Vibrational study on the molecular structure of Zinc -Juglonate [Zn(5-hydroxy-1, 4-naphthoquinone)$_2$] by DFT and HF calculations

A. B. Pawar, K. D. Jadhav and R. G. Sarawadekar

Bharati Vidyapeeth University, Pune (India), Yashwantrao Mohite College, Pune

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ABSTRACT

Zinc -Juglonate (5-hydroxy 1, 4-naphthoquinone) was synthesized. The vibrational wave numbers of chelate have been calculated using Gaussian 09 software code, employing RHF / SDD basis set and DFT / B3LYP/ LAND2DZ. The IR data is compared with experimental values. The predicted infrared intensities and Raman activities are reported. The calculated frequencies are in good agreement with the experimental values. The calculated geometrical parameters are also given. The study is extended to calculate the HOMO-LUMO energy gap, Ionization potential (I), Electron affinity (A), Global hardness (η), chemical potential (µ) and global electrophilicity (ω). The calculated HOMO-LUMO energies show the charge transfer occurs in the molecule. Optimized geometrical parameters of the title compound are in agreement with similar reported structures.

Keywords: 5-hydroxy-1,4-naphthoquinone, IR, HF, Energy gap, Zinc juglonate
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INTRODUCTION

Juglone (5- Hydroxy-1, 4-Naphthoquinone) is a naturally occurring quinine found in leaves, roots, nut-husk and bark of Walnut (Juglan regia) , also in black Walnut (1). Naphthoquinones play an integral role in many biological electron transfer processes (2, 3). The molecular basis of naphthoquinone toxicity is the enzyme catalysed reaction to semi-quinone radicals. It reduces oxygen to superoxide anion radicals which regenerate quinines (4). As some quinine reactions are catalysed by metal ions like copper, iron, manganese and molybdenum these should be characterized and through study was carried out of metal chelates with biologically relevant quinine derivatives (5). Zinc juglonate [Zn (5-hydroxy 1, 4-naphthoquinone) 2] was reported by Bottei and Mc Eacharn as black material (6). They have reported that Zinc–juglonate is formed with two molecules of water (TG data) but DTA endothermic peak is not given. Quantum chemical descriptors have been used in QSAR studies in biochemistry. This is due to reliability and versatility of prediction by the3se descriptors. Net atomic charges, HOMO-LUMO energies, electron density, delocalization of electron have been used to correlate with various biological activities (7). DFT calculations on copper & nickel chelates of Juglone were carried out and the data was compared with experimental values for important infra red wave bands (8). IR and Epr studies on nickel juglonate have been reported by Aizenberg et.al. (9). FTIR spectra of juglone were recorded and the vibration frequencies of it were calculated by HF and DFT methods. A good comparison is shown by A. B. Pawar et. al. (10). Zinc – juglonate IR was recorded in the region 4000 to 500 cm^{-1} in KBr matrix and characteristic wave bands were discussed (11). Density functional theory based descriptors have found immense usefulness in the prediction of reactivity of atoms and molecules as well as site selectivity. The resourcefulness of density functional descriptors in the development of QSAR has been recently reviewed (12)

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This paper describes synthesis and vibrational spectra of zinc- juglonate calculated by DFT basis set, the data is compared with experimental values. The wave number values computed by the DFT/B3LYP/ SDD method contain known systematic errors due to negligence of electron correlation (13). We therefore have used the scaling factor as 0.90. Geometrical parameters, Mulliken atomic charges and HOMO – LUMO energy gap of the chelate is reported.

MATERIALS AND METHODS

The ligand 5-hydroxy -1, 4-naphthoquinone is prepared in our laboratory by well known method. A stock solution of Zinc chloride is prepared by using AR grade chemicals.

2.1 Synthesis of metal chelate
The chelate zinc- juglonate was prepared by mixing metal salt solution and ligand in 1: 2 proportions. The mixture was constantly stirred for one hour on magnetic stirrer. The pH of the mixture was maintained, in between 5.0 – 6.0 by adding ammonia solution to it. The mixture warmed on water bath for about 15 minutes. On cooling it was filtered and found to be colored.

