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Theoretical calculation on a compound formed by methyl alcohol and *simmondsin*

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Abstract: Etheric oil results from the esterification reactions of oil acids with alcohols. In these reactions, one molecule water (H_2O) is composed of H protons from oil acids and OH^- groups which separated from alcohol. Etheric oil is commonly used in food industry, perfume industry and medicine. From this perspective, we need to know physical properties of etheric oil as well as chemical properties. In this study, the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, the electronic properties (total energy, electronegativity, chemical hardness and softness), NBO analysis and thermodynamic parameters of a compound formed by methyl alcohol and *simmondsin* have been performed by using Gaussian 09W program. The structural and spectroscopic data of the molecule in the ground state have been calculated by using density functional method (DFT/B3LYP) with the 6-31++G(d,p) basis set.

Keywords: Simmondsin, DFT, HOMO, LUMO, NBO

1. Introduction

Simmondsin is a flavan-3-ol, a type of natural phenol and antioxidant. It is a plant secondary metabolite. It belongs to the group of flavan-3-ols (or simply flavanols (phenols)), part of the chemical family of flavonoids. In organic chemistry; phenols sometimes called phenolics are the class of chemical compounds consisting of a hydroxyl group ($^-$OH) bonded directly to an aromatic hydrocarbon group. Phenolic compounds are classified as simple phenols or polyphenols which are based on the number of phenol units in the molecule [1-3].

Simmondsin is an extract of jojoba seeds (Simmondsia chinensis), it was traditionally thought to be a toxic substance due to jojoba seed meal which causing weight loss in animals. Although it has been researched as a potential treatment for reducing appetite of obese individuals by helping to reduce craving for food. Several mechanisms of action are thought to be involved in the appetite suppressant effect [4-6].

Etheric oil results from the esterification reactions of oil acids with alcohols. Etheric oil is commonly used in food industry, perfume industry and medicine. From this perspective, we

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need to know physical properties of etheric oil as well as chemical properties. It is also important to understand the properties of the coalescence of *simmondsin* to develop new molecules.

Calculations using large basis sets are more accurate because they are less restrictive on the location of the electrons. Such calculations are also more expensive because they require computing more integrals. DFT methods account for electron correlation by estimating the interaction of an electron with the total electron density. DFT orbitals are formed from basis functions like those used in SCF or MP2. Most popular DFT method is B3LYP (Becke3-Parameter method for calculating that part of the molecular energy due to overlapping orbitals, plus the Lee-Yang-Parr method of accounting for correlation). In this regard, we optimized the methyl alcohol and *simmondsin* by using B3LYP method and 6-31++G(d,p) basis set.

In this study, we investigated theoretically the electronic structure using HOMO-LUMO energies, electron delocalizations using NBO analysis and thermodynamic parameters at different temperatures using B3LYP/6-31++G(d,p) level of a compound formed by *methyl alcohol* and *simmondsin*.

2. Calculation

The electronic and thermal properties of the compound are theoretically examined by means of B3LYP method with 6-31++G(d,p) basis set. All the calculations were performed by using Gaussian 09. Revision C1 program and GaussView 5.0.8 was used for the visualization of the structure and simulation [7]. Gaussian09 package, approximates orbital shapes and orbital energies of a given molecular geometry using a model chemistry consisting of two parts: a basis set and a method.

Methanol, also known as methyl alcohol, is a chemical with the formula CH_3OH (often abbreviated MeOH). The new *simmondsin* form (S2 form) comprise by the reaction of methanol and *simmondsin* (Figure 1).

$$C_{16}H_{25}NO_9 + CH_3OH \longrightarrow C_{17}H_{27}NO_9 + H_2O$$

In these reactions, one molecule water (H_2O) is composed of H protons from oil acids and OH^- groups which separated from alcohol. After the optimization of the new *simmondsin* form we determined that the methyl alcohol added to the nucleophilic region of the *simmondsin* (Figure 3).

