Theoretical Approach to Study the Nature and Structure of Organotin (IV) Derivatives

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Abstract

A theoretical study of semi-empirical calculation of PM3 level was used to characterize three Tin complexes (R_2SnL_2) [where (R): (Phenyl), (butyl) and (methyl) and L: (N-tolyl -m-methoxybenzo hydroxamic acid)]. The comparison of the three complexes that have different (R) had been done on the basis of calculated energies and physical properties of the molecular model systems, such as heat of formation, HOMO-LUMO gap, binding energy, dipole moment, surface area. This present study revealed a clear picture and useful information about the nature of complex stability of the three Tin complexes R_2SnL_2. [DOI: 10.22401/JUNS.21.1.05]

Keywords: AM1 method, Tin complexes, charge transfer complex.

Introduction

Tin (IV) and organo-tin(IV) synthesis are fully known by their pose in chemical matier cultivation and other field of epidermal activities [1-3]. There is deceptively modest area of metal (organic and inorganic) chemistry, have been extradite more attentiveness due to the substantial matier and ecological implementation [4]. The organ tin (IV) complexes compounds with oxygen and nitrogen granter ligand have been extensive study not driven only through their coordination chemistry is interesting but also due to the possible implementation in the field of science material, biological action ,cultivation, pharmaceutical chemistry [5,6], potential antineoplastic and anti-tuberculosis agents [7], and cytotoxicity [8] as well as their industrial and agricultural applications [9-12]. Leading of (Sn) atom to the forming of five - membered ring chelate (Oh.) geometry was suggested for complexes prepared [13].

Seeing that the varied field of implementations or oregano tin complexes, we have study theoretically of ligand(L)[(N-Tolyl-m-methoxybenzohydroxamic)] and its organo-tin(IV) syntheses Di methyl tin(IV) bis (N- tolyl-m-methoxy benzohydroxamate) (F1), Di butyl tin(IV) bis (N- methyl-m-methoxy benzohydroxamate) (F2), Di phenyl tin(IV) bis (N- tolyl-m-methoxy benzohydroxamate) (F3).[13]

Theoretical-study in gas-phase was completed by method using semi - empirical in order to show the most stable conformation [14]. The aims of research to calculate the formation of heat and energy binding to all suggested-geometries, in orderto determine and evaluate the most active sites for the three Tin complexes R_2SnL_2 by using the electrostatic potential calculations. In addition, semi-empirical method was used to calculate dipole moment, surface area and finally bond lengths for all molecular modeling system of Tin complexes [15,16].

Computational Methods

All molecular structures were optimized completely by application method semi-empirical as proceed in the program packing Hyper chem. 7.1 (Hyper cube Inc [17]. GainvilleFL) by using default gradient methods. Hyper chem. offers Ten (IV) semi - empirical orbital molecular tichniques, together with choices of organic all major group synthesis for metal transition complexes and simulation spectral [15]. Choose from parameterization model version3 (PM3), [including metals transition]. (PM3) were hired for the computation of formation heat, energy binding, Frontier Orbital Energies (HOMO, and LUMO) and other parameters for all suggested molecular modeling system of Tin complexes [18-20].

Results and Discussion

The program Hyperchem is included the semi-empirical with PM3 level and molecular mechanics with amber method for obtaining optimized geometries of molecular modeling system in gas phase at the ground state [٢١]. The result of calculations was formation of heat ($\Delta H^o{}_f$) and energy binding (ΔE_b) for ligand and its complexes R_2SnL_2 which are listed in Table (1). The data of Table (1) depicted that the stability of Tin complexes follow the order: F2>F1>F3.

Table (1)
Energetic data in (kJ.mol^{-1}) for all components of R_2SnL_2.

Molecule	$\Delta H^o{}_f$	*Total energy*	ΔE_b
L1	-8.466	-16823.564	-878.456
F1	27.8718	-346876.196	-1885.933
F2	18.144	-40823.433	-2290.533
F3	54.3237	-42728.696	-2318.167

The molecular optimized structure of most stable conformations are shown in Fig.(1). The six coordination number is completed by two carbons at one of (R). Since the all component of R_2SnL_2 are concerning and diverge only in subrogate (R) group, it seems that the stability of complexes reflected by the effect of (R) group to obtain the more stable conformations.