2.2 Instrumental Analysis
Elemental analysis was carried out with a Perkin Elmer 2400 series for C, H, and O & N. The IR spectra were recorded on a JASCO FTIR spectrophotometer in a KBr matrix and in the range of 4000 – 400 cm^{-1}as well as in the range of 1000 – 100 cm^{-1} and FAR IR spectra was recorded on Nicollet D5 with reflection technique.

2.2.1 Computational details
The entire calculations conducted in the present work were performed at Density Functional theory (DFT / B3LYP) basis set in the Gaussian 09 software code. The geometries were first determined at the Hartree – Fock level of employing SDD basis set (14, 15). The wave number value computed theoretically contains known systematic error due to the negligence of electron correlation. We have used the scaling factor value of 0.9393 for HF /SDD basic set. The absence of imaginary wave number on the calculated Vibrational Spectrum confirms that the structure corresponds to minimum energy. HOMO-LUMO energy gap and other related molecular parameters are calculated.

RESULTS AND DISCUSSION

In the range of 4000 to 10 cm^{-1}, code has predicted about 97 infra-red bands by the Zn juglonate chelate which is calculated by RHF and DFT method .The wave numbers of all the calculated and observed frequencies are given in Table 1. The probable modes of vibrations assigned for the observed frequencies are given in the last column of the table. The assignments of the fundamental frequencies made on the basis of intensity considerations and position of observed frequencies with the help of molecular structure as shown in Fig. 1.
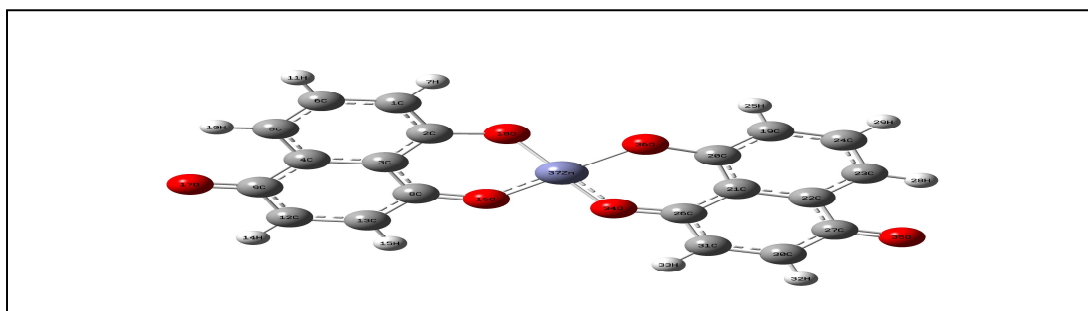

Fig. 1 Molecular structure of Zinc juglonate

C ---H stretching frequencies
Out of ten vibrations of this type in Zn juglonate, the frequencies 3419.33, 3419.40, 3434.12, 3434.21, 3435.58, 3435.61, 3446.46, 3446.51, 3448.50 and 3448.56 cm^{-1} are predicted by HF theory while only one wave number is recorded at 3072.50 cm^{-1}.

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C—C stretching frequencies
The C—C stretching vibrations of this compounds are predicted at 1842.08, 1833.84, 1821.35, 1820.04, 1750.22, 1676.14, 1657.90, 1453.77 and 1448.76 cm^{-1}. While we found bands at 1665.23, 1643.05 and 1453.77 cm^{-1}.

C- Substituted vibrations
 C=O group frequencies. In the C=O stretching region of the infra red spectra of zinc juglonate predicted bands at 1785.47, 1767.89, 1607.74 and 1600.14 cm^{-1} while only one band has been observed at 1599.66 cm^{-1}. The C-O in plane bending vibrations are predicted at 779.61, 775.48, 629.66, 605.31, 591.01, 558.16, 431.93, 160.55 and 94.31 cm^{-1} which are observed at 671.106, 629.444, 600.717, 566.17, 446.00, and 394.08 cm^{-1} . The C=O out-of- plane bending vibration of b_1 type is predicted at 199.96 cm^{-1} and it is found at 209.74 cm^{-1} .