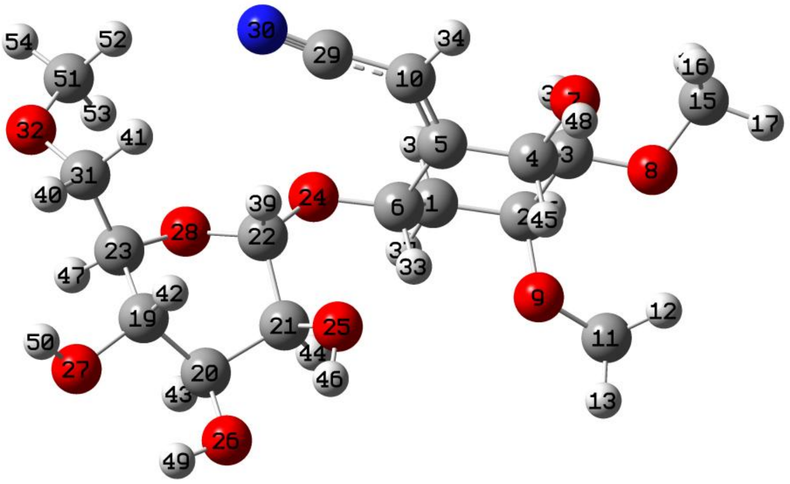


Figure 1. Optimized structure (S2 form) with using B3LYP/6-31++G(d,p) the compound (S2 form) formed by methyl alcohol and *simmondsin*.

2.1. Electronic Properties

In quantum chemistry, HOMO and LUMO energies are very important parameters. LUMO as an electron acceptor represents the ability to obtain an electron, whereas HOMO represents the ability to donate an electron [8]. The HOMO and LUMO energies of the compounds (S1 and S2 form) are calculated by using B3LYP/6-31++G(d,p) level in gas phase and these energies are presented in Table 1.

Table 1. The electronic structure parameters calculated for the molecule.

Electronic parameters	*Simmondsin_1* (S1 form)	*Simmondsin_2* (S2 form)
HOMO	-6.55	-6.77
LUMO	-1.46	-1.63
ΔE(eV)	5.09	5.14
I (eV)	6.55	6.77
A (eV)	1.46	1.63
χ (eV)	4.01	4.20
Hardness (η)	2.55	2.57
Softness (S)	0.12	0.12

