for the iso-inden molecule the parent iso-inden was prepared by flash vacuum pyrolysis of an N-substituted iso-inden. N-Substituted iso-inden, which are easier to handle, can be prepared by dehydration of iso-inden-N-oxides. They also arise by myriad other methods, e.g., starting from xylylenedibromide ( $C_6H_4(CH_2Br)_2$ ) [1]. The structure for iso-inden unlike inden, iso-indens exhibit noticeable alternation in the C-C bond lengths, which is consistent with their description as pyrrole derivatives fused to a butadiene. In solution, the 2H-isoindole tautomer predominates. It resembles a pyrrole more than a simple imine. The degree to which the

2H predominates depends on the solvent, and can vary with the substituent in substituted iso-indens [2].



Current research goals to study of the effect of adding n nitrogen N and sulfur S atoms on the thermal properties of the mono hydroxyl iso-indene molecule.

### 2- Theoretical method and computational details

The statistical thermodynamics is an application of the theory of probability which uses mathematical methods for dealing with large populations to the study of the behavior of many particles systems [3]. Statistical thermodynamics can be used to calculate many properties such as the enthalpy, heat capacity and entropy of a gas-phase molecule according to its relax and vibrational modes in the theory of density function [4][5].

In order to achieve accurate results that can be compared to experimental values, one needs to do accurate electronic structure calculations. For many practical purposes a Density Functional Calculation using the (B3LYP) functional and a correlation consistent-polarized Valance Triple Zeta cc-pVTZ basis set is sufficiently accurate [6].

At last, vibrational temperatures for each normal mode. This all information needed to process the data and calculate heat capacities, entropy, internal energy, enthalpy, Gibbs free energy [6][7].

## 2-1 Thermal properties

The equation below represents thermal correction for thermal properties calculations [8].

$$H_{\text{corr}} = E_{\text{tot}} + K_B T \dots\dots\dots(1)$$

$$G_{\text{corr}} = H_{\text{corr}} - T S_{\text{tot}} \dots\dots\dots(2)$$

Where  $H_{\text{corr}}$  is correction of enthalpy,  $E_{\text{tot}}$  is the total ground state energy,  $K_B$  is the Boltzmann constant and  $T$  is the temperature. In equation 2,  $G_{\text{corr}}$  is the correction of Gibbs free energy and  $S_{\text{tot}}$  is the total entropy.

$$E_{\text{th(tot)}} = E_{\text{ele}} + E_{\text{tra}} + E_{\text{rot}} + E_{\text{vib}} \dots\dots\dots(3)$$

$$S_{\text{th(tot)}} = S_{\text{ele}} + S_{\text{tra}} + S_{\text{rot}} + S_{\text{vib}} \dots\dots\dots(4)$$

In equations (3 and 4),  $E_{\text{th(tot)}}$  is the total thermal energy, its components  $E_{\text{ele}}$  is the electronic energy,  $E_{\text{tra}}$  is the translational energy,  $E_{\text{rot}}$  is the rotational energy and  $E_{\text{vib}}$  is the vibrational energy.  $S_{\text{th(tot)}}$  is the total thermal entropy,  $S_{\text{ele}}$ ,  $S_{\text{tra}}$ ,  $S_{\text{rot}}$  and  $S_{\text{vib}}$  are the electronic, translational, rotational and vibrational entropy, respectively.

The other thermal properties included the interior thermal energy, enthalpy, Gibbs free energy can be calculated according to the equations below [6][7].

$$E_{\text{th(tot)}} = E_{\text{tot}} + \text{ZPE} \dots\dots\dots(5)$$

$$U = E_{\text{tot}} + E_{\text{th(tot)}} \dots\dots\dots(6)$$

Where ZPE is the zero point energy and  $U$  is the interior energy of the system.

$$H_{\text{tot}} = E_{\text{tot}} + H_{\text{corr}} \dots\dots\dots(7)$$

$$G_{\text{tot}} = E_{\text{tot}} + G_{\text{corr}} \dots\dots\dots(8)$$

Where:  $E$  = Sum of total electronic and zero-point Energies.