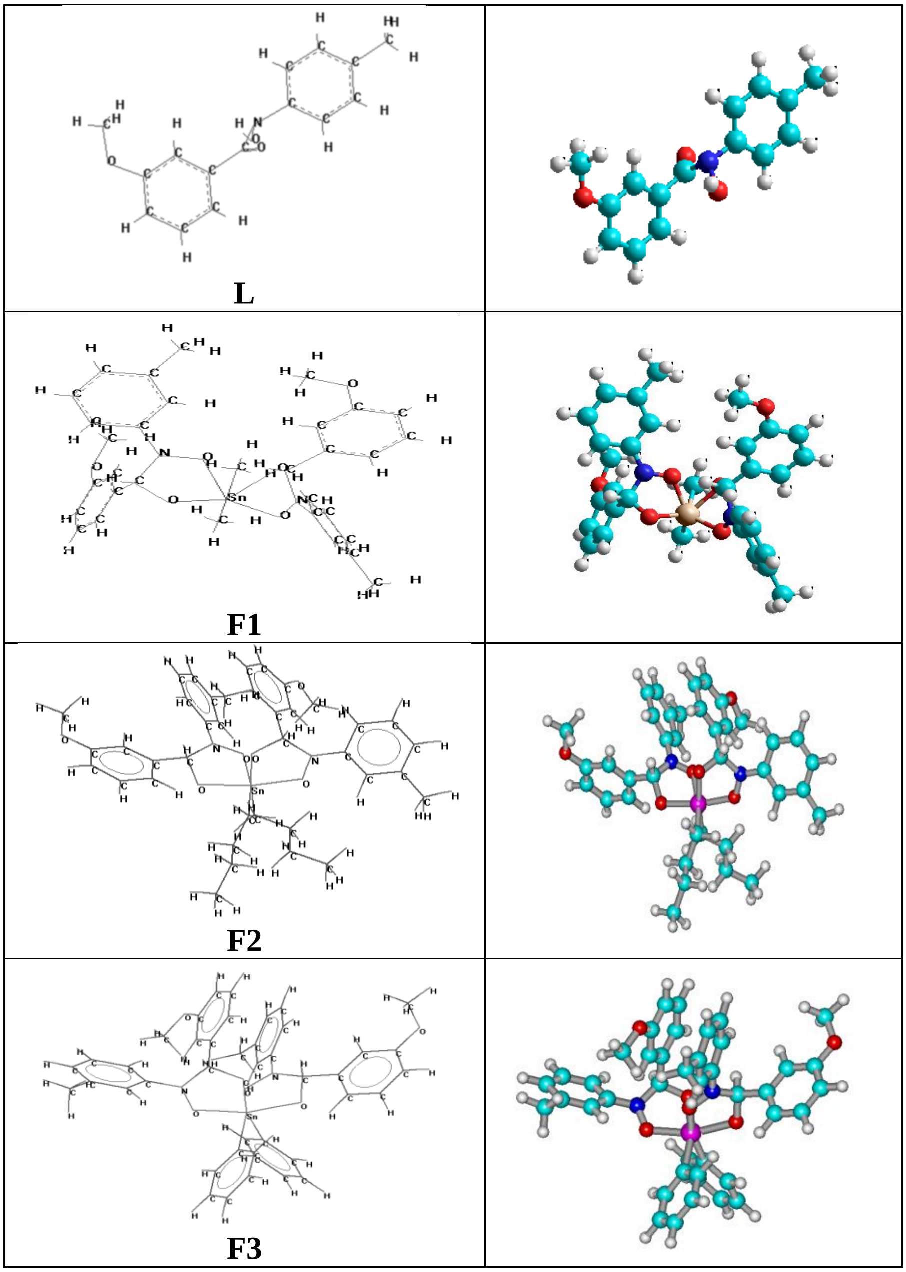


Fig.(1): Optimized molecular structure of all component of R_2SnL_2.

Potential Electrostatic (E.P) of electron allocation judged potential the electrostatic of molecules, and also delineate interaction of the system molecular with a formal charge positive [22]. So it of use for find a site of reaction a molecule charged positive setting tend to attack a molecule where the E.P is strongly negative electro philic offensive. E.P of ligand free was studied and conspired as 2 D contour for discuss the sites active of molecule Fig.(2). It is clear that Fig.(2) gave a whole view for the electrostatic potential of the ligand and the electrostatic potential of complexes R_2SnL_2 had differed due to the rearmament of electron distribution over the each complex.