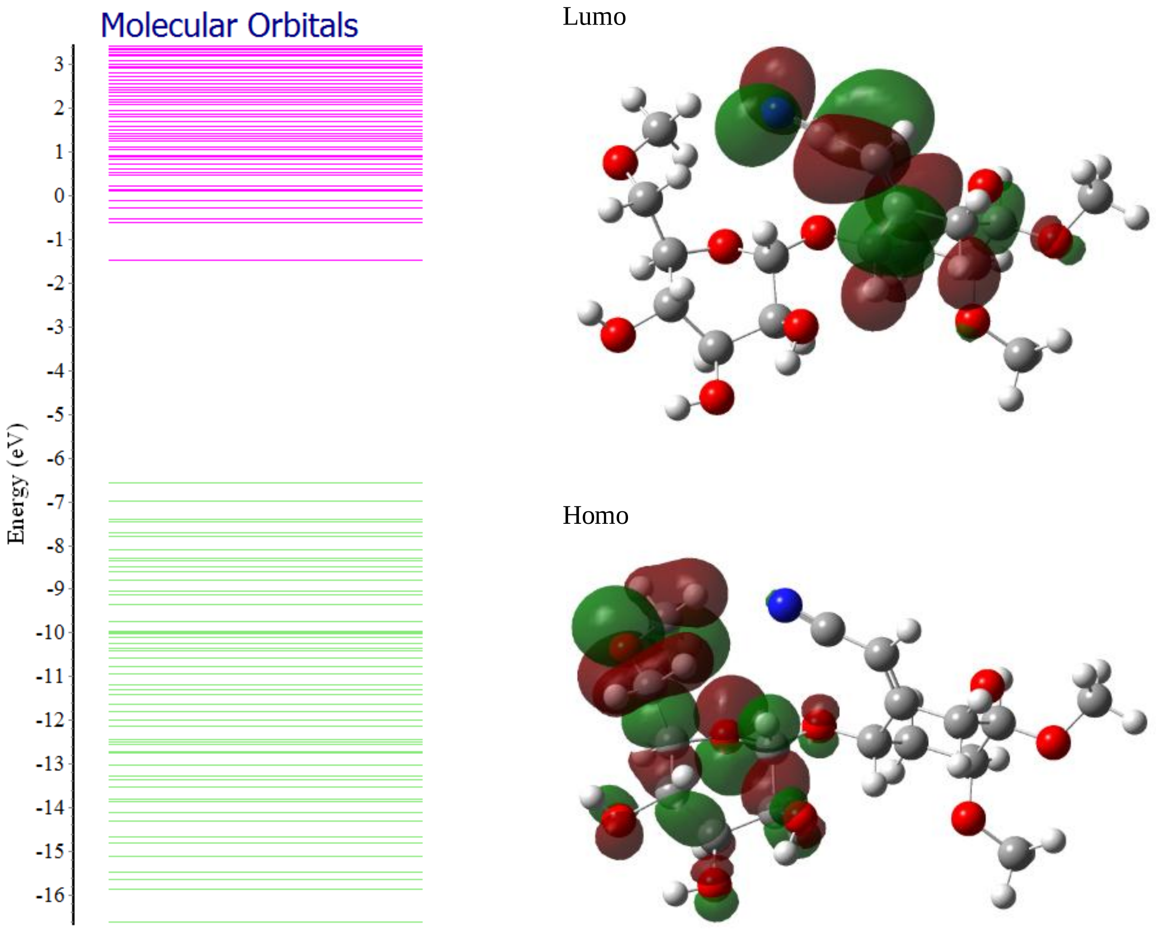


Figure 2. Optained the molecular orbitals of the title compound by using B3LYP/6-311G++(d,p) level in the gas phase.

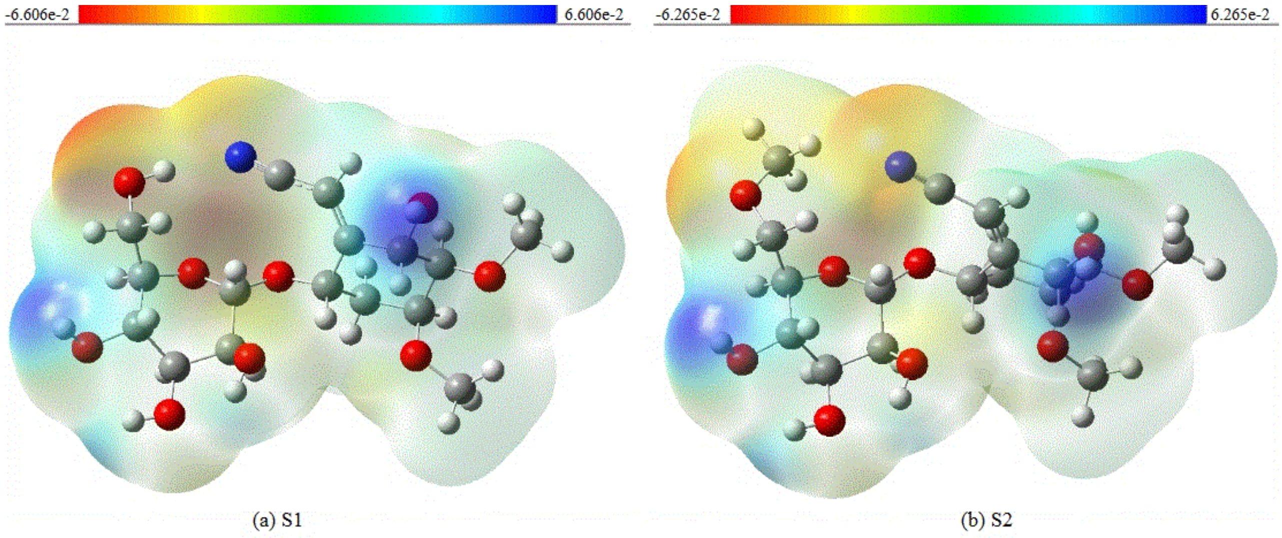
Energy gap (ΔE) between HOMO and LUMO characterizes the molecular chemical stability and electron conductivity. The following parameters can be calculated using HOMO and LUMO energy values: Ionization potential ($I=-E_{HOMO}$) is the minimum energy required to remove an electron from a molecule in gas phase. Electron affinity ($A= -E_{LUMO}$) is the amount of energy increasing when added an electron to a molecule in the gas phase. Electronegativity ($\chi = (I + A)/2$) represents the electron attraction of atom in a molecule. Chemical hardness ($\eta=(I-A)/2$) is a measure of the inhibition of the charge transfer to the molecule. If the value of chemical hardness of a molecule is high, the charge transfer can be less or charge transfer could not take place. Chemical softness is $S=1/\eta$ [9, 10]. The HOMO–LUMO energy gap values of the S1 and S2 form of the molecule are 5.09 and 5.14 eV, respectively. An electronic system with a larger HOMO–LUMO energy gap should be less reactive than one having a smaller gap [11]. The high HOMO–LUMO energy gap value indicates that there is very little or no charge transfer in the molecule. As seen from Fig. 2, the positive phase is symbolized with red and the negative phase green.