C-H in plane bending vibrations
The C-H in plane bending vibrations is predicted at 516.05, 548.09, 1477.86, 1442.39, 1538.92, 1539.41, 1583.26, 1587.14 and 1746.38 cm^{-1} for zinc juglonate chelate. In the infra-red spectrum, one should observe nine vibrations, four being b_{1u} type and five of b_{2u} type. These are observed at 525.48, and 857.20,

C-H bending out of plane vibrations
The C-H bending out of plane vibrations are predicted at 391.23, 515.51, 800.52, 802.08, 871.77, 872.55, 1074.74, 1074.94, 1105.88, 1106.02, and 1077 cm^{-1} for the present compound and recorded at 518.90, 699.09, 835.02, 1079.94, 1103.08, 1155.15, 1229.40, 1291.11, AND 1337.39 cm^{-1}

M-O stretching frequencies
The predicted frequencies for this compound at 680.08, 629.66 and 591.01 cm^{-1}but we found only two at 671.10 and 629.64 cm^{-1}.

M-O bending frequencies
The M-O bending vibrations are predicted at 714.14, 680.08, 591.28, 497.34, 484.30, 458.30, 394.16, 382.75, 348.97, 320.42, 311.14, 282.40, 224.17, 113.10 and 94.71 cm^{-1} but we found peaks at 225.20, 279.07, 303.01, 312.56, 348.97, 382.75, 478.77, 491.94 and 491.94 cm^{-1}.

Table 1: IR frequencies calculated and observed of Zinc juglonate

Sr. No.	RHF cal. cm^{-1}	Into. cal.	Raman Activity	Old. cm^{-1}	Into. Old.	Assignments
1	3448.56	1.39	350.27	--	--	C – H Stretching
2	3448.50	0.60	148.29	--	--	C – H Stretching
3	3446.51	26.10	268.03	--	--	C – H Stretching
4	3446.46	5.23	47.14	--	--	C – H Stretching
5	3435.61	0.38	56.45	--	--	C – H Stretching
6	3435.58	0.45	39.30	--	--	C – H Stretching
7	3434.21	0.38	40.43	--	--	C – H Stretching
8	3434.12	0.19	80.91	--	--	C – H Stretching
9	3419.40	9.77	43.04	--	--	C – H Stretching
10	3419.33	8.75	73.10	3072.05	65.7177	C – H Stretching
11	1842.08	228.86	1017.80	--	--	C = C Stretching
12	1833.84	152.50	626.28	--	--	C = C Stretching
13	1821.35	20.85	1437.97	--	--	C = C Stretching
14	1820.04	0.99	67.65	--	--	C = C Stretching
15	1785.47	235.94	16.70	--	--	C = O Stretching
16	1767.89	1479.65	185.74	--	--	C = O Stretching
17	1750.22	278.98	146.17	--	--	C = C Stretching
18	1746.38	864.66	215.30	--	--	C – H Bending
19	1705.19	41.49	358.37	--	--	C = C Stretching
20	1703.26	9.79	104.93	--	--	C – H Bending IP
21	1676.14	381.94	116.72	1665.23	42.0629	C = C Stretching
22	1657.90	379.09	38.20	1643.05	32.1526	C = C Stretching
23	1607.74	30.37	41.68	--	--	C = O Stretching
24	1600.14	39.38	28.00	1599.66	50.6804	C = O Stretching
25	1587.14	67.64	147.99	--	--	C – H Bending
26	1583.26	32.57	57.42	--	--	C – H Bending
27	1539.41	35.97	31.15	--	--	C – H Bending

