

Vibrational analysis and electronic properties of 2-Decenoic acid and its derivative by first principles

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Abstract. Royal jelly is the mixture of acids like 2-Decenoic acid (DA), 10-Hydroxy 2-Decenoic acid and many others. 10-HDA possesses strong inhibition to the growth of cancer cells, namely transferable AKR leukaemia, TA3 breast cancer, etc. The equilibrium geometry of 2-Decenoic acid and its derivative 10-Hydroxy 2-Decenoic acid in the ground state have been determined and analyzed by Density functional theory (DFT) employing 6-311 G (d, p) as the basis set. The harmonic frequencies of 2-DA and 10-HDA have also been calculated to understand its complete vibrational dynamics. The study of simulated spectra provides important information about the ability of the computational method to describe the vibrational modes.

Keywords: Royal jelly, vibrational analysis, polarizability, hyperpolarizability, electronic properties

1. Introduction

The chemical nature of the components of royal jelly has received considerable attention over the past 20 years. It is a mixture of acids like 2-Decenoic acid, 10-Hydroxy 2-Decenoic acid and many others. 10-Hydroxy-2-Decenoic acid is a kind of special active substance which exists only in royal jelly in nature. It is also called 10-HDA or royal jelly acid. 10-HDA possesses strong inhibition to the growth of cancer cells, namely transferable AKR Leukaemia, TA3 breast cancer etc. Recent studies show that 10-HDA possesses the effect of immuno-regulation and anti-cancer activities. 10-HDA's strong cancer fighting properties were first witnessed by a study published in Nature in May 1959. The scientists mixed 10-HDA with active tumour cells taken from cancerous mice. They reported that an injection of the mixture suppressed mouse leukaemia and inhibited the formation of tumours. 10-HDA has a strong antibacterial property, skin care, skin whitening and antioxidative activity effect. 10-HDA has other function including treatment of AIDS and other immunodeficiency diseases, insulin-like effect for diabetes and hypertension, antiulcer effects and preventive and therapeutic effects on hyperlipidemia [3,6,14,19–21,23,25–35].

In the present communication, the focus has been on the study of the molecular structure of two well-known and biologically important acids of royal jelly: 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid. The study offers different perspectives on what can be done using computational modeling.

The equilibrium geometry, harmonic vibrational frequencies and HOMO–LUMO gap have been calculated by the Density Functional B3LYP method employing 6-311 G (d, p) as the basis set. The detailed

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interpretation of the infrared spectra of 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid in terms of the normal mode analysis has been carried out. The main objective of the present study is to investigate in detail the vibrational spectra of important biological molecules (2-Decenoic acid and 10-Hydroxy 2-Decenoic acid) by DFT [12] method, which can presumably help in understanding its dynamical behavior. To the best of our knowledge no detailed DFT calculations have been performed on 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid so far in the literature.

2. Structure and spectra

The molecular structures of the title compounds 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid is made by molecular modeling. The model molecular structures of the compounds are given in Figs 1 and 2. FTIR spectrum is available only for 2-Decenoic acid in literature [1] and has been given in Fig. 4. FTIR spectra of the compounds has been plotted theoretically, which are given in Figs 3 and 5, respectively.

3. Computational methods

Initial geometry was generated from the standard geometrical parameters and was minimized without any constraint in the potential energy surface. The gradient corrected Density Functional Theory

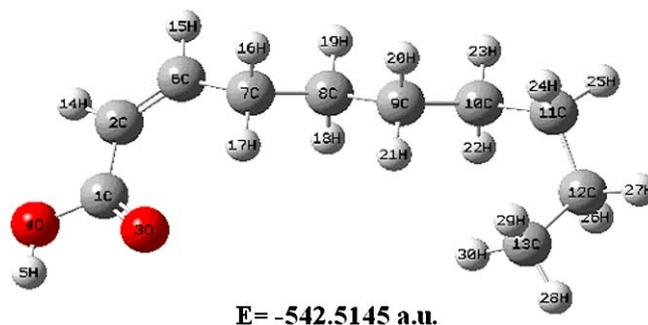


Fig. 1. Molecular structure of 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