2.2. Molecular electrostatic potential (MEP)

MEPs, also known as electrostatic potential maps, show that the molecules have three dimensional charge distributions. In this case the knowledge of charge distribution can be used for determination of molecule interactions. The red color represents the low potential areas and rich electron regions, while blue color represents the high potential areas and poor electron regions and green color represents the regions of zero potential on the map (red < orange < yellow < green < blue). MEP values are calculated by using the following equation

$$V(r) = \sum_A \frac{Z_A}{|\overrightarrow{R_A} - \vec{r}|} - \int \frac{\rho(\overrightarrow{r'})}{|\overrightarrow{r'} - \vec{r}|} d^3r'$$

where Z_A is the charge on nucleus A, located at R_A and $\rho(r')$ is the electronic density function of the molecule, and r′ is the dummy integration variable [12]. MEPs map of the title compound is represented using B3LYP/6-31++ G (d,p) level of theory and are given in Figure 3. As can be seen from Fig. 3, map color range is between from -0.06606 (deepest red region) to +0.06606 (deepest blue region). In the S1 form the red regions are around the OH and N so the methyl alcohol attached the nucleophilic region. The deepest blue regions both in S1 and S2 forms are the electrophilic regions waiting for attract the positive ions.



(a) S1

(b) S2

Figure 3. The total electron density isosurface mapped with molecular electrostatic potential for the title compounds. a) S1 form, b) S2 form

2.3. NBO Analysis

NBO analysis provides an efficient method to study intra- and intermolecular bonding and charge transfer or conjugative interaction in molecular systems [13]. The second order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO analysis [14]. For each donor and acceptor (j), the stabilization energy $E^{(2)}$ associated with the delocalization i→j is estimated as,

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where q_i is the donor orbital occupancy, are ε_j and ε_i diagonal elements and F(i, j) is the off diagonal NBO Fock matrix element [15, 16]. The hyperconjugative σ→σ* interactions playa highly important role. These interactions represent the weak departures from a strictly localized natural Lewis structure that constitutes the primary "noncovalent" effects [17].

The interaction between σ (C29-N30) → σ^* (C10-C29) has 5.02 kcal/mol, σ (C29-N30) shows conjugation with π*(C5-C10) with the stabilization energy of 8.92 kcal/mol in the S1 molecule. Similarly, in the S2 molecule, σ (C29-N30) → σ^* (C10-C29) has 5.00 kcal/mol, σ (C29-N30) shows conjugation with π*(C5-C10) with the stabilization energy of 8.80 kcal/mol.

In S1 and S2, the strongest interaction is between π*(C5-C10) → π*(C29-N30) with the stabilization energy of 11.42 and 11.80 kcal/mol, respectively. In the S1 and S2; the electron donating from LP1 (N30) and LP2 (O24) to the antibonding acceptor σ*(C10-C29) and σ*(C5-C6) with stabilization energy of 13.16, 13.08 and 9.00, 8.95 kcal/mol is the most important interactions. Besides, LP2 (O9) and LP2 (O24) to the antibonding acceptor σ*(C2-C3) and σ*(C22-H39) with stabilization energy of 7.71, 7.75 and 7.50, 7.42 kcal/mol are also important interactions. From the Tables 2 and 3, it is clearly seen that intramolecular (σ→σ*, π→π*, π*→π*, LP → σ* and LP → π*) charge transfer occurs in the title compounds.