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28	1538.92	16.00	18.40	--	--	C – H Bending
29	1442.39	1.20	10.00	--	--	C – H Bending
30	1437.86	104.88	1.23	--	--	C – H Bending
31	1453.77	258.65	473.54	1453.1	52.5522	C = C Stretching
32	1448.76	31.41	75.00	--	--	C = C Stretching
33	1339.27	3.24	1.52	1337.39	66.8233	C – H Bending
34	1347.31	12.73	2.86	--	--	C – H Bending
35	1289.60	48.10	21.78	1291.11	48.3606	C – H Bending
36	1289.25	0.74	35.53	--	--	C – H Bending
37	1273.76	28.71	21.60	--	--	C – H Bending
38	1271.70	15.44	24.90	--	--	C – H Bending
39	1243.78	466.71	115.26	1229.4	59.798	C – H Bending
40	1222.81	4.61	33.75	--	--	C – H Bending
41	1191.29	13.00	126.00	--	--	C – H Bending
42	1190.71	4.14	8.14	--	--	C – H Bending
43	1145.67	1.73	13.51	1155.15	65.2822	C – H Bending OOP
44	1145.44	4.86	7.80	--	--	C – H Bending OOP
45	1139.99	30.94	87.87	--	--	C – H Bending IP
46	1134.02	76.28	4.72	--	--	C – H Bending IP
47	1106.02	0.19	12.32	1103.08	69.1815	C – H Bending OOP
48	1105.88	0.18	14.20	--	--	C – H Bending OOP
49	1074.94	0.70	2.30	1079.94	70.567	C – H Bending OOP
50	1074.74	0.84	2.47	--	--	C – H Bending OOP
51	997.23	43.68	9.45	--	--	C – O Stretching
52	981.32	426.32	1.50	--	--	C – O Stretching
53	965.15	41.45	0.00	--	--	C – H Bending OOP
54	964.73	2.00	7.85	--	--	C – H Bending OOP
55	943.07	1.10	24.46	--	--	C – O Stretching
56	942.11	2.70	5.10	--	--	C – H Bending OOP
57	938.14	16.12	50.18	938.199	89.5907	Zn-O Stretching
58	920.26	4.28	6.99	--	--	Zn-O Stretching
59	881.55	3.53	2.27	--	--	C – H Bending IP
60	878.17	30.50	0.20	857.204	58.6249	C – H Bending IP
61	872.55	3.81	9.00	--	--	C – H Bending OOP
62	871.77	37.46	3.11	835.026	50.5563	C – H Bending OOP
63	802.08	8.00	1.86	--	--	C – H Bending OOP
64	800.52	1.43	8.90	--	--	C – H Bending OOP
65	779.61	37.33	3.15	--	--	C – O Bending OOP
66	775.48	8.19	23.63	754.031	47.8687	C – O Bending OOP
67	714.14	19.00	45.47	--	--	--
68	705.31	7.60	4.60	--	--	C – H Bending OOP
69	704.63	1.56	4.52	699.069	62.6605	C – H Bending OOP
70	690.23	32.61	10.84	671.106	83.678	Zn–O Stretching
71	680.08	24.76	47.32	--	--	--
72	629.66	10.76	47.33	629.644	56.885	Zn–O Stretching
73	605.31	1.27	6.43	600.717	73.8844	C – O Bending OOP
74	591.28	21.91	31.21	--	--	C – H Bending OOP
75	591.01	63.26	12.68	--	--	Zn O Bending
76	558.16	43.87	1.77	566.17	0.60	C – O Bending OOP
77	548.08	55.84	5.38	--	--	C – H Bending IP
78	516.05	2.67	11.62	525.41	2.00	C – H Bending IP
79	515.51	0.85	1.92	518.90	2.20	C – H Bending IP
80	497.34	77.97	26.57	--	--	Zn O Bending
81	484.30	2.73	12.26	491.94	0.20	Zn O Bending
82	458.30	19.42	6.76	478.77	0.20	Zn O Bending
83	431.93	11.69	1.30	446.00	19.60	C – O Bending OOP
84	394.16	13.95	3.46	414.87	8.20	Zn O Bending
85	394.08	4.62	1.21	397.54	2.30	C – O Bending OOP
86	391.23	0.52	5.40	--	--	C – H Bending OOP
87	382.75	17.78	0.80	372.23	19.00	Zn O Bending
88	348.97	2.81	2.13	350.82	5.20	Zn O Bending
89	320.42	9.75	0.18	312.56	3.8	Zn O Bending
90	311.14	0.46	3.42	303.01	3.90	Zn O Bending
91	282.40	56.89	2.93	279.01	4.20	Zn O Bending
92	224.17	21.70	0.33	225.20	1.20	Zn O Bending
93	199.96	0.18	5.00	209.74	2.80	C –O Stretching