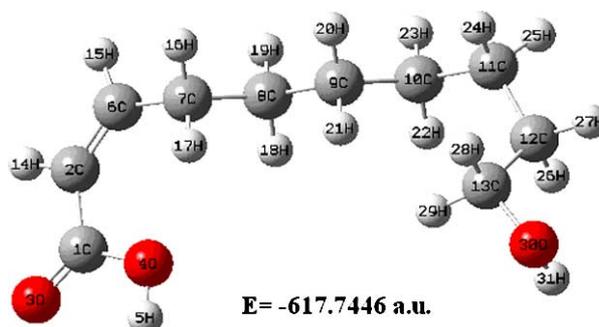


Fig. 2. Molecular structure of 10-Hydroxy 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

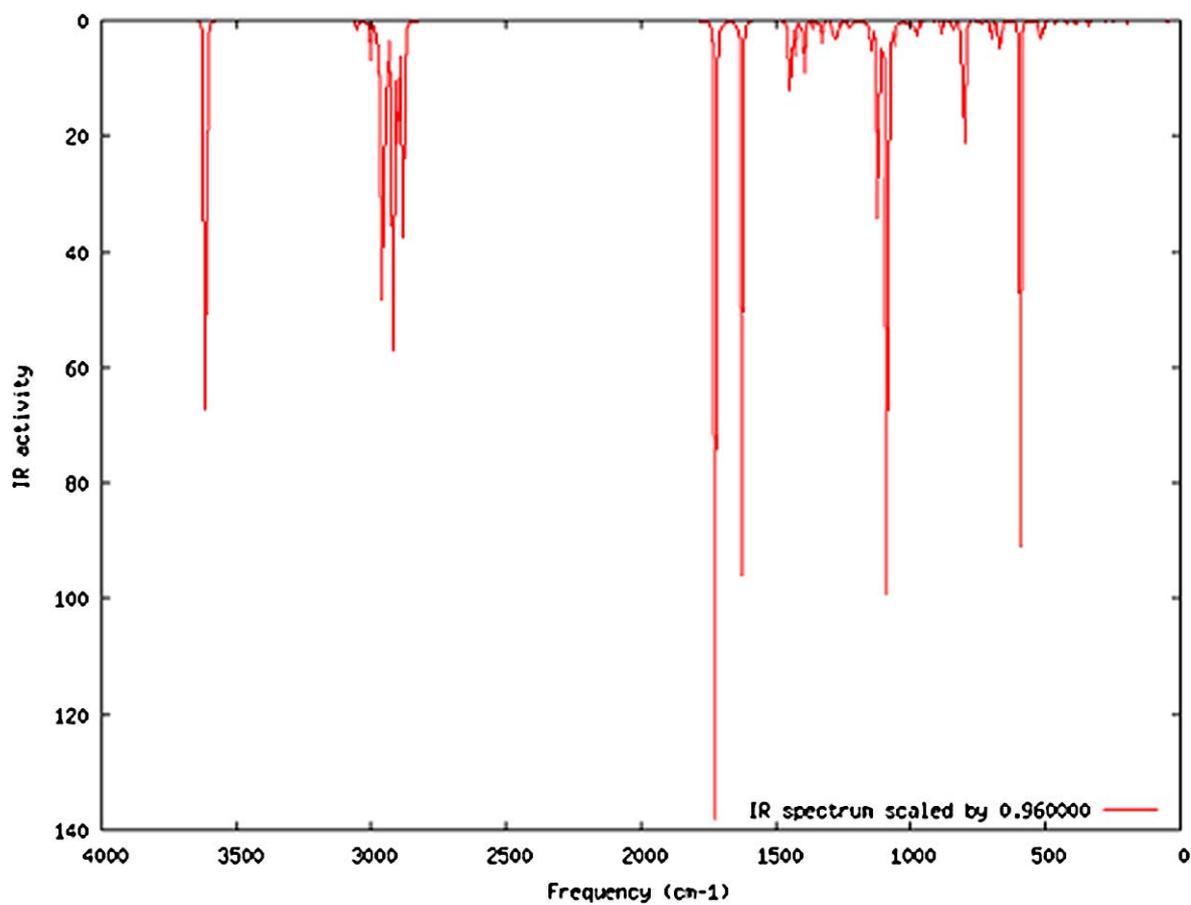


Fig. 3. Calculated spectra of 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