Table 2. Second order perturbation theory analysis of Fock matrix in NBO for the molecule S1 in gas phase basis for 6-31++G(d,p)

Donor(i)	Type	ED/e	Acceptor(j)	Type	ED/e	E^2 (kcalmol^{-1})	E_j-E_i(a.u.)	F_{ij} (a.u.)
C2-O9	σ	1.98935	C1-H38	σ*	0.01084	0.98	1.25	0.031
			C3-H35	σ*	0.02883	0.88	1.22	0.029
			C11-H13	σ*	0.00865	0.68	1.27	0.026
C23-O28	σ	1.98183	C19-O27	σ*	0.02448	1.31	1.06	0.033
			C22-O24	σ*	0.03862	1.74	1.11	0.040
			C23-O28	σ*	0.03186	0.67	1.21	0.025
C29-N30	σ	1.99557	C10-C29	σ*	0.02746	5.02	1.55	0.079
	π	1.98565	C5-C10	σ*	0.02248	2.79	0.97	0.046
	π	1.98565	C10-H34	σ*	0.02042	2.76	0.80	0.042
	π	1.95787	C5-C10	π*	0.10697	8.92	0.36	0.052
O9	LP1	1.96597	C1-C2	σ*	0.02062	0.86	0.94	0.025
			C2-H36	σ*	0.02634	2.57	0.98	0.045
			C11-H12	σ*	0.01946	0.85	1.02	0.026
			C11-H13	σ*	0.00865	1.95	1.02	0.040
			C11-H14	σ*	0.01830	0.89	0.99	0.027
	LP2	1.92590	C1-C2	σ*	0.02062	1.51	0.67	0.029
			C2-C3	σ*	0.04240	7.71	0.65	0.064
			C2-H36	σ*	0.02634	1.99	0.72	0.034
			C3-H35	σ*	0.02883	0.76	0.71	0.021
			C11-H12	σ*	0.01946	5.52	0.75	0.058
			C11-H14	σ*	0.01830	5.21	0.73	0.056
O24	LP1	1.95117	C1-C6	σ*	0.02494	0.76	0.90	0.024
			C6-H33	σ*	0.03129	3.56	0.97	0.053
			C21-C22	σ*	0.05197	3.38	0.89	0.049
			C22-O28	σ*	0.03404	3.94	0.85	0.052
	LP2	1.91287	C1-C6	σ*	0.02494	1.75	0.66	0.031
			C5-C6	σ*	0.04501	9.00	0.70	0.072
			C6-H33	σ*	0.03129	1.47	0.74	0.030
			C21-C22	σ*	0.05197	3.38	0.66	0.042
			C22-O28	σ*	0.03404	2.11	0.61	0.032
			C22-H39	σ*	0.04670	7.50	0.73	0.067
			C29-N30	π*	0.03404	0.88	0.42	0.017
N30	LP1	1.96404	C10-C29	σ*	0.02746	13.16	1.02	0.104
			C31-H41	σ*	0.01908	0.73	0.97	0.024
C5-C10	π*	0.10697	C1-C6	σ *	0.02494	0.53	0.32	0.045
			C3-C4	σ *	0.04952	0.60	0.30	0.043
			C29-N30	π *	0.08480	11.42	0.07	0.083

Table 3. NBO analysis for the molecule S2 in gas phase basis for 6-31++G(d,p)