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94	165.31	0.10	0.68	--	--	C – H Bending OOP
95	160.55	2.87	1.75	--	--	C = O Bending
96	113.10	26.78	0.55	--	--	Zn-O Bending
97	94.71	2.26	4.18	--	--	Zn-O Bending

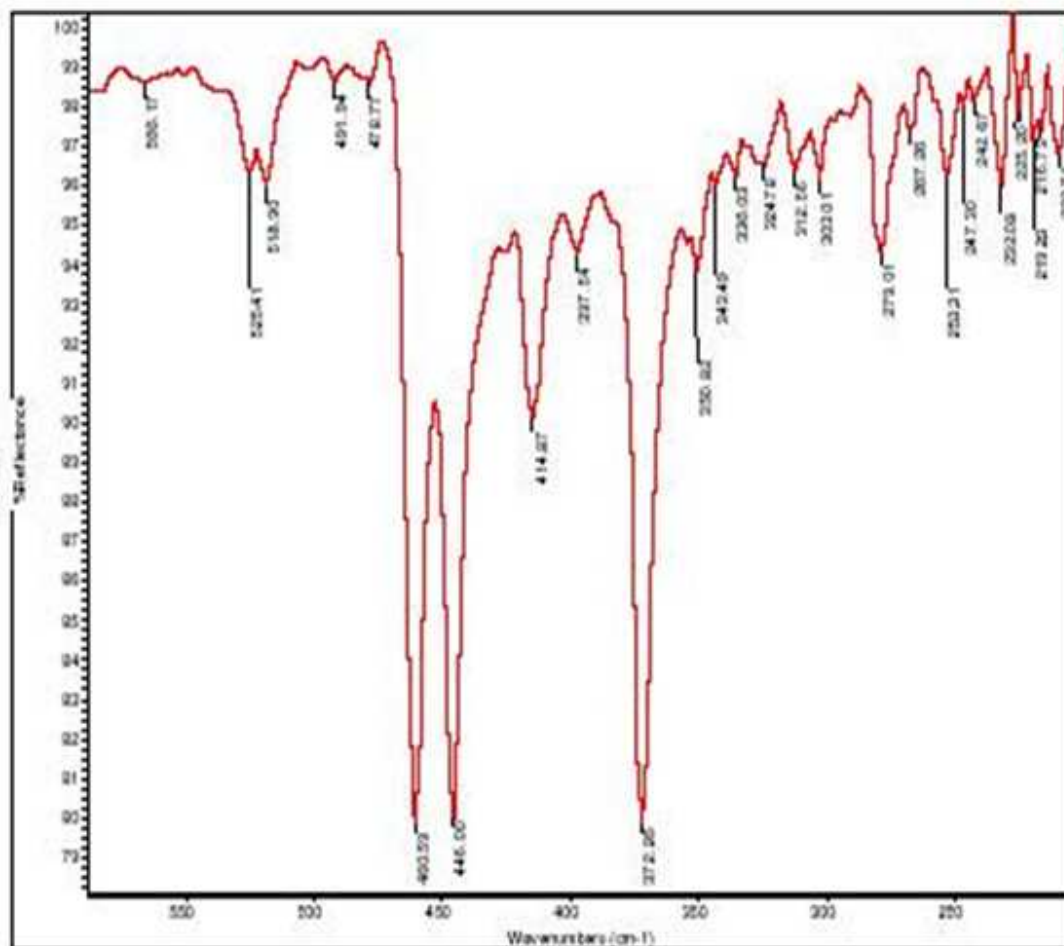*OOP = OUT OF PLANE   IP = IN PLANE*

Fig. 2: FAR IR spectra of Zinc juglonate

Molecular geometry.
The optimized structure parameters of Zinc lawsonate calculated by ab initio, HF/SDD basis set are listed in Table 2 in accordance with the atom numbering scheme given in Fig -1.

The values of bond length in A^0 and bond angles in degree are given in Table 2.