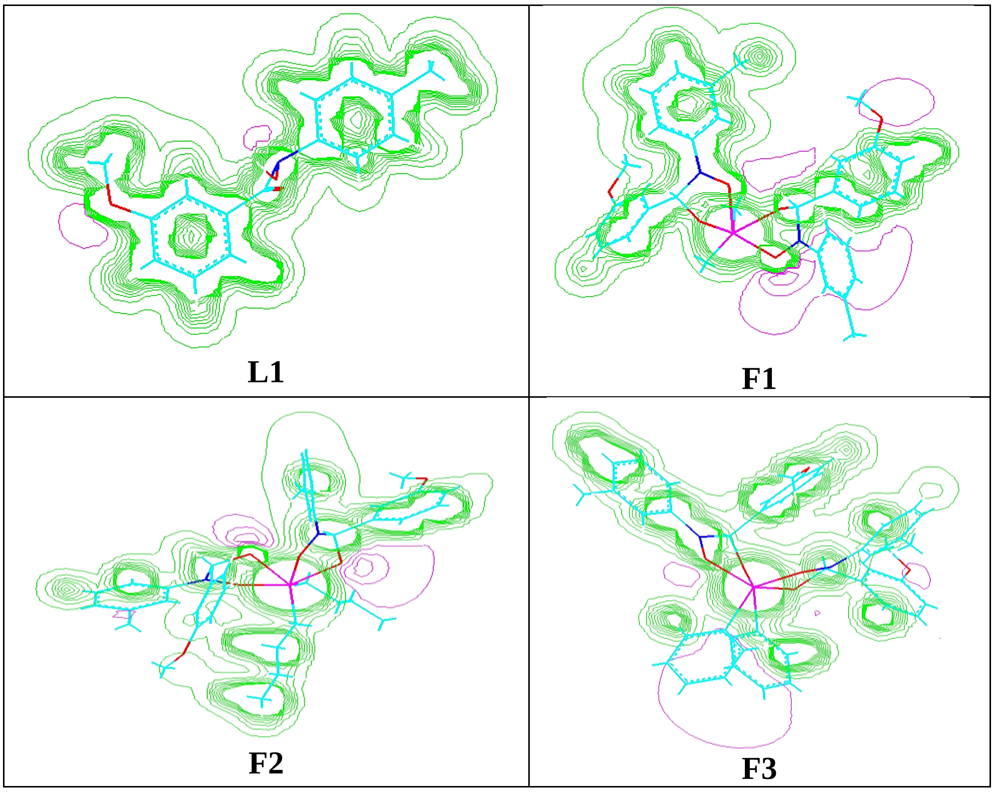


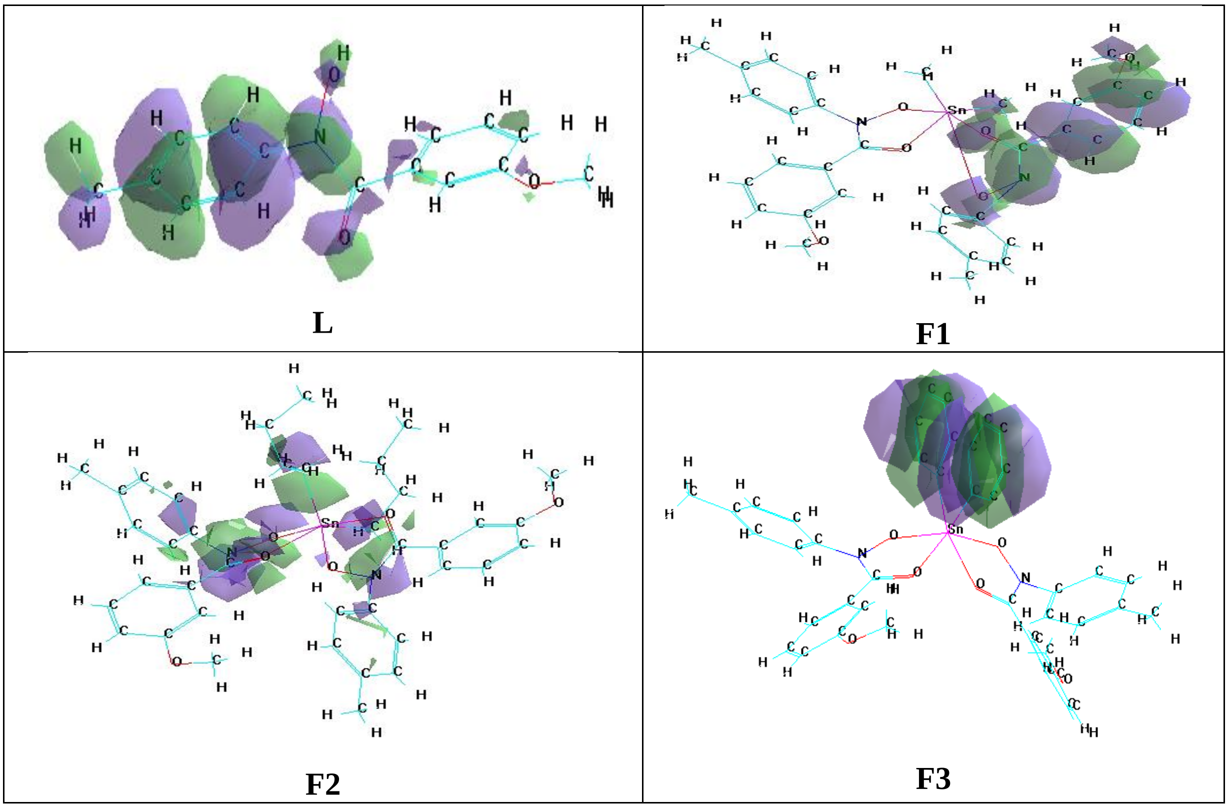
Fig.(2): Electrostatic potential (E.P) as 2D of all compounds.