Donor(i)	Type	ED/e	Acceptor(j)	Type	ED/e	E^2 (kcalmol^{-1})	E_j-E_i(a.u.)	F_{ij} (a.u.)
C2-O9	σ	1.98936	C1-H38	σ*	0.01086	0.99	1.25	0.031
			C3-H35	σ*	0.02886	0.88	1.22	0.029
			C11-H13	σ*	0.00865	0.67	1.27	0.026
C23-028	σ	1.98123	C19-O27	σ*	0.02406	1.33	1.06	0.034
			C22-O24	σ*	0.03871	1.78	1.10	0.040
			C31-H40	σ*	0.01688	0.62	1.23	0.025
C29-N30	σ	1.99556	C10-C29	σ*	0.02746	5.00	1.55	0.079
	π	1.98631	C5-C10	σ*	0.02248	2.76	0.97	0.046
	π	1.98631	C10-H34	σ*	0.02040	2.75	0.80	0.042
	π	1.95869	C5-C10	π*	0.10715	8.80	0.37	0.052
C31-O32	σ	1.99214	C19-C23	σ*	0.04336	0.98	1.15	0.030
			C51-H54	σ*	0.00897	0.72	1.27	0.027
C31-H40	σ	1.97481	C23-O28	σ*	0.03258	4.47	0.79	0.053
			O32-C51	σ*	0.00750	3.17	0.82	0.046
O32-C51	σ	1.99298	C31-H40	σ*	0.01688	1.00	1.20	0.031
C51-H54	σ	1.995501	C31-O32	σ*	0.01690	3.10	0.82	0.045
O9	LP1	1.96570	C1-C2	σ*	0.02058	0.88	0.93	0.026
			C2-H36	σ*	0.02644	2.56	0.98	0.045
			C11-H12	σ*	0.01941	0.82	1.02	0.026
			C11-H13	σ*	0.00865	1.95	1.02	0.042
			C11-H14	σ*	0.01818	0.92	0.99	0.027
	LP2	1.92576	C1-C2	σ*	0.02058	1.46	0.67	0.028
			C2-C3	σ*	0.04258	7.75	0.65	0.064
			C2-H36	σ*	0.02644	2.05	0.72	0.035
			C3-H35	σ*	0.02886	0.76	0.71	0.021
			C11-H12	σ*	0.01941	5.56	0.76	0.059
			C11-H14	σ*	0.01818	5.13	0.73	0.055
O24	LP1	1.95191	C1-C6	σ*	0.02511	0.75	0.90	0.023
			C6-H33	σ*	0.03143	3.44	0.98	0.052
			C21-C22	σ*	0.05228	2.89	0.90	0.046
			C22-O28	σ*	0.03767	4.12	0.86	0.053
	LP2	1.91452	C1-C6	σ*	0.02511	1.82	0.66	0.031
			C4-C5	σ*	0.04146	0.51	0.69	0.017
			C5-C6	σ*	0.04482	8.95	0.70	0.071
			C6-H33	σ*	0.03143	1.49	0.74	0.030
			C21-C22	σ*	0.05228	3.90	0.65	0.045
			C22-O28	σ*	0.03767	1.50	0.61	0.027
			C22-H39	σ*	0.04615	7.42	0.73	0.066
			C29-N30	π*	0.03527	0.94	0.41	0.018
N30	LP1	1.96417	C10-C29	σ*	0.02746	13.08	1.03	0.104
			C51-H52	σ*	0.01718	0.51	0.99	0.020
O32	LP1	1.96774	C31-H40	σ*	0.01688	1.73	0.97	0.037
			C31-H41	σ*	0.02623	2.32	0.99	0.043
			C51-H52	σ*	0.01718	1.20	1.02	0.031
			C51-H54	σ*	0.00897	1.78	1.02	0.038
	LP2	1.92728	C19-C23	σ*	0.04336	0.66	0.62	0.018
			C23-C31	σ*	0.04522	8.49	0.65	0.067
			C31-H40	σ*	0.01688	0.55	0.71	0.018
			C31-H41	σ*	0.02623	3.66	0.72	0.047
			C51-H52	σ*	0.01718	4.07	0.76	0.050
			C51-H53	σ*	0.01855	6.18	0.75	0.062
C5-C10	π*	0.10715	C1-C6	σ*	0.02511	0.54	0.32	0.046
			C3-C4	σ*	0.04976	0.61	0.30	0.043
			C29-N30	π*	0.08638	11.80	0.07	0.083

2.4. Thermodynamic Properties

The heat formation is one of the most important parameter of thermochemical properties of the molecule. The heat formation values of many organic compounds are not known. The importance of the quantum chemical calculations are increased by the heat effect investigations. In the study of the organic reaction mechanisms the thermodynamic quantum chemical data are extensively used.

Thermodynamic parameters; thermal energy, specific heat capacity, rotational constants, entropy and sum of electronic and thermal enthalpy of the S1 and S2 forms were calculated by using the B3LYP/6-31++G(d,p) level in the gas phase. Thermodynamic parameters such as change in the free energy (ΔG) in Cal.Mol^{-1}, and entropy (ΔS) in $\text{Cal.Mol}^{-1}.\text{K}^{-1}$ were determined using the following equations [18]:

$$\Delta G = \sum(\varepsilon_o + G)_{\text{products}} - \sum(\varepsilon_o + G)_{\text{reactants}}$$

$$\ln K_d = -\Delta G/(RT)$$

Where ε_o for the total electronic energy, K_d is the equilibrium constant, ΔG is the internal energy, T is the temperature in Kelvin and R is the gas constant [19]. The values of the thermodynamic parameters are depended on temperature of the compound were given in Table 4.