The bond length of Zn-O is showing a difference of 0.16 $A^0.$ The naphthalene carbon ring is relatively planar, the largest deviation from the mean plane being 0.023 A ^{o} for the C1 carbon atom. A further interesting finding is that the outside angle O36-C20-O21 [122.320o] is significantly larger than the inside angle O36-C20-C21 [117.649o]. It may be noted that almost the same differences are predicted.

237

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Table No:-2   Bond Length and Bong Angles of Zinc juglonate

Sr. No.	Bond	Bond Length A^0	Sr. No	Bong Angle	(0)
1	Zn37O18	1.90521	1	O18Zn37O16	94.032
2	Zn37O16	1.74548	2	O36Zn37O34	93.542
3	Zn37O34	1.74757	3	O18Zn37O36	86.592
4	Zn37O36	1.90747	4	O16Zn37O34	86.186
5	C2O18	1.42458	5	O18C2C3	122.267
6	C8O16	1.26490	6	C2C3C8	121.932
7	C26O34	1.26478	7	C8O16Zn37	127.089
8	C20O36	1.42424	8	O36C20C21	122.320
9	C9O17	1.2584	9	O36c20c19	117.649
10	C27O35	1.2584	10	C26O34Zn37	127.879
11	C26C21	1.40756	11	C20C19H25	119.741
12	C21C20	1.40753	12	C26C31H33	119.620
13	C8C3	1.40994	13	C8C13H15	119.627
14	C3C2	1.40342	14	C2C1H7	119.744
15	C13H15	1.0700			
16	C31H33	1.0700			
17	C1H7	1.0700			
18	C19H25	1.0700			

Mulliken Atomic Charges

Mulliken charges arise from the Mulliken population analysis (16,17) and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry, particularly those based on the linear combination of atomic orbital's molecular orbital method, and are routinely used as variables in linear regression QSAR procedures(18). In the application of quantum mechanical calculation to molecular system, the calculation of effective atomic charges plays an important role. The electron distribution of Zinc lawsonate is compared in the two different   mechanical methods and the sensitivity of the calculated charges to charge in choice of methods is studied. By determining electron population of each atom in the defined basis function, the Mulliken charges are calculated by HF/SDD. The results are presented in Table-3 which the values of atomic charges of each atom of the concerned molecule.

Table-3:- Mulliken Atomic Charges of Zinc juglonate

1	1C	-0.335288	20	20C	0.206073
2	2C	0.205547	21	21C	0.055155
3	3C	0.048605	22	22C	0.247481
4	4C	0.249150	23	23C	-0.36823
5	5C	-.368260	24	24C	-0.17593
6	6C	-0.175843	25	25H	0.273051
7	7H	0.273359	26	26C	0.290699
8	8C	0.290941	27	27C	0.047492
9	9C	0.047677	28	28H	0.292485
10	10H	0.292641	29	29H	0.245261
11	11H	0.245479	30	30C	-0.294506
12	12C	-.293684	31	31C	-0.30939
13	13C	-0.30959	32	32H	0.275225
14	14H	0.275531	33	33H	0.273007
15	15H	0.273543	34	34O	-0.461568
16	16O	-0.459383	35	35O	-0.248807
17	17O	-0.24828	36	36O	-0.532456
18	18O	-0.529929	37	37Zn	1.038426
19	19C	-0.335661			

HOMO-LUMO energy gap and related molecular properties.

The HOMO-LUMO energy gap of the molecule Zinc juglonate in the HF and SDD basis set has been calculated. The HOMO-LUMO energy gap is constant in both methods. It is known that the value of E_{HOMO} is often associated with the electron donating ability of inhibitor molecule, higher values of E_{HOMO} is an indication of the greater ease of donating electrons to the unoccupied d orbital of the receptor. The value of E_{LUMO} is related to the ability of the molecule to accept electrons, lower values of E_{LUMO} shows the receptor would accept electrons. Consequently, the value of *E gap* provides a measure for the stability of the formed complex on the metal surface. The frame work of