$U$  = Sum of total electronic and thermal Energies.

$H$  = Sum of total electronic and thermal Enthalpies.

$G$  = Sum of total electronic and thermal Gibbs Free Energies [8].

These functions (last three) are sometimes useful to be known because of the thermodynamic identity between Gibbs energy  $G$ , enthalpy  $H$  and entropy [7]. The Gibbs free energy is particularly relevant to calculate activation energies. In both cases (free energies and enthalpies) are very important to calculate accurate electronic energies, which are 'converged' with respect to the basis set [8].

## 2-2 Electronically motion

The electronic partition function is [6]:

$$q_{\text{ele}} = \omega_0 \dots\dots\dots(9)$$

$$E_{\text{ele}} = N_A K_B T^2 \left( \frac{\partial \ln q_{\text{ele}}}{\partial T} \right) = 0 \dots\dots\dots(10)$$

$$C_{\text{ele}} = \left( \frac{\partial E_{\text{ele}}}{\partial T} \right) = 0 \dots\dots\dots(11)$$

Where:  $\omega_0$  degeneracy of the ground state, ( $N_A = 6.022 \times 10^{22} \text{ mole}^{-1}$ ) is the Avogadro's number.

$E_{\text{ele}}$  Internal thermal energy due to electronically motion.

$C_{\text{ele}}$  Contribution to the heat capacity due to electronically motion.

If there is an independent temperature, the heat capacity and the interior thermal energy due to electronically motion are zero. The entropy due to electronically motion is [6]:

$$S_{\text{ele}} = R \ln q_{\text{ele}} \dots\dots\dots(12)$$

Where:  $S_{\text{ele}}$  the entropy due to electronic motion and ( $R = 8.3145 \times 10^{-7} \text{ erg mol}^{-1} \text{ K}^{-1}$ ) is the gas constant.

### 3-2 Translational motion

The translational partition function takes the form [6]:

$$q_{tra} = \left( \frac{2\pi m K_B T}{h^2} \right)^{3/2} * \frac{K_B T}{P} \dots\dots\dots(13)$$

The influence of the interior thermal energy and the constant volume heat capacity, due to translational motion is [6]:

$$E_{tra} = \frac{3}{2} RT \dots\dots\dots(14)$$

$$C_{tra} = \frac{3}{2} R \dots\dots\dots(15)$$

Where:  $E_{tra}$  Internal thermal energy due to translational motion.

$C_{tra}$  Contribution to the heat capacity due to translational motion.

The translational entropy is calculated as [6]:

$$S_{tra} = R (\ln q_t + 5/2) \dots\dots\dots(16)$$

Where:  $S_{tra}$  Entropy due to translation motion.

### 4-2 Rotational motion

The rotational partition function for a molecule is [6]:

$$q_{rot} = \frac{\pi^{1/2}}{\sigma r} \left( \frac{T^{3/2}}{(\theta_{r,x} \theta_{r,y} \theta_{r,z})^{1/2}} \right) \dots\dots\dots(17)$$

Where  $q_{rot}$  changes with the change of the number of electrons in a molecule and the position of subgroup,  $\sigma r$  symmetry number for rotation and  $\theta_{r,x}$   $\theta_{r,y}$   $\theta_{r,z}$  typical temperature for rotational motion. The impact to the interior thermal energy and heat capacity, respectively [8]:

$$E_{rot} = \frac{3}{2} RT \dots\dots\dots(18)$$

$$C_{rot} = \frac{3}{2} R \dots\dots\dots(19)$$

Where:  $E_{rot}$  Interior thermal energy from the rotational motion.

$C_{rot}$  Influence to the heat capacity from the rotational motion.