If the reaction is endothermic, the value of ΔE is positive. But, if the reaction is spontaneous, the value of ΔG is negative. The high equilibrium constant (K_d) indicates that the spontaneity of the reaction increases at high temperature. The plotting 1/T against $\ln K_d$ is shown in Fig 4 ($y = 1.3759x - 0.6114$; $R^2 = 0.9999$). R^2 value which obtained by using the least squares method is very close to 1. It means that the data obtained the K_d equilibrium constant values are consistent with each other and have a linear relationship between the variable.

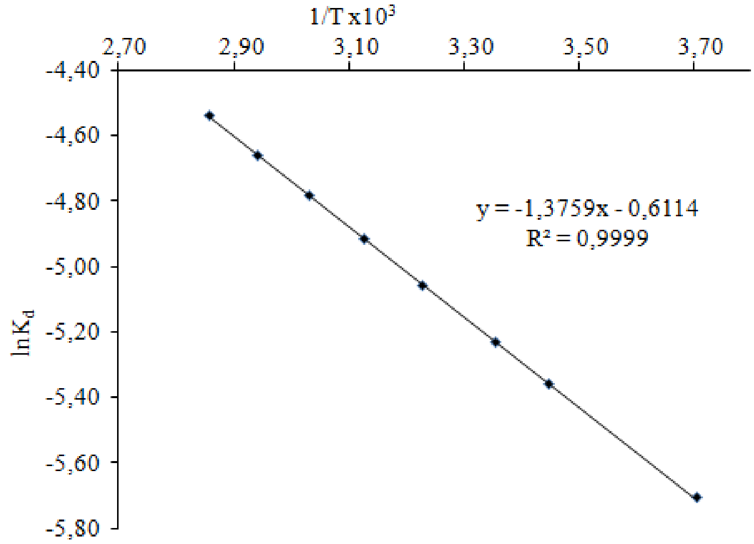


Figure 4. The thermodynamic behavior of the title compound is illustrated by plotting 1/T against $\ln K_d$ graph.

Table 4. The values of the thermodynamic parameters [the internal thermal energy (E_{tot}), constant volume heat capacity (C_{tot}) and entropy (S_{tot})] depended on temperature of the compound (in the S1 and S2 forms).

(a) for S1 form

T(K)	E_{tot} (KCal/Mol)	C_{tot} (Cal/Mol-Kelvin)	S_{tot} (Cal/Mol-Kelvin)
270	277,923	94,592	170,871
290	279,871	100,238	177,971
298,15	280,697	102,54	180,837
320	283,005	108,697	188,444
330	284,106	111,5	191,893
340	285,235	114,286	195,323
350	286,392	117,054	198,733

(b) for S2 form

T(K)	E_{tot} (KCal/Mol)	C_{tot} (Cal/Mol-Kelvin)	S_{tot} (Cal/Mol-Kelvin)
270	296,273	99,578	180,893
290	298,322	105,393	188,355
298,15	299,191	107,771	191,364
320	301,616	114,15	199,35
330	302,772	117,061	202,968
340	303,957	119,96	206,565
350	305,171	122,844	210,142

3. Conclusion

The aims of this study are to give a complete description of the physical and chemical properties of the *methanol and simmondsin* complex theoretically. This study will be helpful to systematically understanding of the structures of *methanol and simmondsin* for studying the structure-activity relationship. The electronic and thermodynamic properties of the compound were also investigated in the gas phase at B3LYP/6-31++G(d,p) level. The thermodynamic properties of the title compound were calculated in the gas phase and were interpreted in different temperatures.

HOMO–LUMO energy gap is calculated as 5.14 eV at B3LYP/6-31++G(d,p) level. This high energy gap value show us the charge transfer in the molecule is very little or not exist. The high electron density is mostly localized on the OH group around the N atom as can be seen in Figure 3. On the other hand, this reaction has been found out that the formation of *methanol and simmondsin* complex compound is endothermic, and it is easy to obtain this complex as the temperature increases.

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