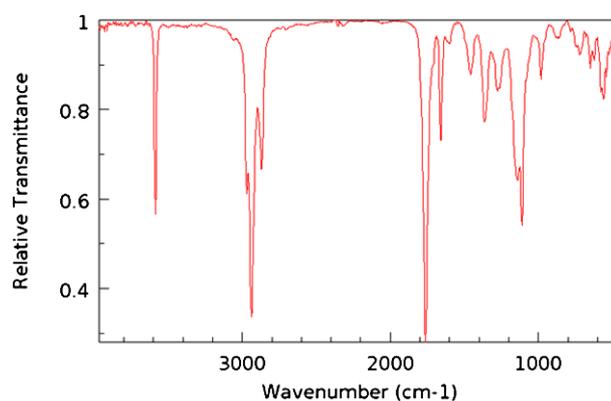


Fig. 4. Experimental FTIR spectrum of 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

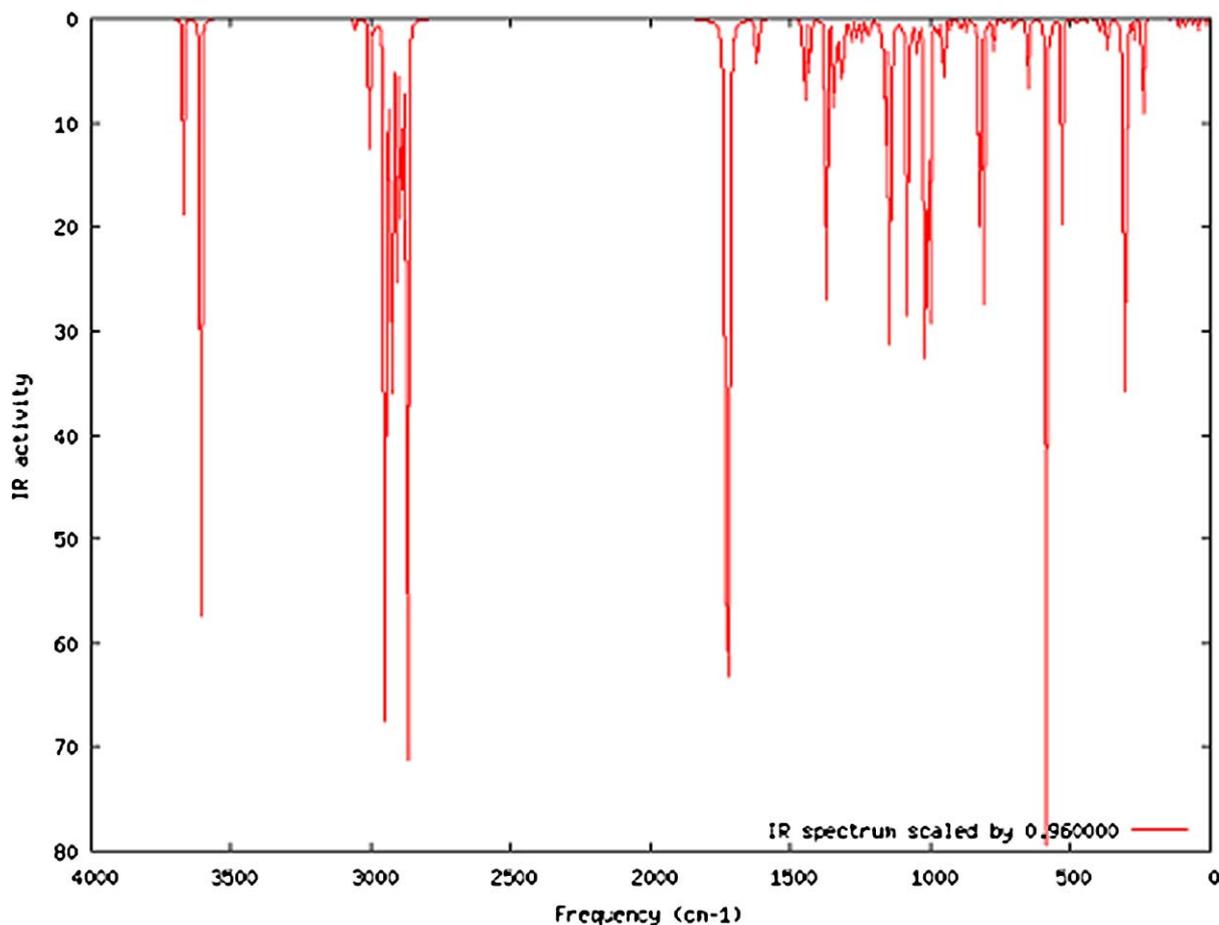


Fig. 5. Calculated spectra of 10-Hydroxy 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

(DFT) with the three-parameter hybrid functional (B3) [2] for the exchange part and the Lee–Yang–Parr (LYP) correlation function [17] has been employed for the computation of molecular structure, vibrational frequencies, HOMO–LUMO and energies of the optimized structures, using Gaussian’09 [10]. The calculated vibrational frequencies have also been scaled by a factor of 0.963 [7]. By combining the results of the GAUSSVIEW’S program [9] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. The prediction of IR frequencies of title compound has been found to be very straightforward using this approach. To determine the form of the modes we used the potential energy distribution (PED) calculations and applied the VEDA program performing both the PED analysis and its optimization [13]. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compound if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for anharmonicity. A number of studies have been carried out regarding calculations of vibrational spectra by using B3LYP methods with 6-311 G (d, p) basis set. The scaling factor (0.963) was applied successfully for B3LYP method and was found to be easily transferable in a number of molecules. Thus vibrational frequencies calculated by using the B3LYP functional with 6-311 G (d,

p) as basis set, can be utilized to eliminate the uncertainties in the fundamental assignment in the IR spectra.

4. Results and discussion

4.1. Geometrical structure