The average influence to the interior thermal energy from every rotational degree of freedom is  $RT/2$ . The rotational entropy for rotational partition function is [8]:

$$S_{rot} = R (\ln q_{rot} + 3/2) \dots\dots\dots(20)$$

Where:  $S_{rot}$  Entropy due to rotational motion. (Change with temperature and subgroup position).

### 5-2 Vibrational motion

The vibrational partition function [9]:

$$q_{vib} = \prod_K \frac{e^{-\theta_{vib,K}/2T}}{1 - e^{-\theta_{vib,K}/T}} \dots\dots\dots(21)$$

Where:  $\theta_{vib}$ , Characteristic temperature for vibration K.

The influence to interior thermal energy from the vibrational motion is [9]:

$$E_{vib} = R \sum_K \theta_{vib,K} \left( \frac{1}{2} + \frac{1}{e^{\theta_{vib,K}/T} - 1} \right) \dots\dots(22)$$

The contribution to constant volume heat capacity is [6]:

$$C_{vib} = R \sum_K e^{\theta_{vib,K}/T} \left( \frac{\theta_{vib,K}/T}{e^{\theta_{vib,K}/T} - 1} \right)^2 \dots\dots(23)$$

The total entropy contribution from the vibrational partition function is [9]:

$$S_{vib} = R \sum_K \left( \frac{e^{\theta_{vib,K}/T}}{e^{\theta_{vib,K}/T} - 1} - \ln(1 - e^{-\theta_{vib,K}/T}) \right) \dots\dots\dots(24)$$

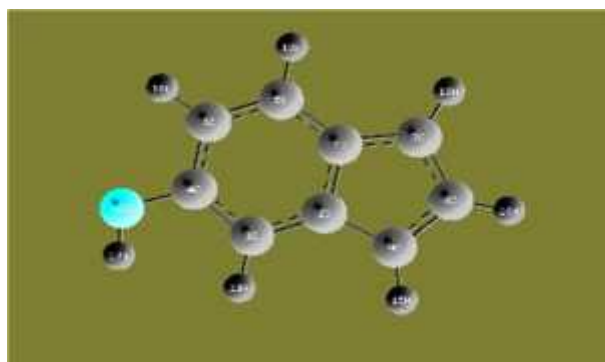
Where:  $E_{vib}$  Interior thermal energy from vibrational motion.

$C_{vib}$  Contribution to the heat capacity from vibrational motion.

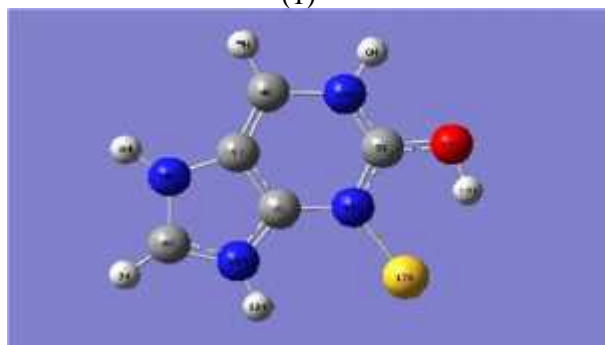
$S_{vib}$  Entropy.

### 3- Results and Discussion

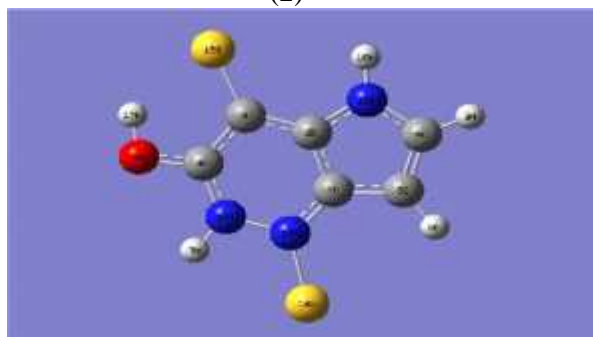
Figure 1 shows the relax structures under study. They are labeled (2-7), where structure 1 represents the reference molecule (mono hydroxyl iso-indene).