Molecular orbital accounts submitted an energetic description of the orbitals including the spatial characteristics model patterns and single atom contribution. Frontier Energies Orbital of top of an occupied molecular orbital (HOMO) and the least part is not occupied molecular orbital (LUMO) are listed in Table (2). The contour plots of border orbits for the state ground of all component of R_2SnL_2 complexes shown in Fig.(3).

Table (2)
Frontier Orbital Energies (HOMO, LUMO) (in Ev).

Molecule	*HOMO*	*LUMO*	*HOMO-LUMO gap*
L1	-9.327	-0.09322	-9.23378
F1	-6.677	-3.176	-3.176
F2	-6.541	-3.331	-3.21
F3	-7.169	-3.972	-3.197

The HOMO-LUMO gap data in Table (2) is in consistency with the stability order of three R_2SnL_2 complexes with F2>F1>F3. In addition, Fig.(3) revealed that high electron density of frontier Orbital HOMO is focused on donating atoms of suggested molecular modeling system of Tin complexes.



L **F1**

F2 **F3**

Fig.(3): HOMO and LUMO as 3D of all compounds.

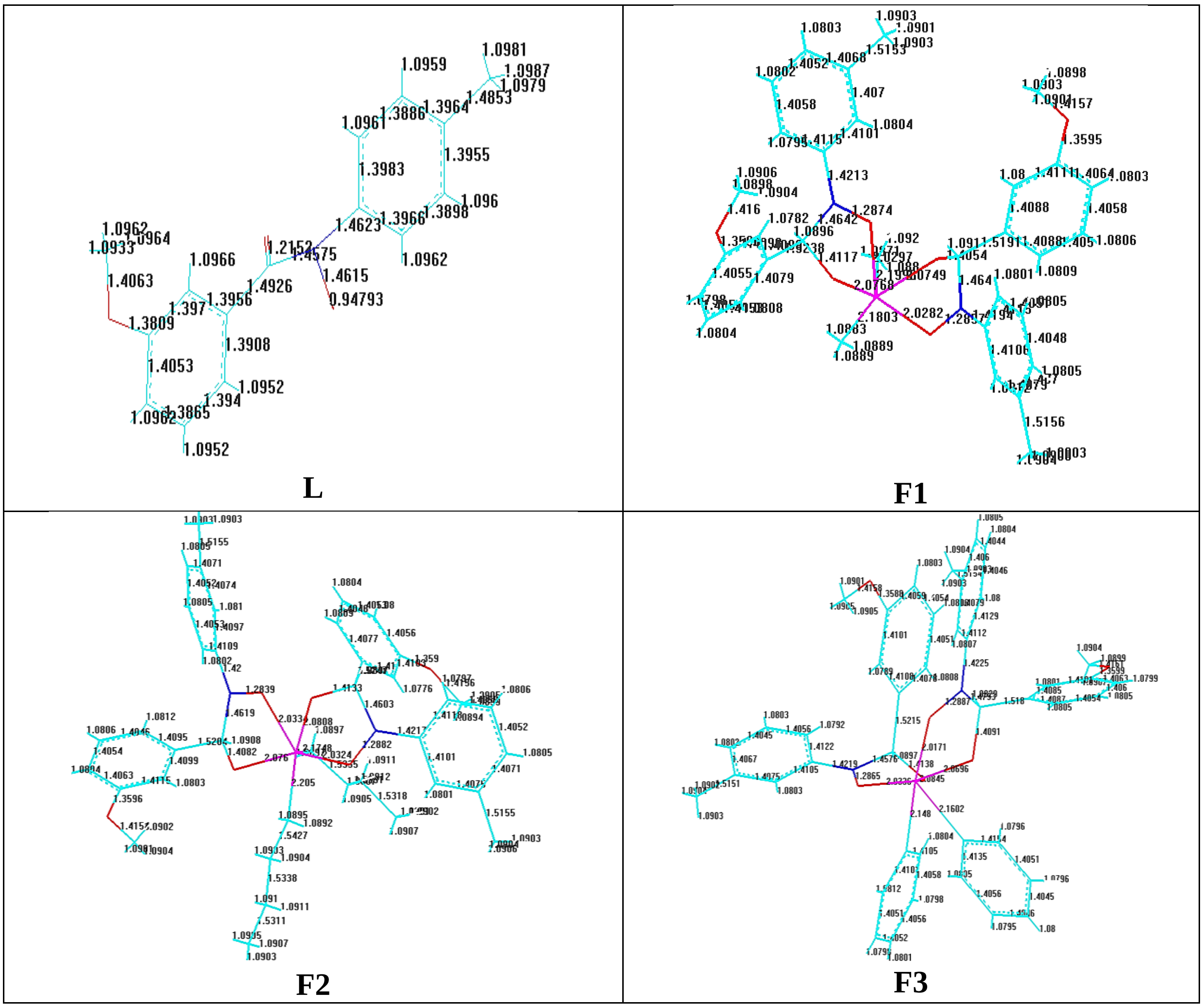
Also, the lower value in the HOMO and LUMO power gap would explain in the end charge transfer the interaction that occurs in side molecular model systems [23]. In Table (3) set forth Infrared-Spectroscopic study of all compounds that are favorite practically, theoretically and mistake percentage. The Fig.(4) shows the calculate bond lengths of the all compounds (L, F1, F2 and F3).

In quantitative structure–property relationships (QSPR) design, forecasts are made up of physic-chem. characteristics or theoretical molecular descriptors of chemicals. QSPR is involving in Hyperchem software and the results of calculations are listed in Tables (3-6). The data in Tables (1,2) is in consistency with the stability order of three R_2SnL_2 complexes with the results of tables (٤-٧).