An extremely important property of molecules, i.e., conformation has been given due importance in the present study. The study of conformation bears significance as far as their interaction with biological system is concerned. This can further provide information about the possible receptor binding site. Even a minor change in the bond or torsion angle can presumably help in explaining the bioactivity. Different structures (Fig. 6) of both the compounds were modeled taking all of the conformational possibilities into consideration. The optimized structure parameters and thermodynamic properties of the lowest energy conformer of 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid were calculated by DFT/B3LYP levels with the 6-311 G (d, p) basis set and are listed in Tables 1 and 2, in accordance with the atom numbering scheme given in Figs 1 and 2. No imaginary frequencies were found in the vibrational mode calculation. Subsequently, the global minimum energy obtained after structure optimization in case of 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid with 6-311 G (d, p) basis sets was approximately -542.5145 and -617.7446 a.u., respectively. This is due to the fact that all the conformers were more planar than the given conformers and became linear structures but the given conformer was inclined in its plane and hence the surface strain was minimized. However, another change which was noticeable in both the conformers was that the CO_2 group rotates by 180° from its plane in case of 2-Decenoic acid than the 2-HDA and also the hydrogen attached to one of the oxygen in CO_2 was perpendicular to the molecular plane, thereby reducing the strain created by the other hydrogen attached to the given chain. The global