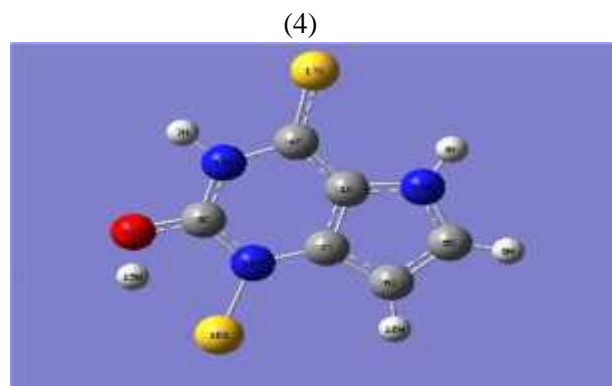
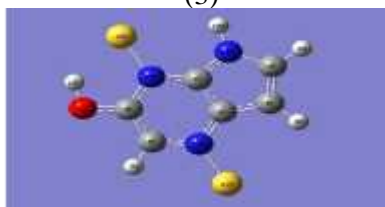
(1)



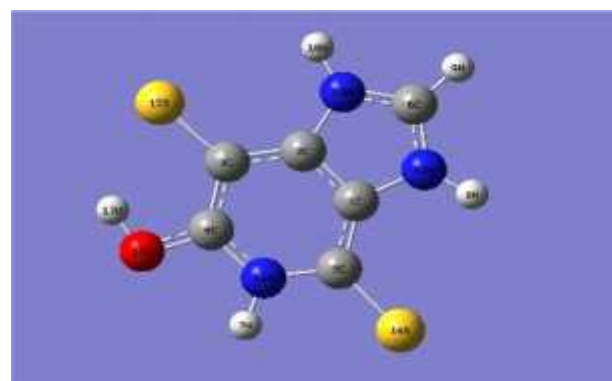
(2)



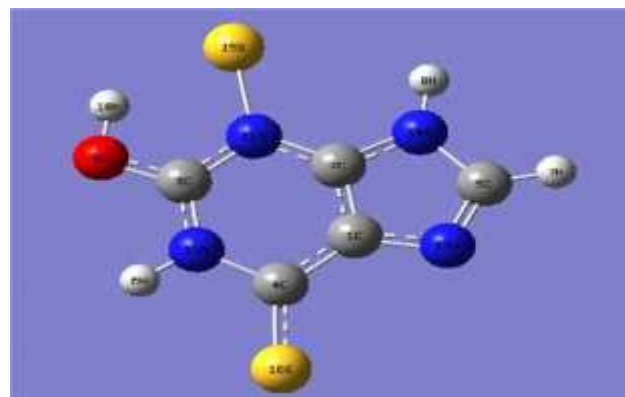
(3)



(5)



(6)



(7)

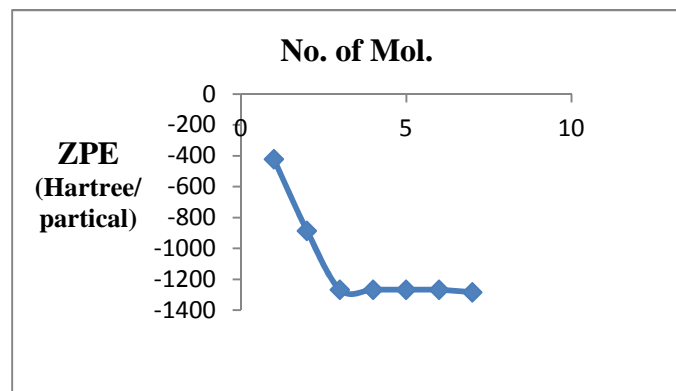
Fig. 1 : Relax structures under study.

The calculated values of total energy, zero point energy, thermally energies, enthalpies and free energies are illustrated in Table 1.