238

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SCF MO theory, the ionization energy and electron affinity can be expressed through HOMO and LUMO energies AS $I = -E_{HOMO}$, $A = -E_{LUMO}$. The hardness compounds to the gap between the HOMO and LUMO orbital energies. If the gap energy is higher than the Hardness is also larger. The global hardness $\eta = \frac{1}{2}(E_{HOMO} - E_{LUMO})$. The hardness is associated with the stability of chemical potential (μ) can be expressed in combination of electron affinity and ionization potential. Recently Parr et al. (19)have defined a new descriptor to quantify the global electrophilic power of the molecule as electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a molecule within a relative scale ($_\omega = \mu^2 / 2\eta$) is also calculated and listed in table- 4. The earlier works of Maynard et al. (20) have formed the strong foundation for the electrophilicity index, which provided the direct relationship between the rates of reaction and the ability to identify the function or capacity of an electrophile and the electrophilic power of the inhibitors. Using the properties of FF, more powerful descriptors of reactivity were discussed.

Table No: - 4 Molecular Properties of Zinc juglonate and juglone

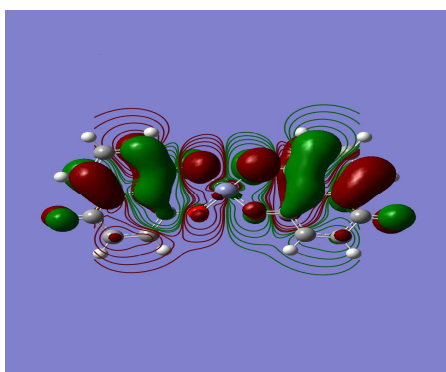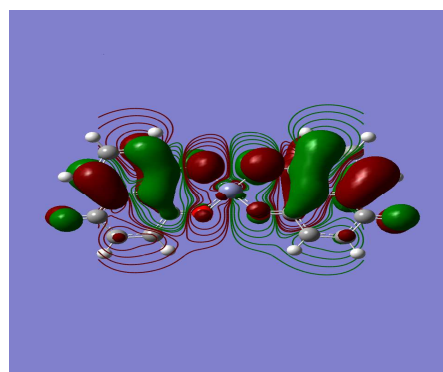| Molecular Properties	Zinc juglonate eV	Juglone eV
HOMO eV	-0.31656	-0.34747
LUMO eV	-0.04238	-0.00836
Energy gap	0.27418	0.33911
Ionisation Potential (I)	-0.04238	-0.00836
Electron Affinity(A)	-0.31656	-0.34747
Global Hardness (η)	0.13709	0.16955
Chemical Potential (μ)	0.17947	0.17791
Global Electrophilicity (ω)	0.11747	0.09334
Electronegativity (x)	0.17947	0.17791

Fig.3 1) HOMO contour   **2) LUMO contour**

Thermodynamic properties
On the basis of vibrational analysis at B3LYP / SDD and HF / SDD level, several thermodynamic parameters are calculated and are presented in Tabl-5. The zero point vibration energy (ZPVE) and the entropy, Svib. (T) are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in total entropy of Zinc lawsonate at room temperature at different methods is only marginal.

Table 5 theoretically computed Energies (a.u.), Zero point Energy (Kcal / mol)
Rotational Constants (GHz), Entropy (cal mlo^{-1}K^{-1}) and Dipole moment D (Debye)

Parameter	HF/SDD
Total Energy e.u.	-1275.515
Zero Point Energy	162.69479
Rotational constants(GHZ)	0.50326
	0.09279
	0.07933
Entropy Total	120.713
Translational	0.889
Rotational	0.889
Vibrational	170.085
Dipole movement (D)	2.5963 Debye

239

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CONCLUSION

The chemical potential of zinc juglonate and juglone are almost equal. The calculated vibration frequencies are compared with experimental data and found most of them are in good agreement. The assignments were confirmed with the help of animation process which is available in Gaussian 09 computer code. The results suggest that it shows the formation of chelates. The molecular geometry of Zinc juglonate is best at the HF/ SDD level. The HOMO- LUMO energy was calculated and other related molecular properties were also discussed. The Mullikan atomic charges were calculated and the results were discussed. Thermodynamic parameters were calculated.

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