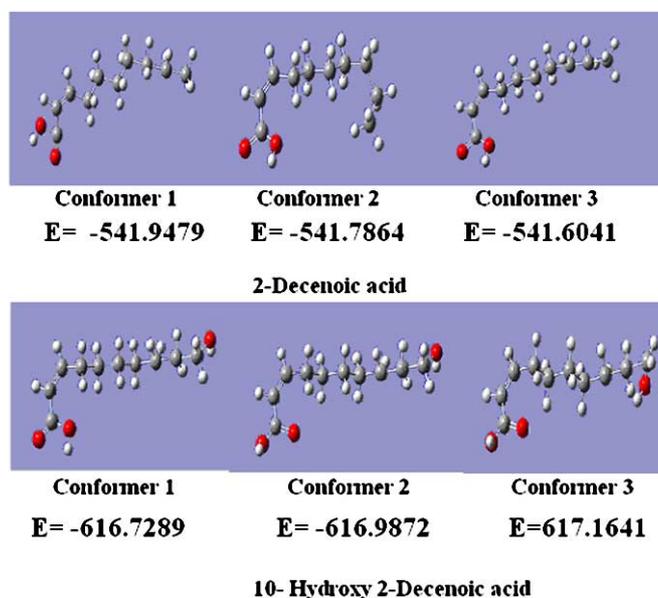


Fig. 6. Different conformers of 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

Table 1
 Optimized geometrical parameters of 2-Decenoic acid (2-DA) and 10-Hydroxy 2-Decenoic acid (10-HDA)

S. No.	2-Decenoic acid parameters		10-Hydroxy 2-Decenoic acid parameters	
	Bond lengths	Calculated	Bond lengths	Calculated
1	R(1, 2)	1.4774	R(1, 2)	1.4769
2	R(1, 3)	1.2105	R(1, 3)	1.2085
3	R(1, 4)	1.3602	R(1, 4)	1.3616
4	R(2, 6)	1.3401	R(2, 6)	1.3405
5	R(2, 14)	1.0836	R(2, 14)	1.0838
6	R(4, 5)	0.9684	R(4, 5)	0.9688
7	R(6, 7)	1.4975	R(6, 7)	1.5000
8	R(6, 15)	1.0898	R(6, 15)	1.0894
9	R(7, 8)	1.5423	R(7, 8)	1.5441
10	R(7, 16)	1.0990	R(7, 16)	1.0967
11	R(7, 17)	1.0886	R(7, 17)	1.0886
12	R(8, 9)	1.5326	R(8, 9)	1.5327
13	R(8, 18)	1.0961	R(8, 18)	1.0952
14	R(8, 19)	1.0976	R(8, 19)	1.097
15	R(9, 10)	1.5356	R(9, 10)	1.5354
16	R(9, 20)	1.0977	R(9, 20)	1.0975
17	R(9, 21)	1.0941	R(9, 21)	1.0948
18	R(10, 11)	1.5442	R(10, 11)	1.5431
19	R(10, 22)	1.0978	R(10, 22)	1.0976
20	R(10, 23)	1.0964	R(10, 23)	1.0962
21	R(11, 12)	1.5385	R(10, 25)	2.1558
22	R(11, 24)	1.0977	R(11, 12)	1.5388
23	R(11, 25)	1.0954	R(11, 24)	1.0975
24	R(12, 13)	1.5324	R(11, 25)	1.0947
25	R(12, 26)	1.0971	R(12, 13)	1.5288
26	R(12, 27)	1.0962	R(12, 25)	2.1335
27	R(13, 28)	1.0937	R(12, 26)	1.0991
28	R(13, 29)	1.0947	R(12, 27)	1.0952
29	R(13, 30)	1.0928	R(13, 28)	1.0934
30	–	–	R(13, 29)	1.0981
31	–	–	R(13, 30)	1.4266
32	–	–	R(30, 31)	0.9623
	Bond angles		Bond angles	
33	A(2, 1, 3)	128.1958	A(2, 1, 3)	123.2843
34	A(2, 1, 4)	110.3225	A(2, 1, 4)	115.2921
35	A(3, 1, 4)	121.4815	A(3, 1, 4)	121.4174
36	A(1, 2, 6)	125.696	A(1, 2, 6)	129.4518
37	A(1, 2, 14)	114.6693	A(1, 2, 14)	111.3544
38	A(6, 2, 14)	119.6347	A(6, 2, 14)	119.1903
39	A(1, 4, 5)	106.0578	A(1, 4, 5)	105.5894
40	A(2, 6, 7)	129.1042	A(2, 6, 7)	130.0523

Table 1
(Continued)