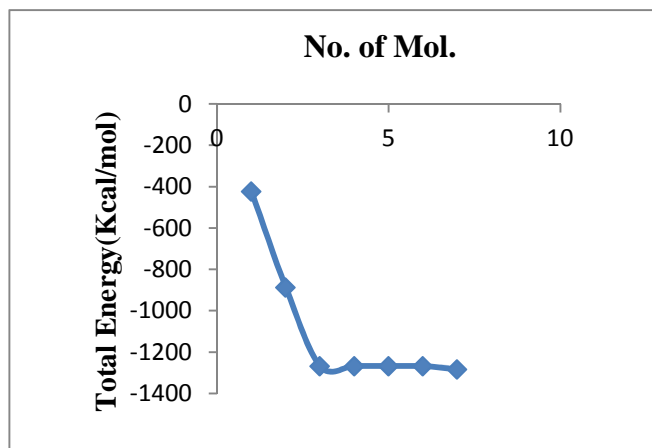
Mol.	Total Energies (Kcal/Mol)	ZPE (Hartree/partical)	Thermal Energies(Kcal/Mol)	Thermal Enthalpies(Cal/Mol .K)	Thermal Free Energies(Cal/Mol . K)
1	-422.402	-422.271	-422.263	-422.262	-422.303
2	-886.527	-886.408	-886.398	-886.397	-886.443
3	-1267.52	-1267.411	-1267.402	-1267.401	-1267.447
4	-1267.53	-1267.418	-1267.408	-1267.407	-1267.453
5	-1267.57	-1267.461	-1267.451	-1267.450	-1267.496
6	-1267.58	-1267.461	-1267.451	-1267.451	-1267.497
7	-1283.61	-1283.510	-1283.501	-1283.500	-1283.546

**Table 1 : Total energy, ZPE, thermally energies, enthalpies and free energies.**

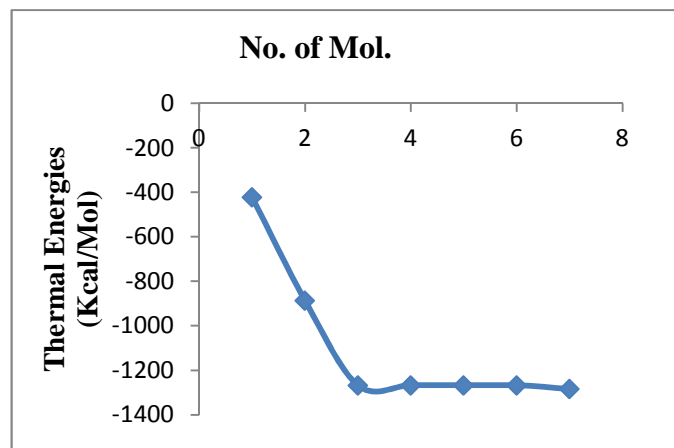
As seen in table 1, all above thermal properties were decreased with increasing the number of atoms in the structure. So, the total energy is approximately independent on the position of atoms added to the reference mono hydroxyl iso-indene molecule. Figures 2-6 show the calculated thermal properties of iso-indene and it is adducts from DFT calculations.



**Fig. 3 : The ZPE of the studied molecules.**



**Fig. 2: The total energy of the studied molecules.**



**Fig. 4 : The thermal energy of the studied molecules.**

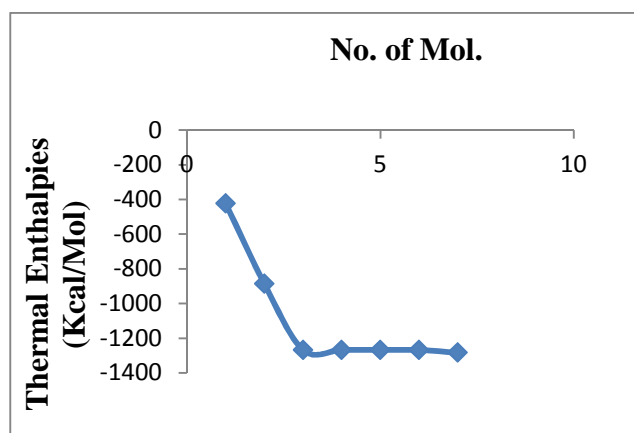


Fig.5 : Thermal enthalpy of the molecules.