Table (3)
Comparison of experimental and theoretical vibration frequencies.

Symb.	υ (O-H)	υ (C=O)	υ (C-N)	υ (N-O)	υ (Sn-C)	υ (Sn-O)
L1	٣٢٥١* 3900** 19.9***	1617* 1930** 19.3***	1429* 1278** -10.2***	953* 959** 0.62***	-	-
F1	-	١٩٦٣* ١٥٧٣** -7.08***	1430* 1588** 11.04***	934* 996** 6.63***	545* 550** 1.83***	455*
F2	-	1691* 1816** 7.39***	1428* 1337** -6.37***	927* 991** 6.9***	573* 591** 3.1***	454* 512** 12.77***
F3	-	1724* 1687** -2.1***	1442* 1362** -5.54***	922* 904** -1.95	569* 545** -4.2***	443* 519** 17.1***

Where:
****: Experimental frequency***
*****: Theoretical frequency***
******: Error% due to main difference in the experimental measurements and theoretical treatment of vibration spectrum.***



L **F1** **F2** **F3**

Fig.(4): Bond lengths of compounds.

Table (4)
Molecular properties and QSAR properties of L.

1.	Total Energy	-16823.564 (kJ/mol)
2.	Binding Energy	-878.456 (kJ/mol)
3.	Isolated Atomic Energy	-66650.5562850 (kcal/mol)
4.	Electronic Energy	-459585.9429265 (kcal/mol)
5.	Core-Core Interaction	389263.5238957 (kcal/mol)
6.	Heat of Formation	-8.466 (kJ/mol)
7.	Gradient	0.0970670 (kcal/mol/Ang)
8.	Surface area	239.6
9.	Volume	799.73 A^{03}
10.	Dipole moment	2.466 D
11.	Surface area (Grid)	495.74 (A^{02})
12.	Surface area (approx)	439.12 (A^{02})
13.	Hydration energy	-8.68 (kcal/mol)
14.	Log p	3.51
15.	Refractivity	72.30 (A^{03})
16.	Polarizability	28.31 (A^{03})
17.	Mass	257.29 (amu)
18.	Nuclear Energy	38979.43 (kcal/mol)
19.	Net Charge	0.00 e
20.	RMS	0.09175 (Kcal/mol)
21.	HOMO	-9.327 (ev)
22.	LUMO	-0.09322 (ev)

Table (5)
Molecular properties and QSAR properties of F1.