S. No.	2-Decenoic acid parameters		10-Hydroxy 2-Decenoic acid parameters	
	Bond lengths	Calculated	Bond lengths	Calculated
41	A(2, 6, 15)	116.0608	A(2, 6, 15)	115.3904
42	A(7, 6, 15)	114.8285	A(7, 6, 15)	114.5452
43	A(6, 7, 8)	111.9149	A(6, 7, 8)	111.8648
44	A(6, 7, 16)	107.7776	A(6, 7, 16)	108.1041
45	A(6, 7, 17)	110.6059	A(6, 7, 17)	110.9826
46	A(8, 7, 16)	108.3322	A(8, 7, 16)	108.6398
47	A(8, 7, 17)	110.3329	A(8, 7, 17)	109.263
48	A(16, 7, 17)	107.7243	A(16, 7, 17)	107.8706
49	A(7, 8, 9)	112.7254	A(7, 8, 9)	112.7518
50	A(7, 8, 18)	108.8336	A(7, 8, 18)	108.4674
51	A(7, 8, 19)	109.7148	A(7, 8, 19)	109.708
52	A(9, 8, 18)	109.5574	A(9, 8, 18)	109.6884
53	A(9, 8, 19)	109.4908	A(9, 8, 19)	109.5462
54	A(18, 8, 19)	106.3134	A(18, 8, 19)	106.4798
55	A(8, 9, 10)	113.055	A(8, 9, 10)	112.9235
56	A(8, 9, 20)	109.1743	A(8, 9, 20)	109.3229
57	A(8, 9, 21)	109.0485	A(8, 9, 21)	108.9024
58	A(10, 9, 20)	108.8485	A(10, 9, 20)	108.8619
59	A(10, 9, 21)	110.4067	A(10, 9, 21)	110.4815
60	A(20, 9, 21)	106.0627	A(20, 9, 21)	106.1178
61	A(9, 10, 11)	115.2893	A(9, 10, 11)	115.4141
62	A(9, 10, 22)	109.4968	A(9, 10, 22)	109.5434
63	A(9, 10, 23)	107.8293	A(9, 10, 23)	107.7937
64	A(11, 10, 22)	109.3379	A(9, 10, 25)	138.8584
65	A(11, 10, 23)	108.7825	A(11, 10, 22)	109.3243
66	A(22, 10, 23)	105.6586	A(11, 10, 23)	108.6232
67	A(10, 11, 12)	116.0906	A(22, 10, 23)	105.6859
68	A(10, 11, 24)	109.3051	A(22, 10, 25)	104.9484
69	A(10, 11, 25)	108.5175	A(23, 10, 25)	83.1199
70	A(12, 11, 24)	109.3819	A(10, 11, 12)	116.4159
71	A(12, 11, 25)	107.3088	A(10, 11, 24)	109.4265
72	A(24, 11, 25)	105.7224	A(12, 11, 24)	109.3586
73	A(11, 12, 13)	116.0069	A(11, 12, 13)	116.4256
74	A(11, 12, 26)	108.6769	A(11, 12, 26)	108.9329
75	A(11, 12, 27)	107.9972	A(11, 12, 27)	108.9993
76	A(13, 12, 26)	109.1622	A(13, 12, 25)	145.4345
77	A(13, 12, 27)	108.6704	A(13, 12, 26)	108.7391
78	A(26, 12, 27)	105.8525	A(13, 12, 27)	106.9466
79	A(12, 13, 28)	110.7339	A(25, 12, 26)	94.5782
80	A(12, 13, 29)	111.2933	A(25, 12, 27)	89.7274
81	A(12, 13, 30)	112.0533	A(26, 12, 27)	106.3345
82	A(28, 13, 29)	107.5922	A(12, 13, 28)	110.2259
83	A(28, 13, 30)	107.2236	A(12, 13, 29)	111.0678
84	A(29, 13, 30)	107.7337	A(12, 13, 30)	112.078

Table 1
(Continued)