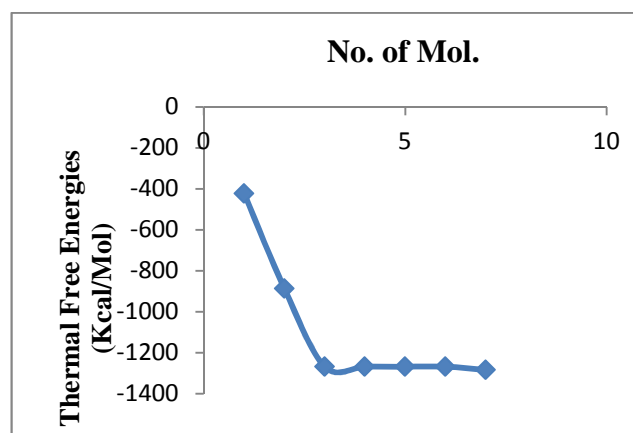


Fig.6 : The thermal free energy of the molecules under study.

Table (2) declare the thermally properties included the interior thermally energy  $E_{th}$ , specific heat  $C_v$  and entropy  $S_{th}$  of the set of mono hydroxyl iso indene molecules. As shown, the values of interior thermally energy  $E_{th}$  of molecules are lessening with addition the (S, N) atoms to the original iso indene. We found that the values of specific heat  $C_v$  cumulative with replaced (N,S) atoms instead of H atom. The values of entropy for the molecules sequence of the form increasing. The rise of electrons number in a molecule means the growth of the ability of the molecule to

appear heat capacity. So, the position of the subgroup in a molecule effects on the specific heat values according to electron population according to linear combine of atomic orbital - molecular orbital. The entropy for the two groups of molecules in Table (2) shows good agreement with the equation (17). The change of the values according to the number of electrons in a molecule and the position of subgroup. Figures (7-9) illustrate the behavior of thermal energy,  $C_v$  and  $S$  for the studied structures, respectively.

Mol.	E (Thermal) Kcal/Mol	$C_v$ Cal/Mol-Kelvin	S Cal/Mol-Kelvin
1	87.049	31.070	85.917
2	80.663	35.179	95.994
3	78.315	37.749	96.778
4	77.965	37.489	97.779
5	78.245	37.151	97.129
6	79.231	37.281	97.494
7	70.943	36.116	97.900

Table (2) : Thermal energy, specific heat  $C_v$  and entropy  $S$  of the molecules.