1.	Total Energy	-346876.196 (kJ/mol)
2.	Binding Energy	-1885.933 (KJ/mol)
3.	Isolated Atomic Energy	-142059.3575160 (kcal/mol)
4.	Electronic Energy	-1442767.3460422 (kcal/mol)
5.	Core-Core Interaction	1292661.2523975 (kcal/mol)
6.	Heat of Formation	27.8718 (J/mol)
7.	Gradient	-47.0301288 (kcal/mol)
8.	Surface area	537.32
9.	Volume	1732.50(A^{03})
10.	Dipole moment	9.714 (D)
11.	Surface area (Grid)	922.58(A^{02})
12.	Surface area (approx)	860.36(A^{02})
13.	Hydration energy	-10.62(Kcal/mol)
14.	Log p	7.61
15.	Refractivity	154.38(A^{03})
16.	Polarizability	64.45(A^{03})
17.	Mass	663.34 (amu)
18.	Nuclear Energy	1453906.3 (Kcal/mol)
19.	Net Charge	0.00 (e)
20.	RMS grid	0.0974(Kcal/mol)
21.	HOMO	-7.304606 (ev)
22.	LUMO	-3.643403 (ev)

Table (6)
Molecular properties and QSAR properties of F2.

1.	Total Energy	-40823.433(kJ/mol)
2.	Binding Energy	-2290.533 (kJ/mol)
3.	Isolated Atomic Energy	-161067.5251320 (kcal/mol)
4.	Electronic Energy	-1951076.3423094 (kcal/mol)
5.	Core-Core Interaction	1780282.7827173 (kcal/mol)
6.	Heat of Formation	18.144 (kJ/mol)
7.	Gradient	0.0889641 (kcal/mol/Ang)
8.	Surface area	638.95
9.	Volume	2000.26(A^{03})
10.	Dipole moment	6.116 (D)
11.	Surface area (Grid)	1058.10 (A^{02})
12.	Surface area (approx)	1041.41(A^{02})
13.	Hydration energy	-5.32 (Kcal/mol)
14.	Log p	10.03
15.	Refractivity	182.12(A^{03})
16.	Polarizability	75.49(A^{03})
17.	Mass	747.50(amu)
18.	Nuclear Energy	178263.625 (Kcal/mol)
19.	Net Charge	0.00 (e)
20.	RMS	0.1005(Kcal/mol)
21.	HOMO	-6.541
22.	LUMO	-3.331

Table (7)
Molecular properties and QSAR properties of F3.

1.	Total Energy	-42728.696(kJ/mol)
2.	Binding Energy	-2318.167 (kJ/mol)
3.	Isolated Atomic Energy	-168916.0136280 (kcal/mol)
4.	Electronic Energy	-2090228.5758124 (kcal/mol)
5.	Core-Core Interaction	1911419.8934860 (kcal/mol)
6.	Heat of Formation	54.3237 (kJ/mol)
7.	Gradient	0.0963155 (kcal/mol/Ang)
8.	Surface area	651.57
9.	Volume	1977.76
10.	Dipole moment	7.267
11.	Surface area (Grid)	1016.29(A^{02})
12.	Surface area (approx)	903.36 (A^{02})
13.	Hydration energy	-10.59(Kcal/mol)
14.	Log p	10.98
15.	Refractivity	193.93(A^{03})
16.	Polarizability	80.10(A^{03})
17.	Mass	787.48(amu)
18.	Nuclear Energy	1928784.75 (Kcal/mol)
19.	Net Charge	0.00 (e)
20.	RMS	0.08833 (Kcal/mol)
21.	HOMO	-7.169
22.	LUMO	-3.972

Conclusion

Theoretical quantum calculations for all suggested molecular modeling system of Tin complexes R_2SnL_2 have successful results to give useful information about of physico-chemical properties and energetic data to predict the optimum conformations of Tin complexes R_2SnL_2.

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