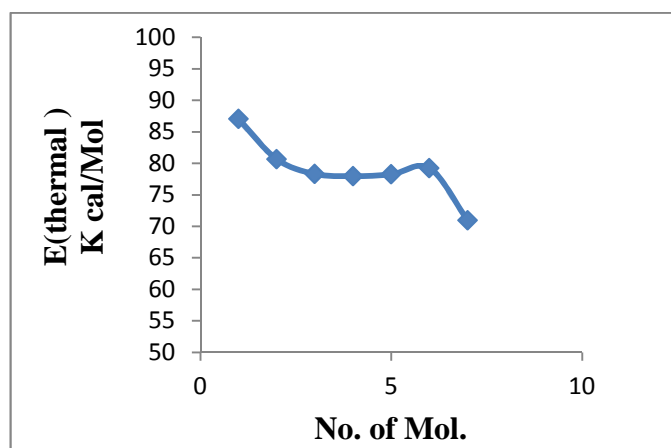


Fig. 7 : Thermal energy of the molecules under study

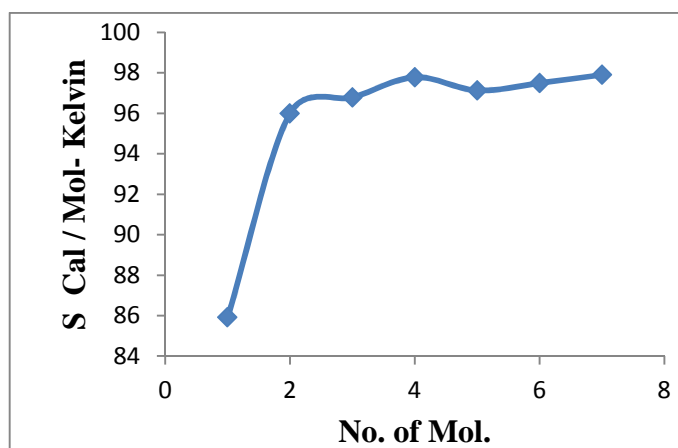


Fig. (9) : S of the molecules under study.

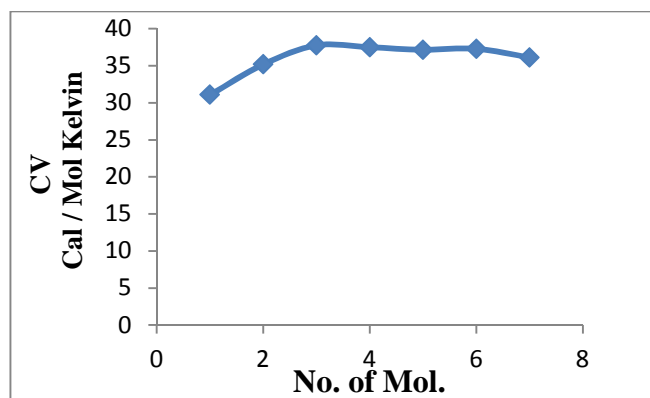
Fig. 8 :  $C_v$  of the molecules under study.

Table 3 shows the three components of energies of the studied structures, these components are translation, rotation and vibration. As seen, there is no effect for increasing the number of replacing atoms on both the translational and rotational energies and this agree with the above equations.

Mol.	Translational	Rotational	Vibrational
1	40.524	29.081	14.934
2	41.300	30.280	24.414
3	41.769	31.424	24.585
4	41.769	31.365	23.645
5	41.769	31.403	23.957
6	41.769	31.456	24.269
7	41.784	31.386	23.730

Table (3) : Translational, rotational and vibrational energies of the molecules

### Conclusions

This search deals with the theory of density function theoretical investigation of (mono hydroxyl iso-indene) and it was included the original molecule with adding (N & S) atoms. The study focuses on determining and computing the

thermal properties and energetic features for various position of mono hydroxyl iso- indene and mono hydroxyl iso- indene with adding (N&S) atoms to the original molecule . The calculated properties based on the factors influence the values of the thermal properties such as internal thermal

energy, enthalpy, Gibbs free energy, specific heat and entropy were calculated using Gaussian 09 package of program. From the results, one can conclude the following:

1. The density functional theoretical methodology has been proved its validity in calculating the thermal properties for mono hydroxyl iso-indene.
2. The specific heat  $C_v$  for the molecules study is increasing with adding atoms to the original molecule. On the other hand, it is directly proportional to the number of atoms in the molecule. The subgroup's position affects the specific heat value increases.

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3. In general, the entropy  $S$  values of molecules increases by adding subgroups and atoms to the reference molecule. Besides, the subgroup's position affects the entropy value.
4. The internal thermal energy  $E_{th}$  is of the molecules under study is decreasing that means these values are dependent on the number of atoms in the molecule and subgroup's position. Furthermore, it is directly proportional to the enthalpy  $H$  because all molecules are under standard conditions.
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