S. No.	2-Decenoic acid parameters		10-Hydroxy 2-Decenoic acid parameters	
	Bond lengths	Calculated	Bond lengths	Calculated
85	–	–	A(28, 13, 29)	107.4371
86	–	–	A(28, 13, 30)	105.4471
87	–	–	A(29, 13, 30)	110.3373
88	–	–	A(10, 25, 12)	75.2793
89	–	–	A(13, 30, 31)	107.6689

Table 2

Calculated thermodynamic properties of 2-Decenoic acid (2-DA) and 10-Hydroxy 2-Decenoic acid (10-HDA) by (B3LYP)/6-311 G (d, p) methods

	E (Thermal) (kcalmol ⁻¹)		CV (cal K ⁻¹ mol ⁻¹)		S (cal K ⁻¹ mol ⁻¹)	
	2-DA	10-HDA	2-DA	10-HDA	2-DA	10-HDA
Total	176.066	180.133	51.110	54.664	127.284	132.226
Translational	0.889	0.889	2.981	2.981	41.302	41.570
Rotational	0.889	0.889	2.981	2.981	32.244	32.887
Vibrational	174.289	178.356	45.148	48.703	53.738	57.769

minimum energy difference between the two conformers was found to be 75.2304 a.u. This is due to the replacement of the hydrogen atom with OH group, making 10-HDA, more stable than 2-DA. In case of 2-DA, molecular structure of lowest energy conformer has C₁ molecular symmetry as visualized by the Gauss view. However, in case of 10-HDA, one hydrogen is replaced at position C₁₃ by the OH group. Both conformers have no point group symmetry. The optimized bond lengths of 10-HDA of C–C bonds is higher than that of 2-DA.

4.2. Vibrational spectra analysis

There are a number of Quantum chemical codes from where spectroscopic properties can be calculated and act as an alternative to experimentally obtained values. The vibrational frequency calculations of 2-Decenoic acid (2-DA) and 10-Hydroxy 2-Decenoic acid (10-HDA) are carried out with the B3LYP and 6-311 G (d, p) as the basis set and are listed in Tables 3 and 4, respectively. 2-DA has 30 atoms and 84 normal modes of fundamental vibration whereas 10-HDA has 31 atoms and 87 normal modes of fundamental vibrations.

4.2.1. Spectral region above 2800 cm⁻¹

The characteristic ν_{CH} stretching vibrations of both the structures are expected to appear in the 2800–3500 cm⁻¹ frequency range. The bands located in the high frequency region of the calculated spectra of 2-DA and 10-HDA are easy to identify and belong to O–H and C–H stretching modes.

For 2-DA, an intense band due to O–H stretching vibration polarized in the plane of molecule is calculated at 3615 cm⁻¹ with a PED (Potential Energy Distribution) of 100% matches well with the 3595 cm⁻¹ in experimental spectrum and for C–H stretching vibrations, intense bands are calculated at 2875, 2922 and 2946 cm⁻¹ with PED of 96, 93 and 92%, respectively matches well with the experimental frequencies 2850, 2925 and 2940 cm⁻¹.

Table 3

Comparison of the observed and calculated vibrational spectra of 2-Decenoic acid with B3LYP/6-311 G (d, p)

B3LYP (Calculated)	IR (Int.)	IR (Exp.)	Vibrational assignments [P.E.D.]
9	0.199	–	τ (C–C–C) [63]
23	0.157	–	τ (C–C–C) [78]
44	1.587	–	twist (OH–C=O) [88]
55	0.039	–	twist in whole molecule
82	0.097	–	twist (CH ₂ –CH ₃) [68]
91	0.125	–	twist in whole molecule
117	0.092	–	τ (H–C–C–H) [63]
132	0.031	–	twist (CH ₃) [78]
203	1.930	–	τ (C=C–C=O) [59] + τ (C–C–C–C) [22]
218	0.185	–	τ (C–C–C–C) [65]
247	0.370	–	twist (CH ₃) [62]
274	0.388	–	τ (C–C–C–C) [79]
301	0.675	–	τ (H–C–C–H) [63]
339	2.452	–	τ (C–C–C–C) [69]
388	4.395	–	τ (C–C–C–C) [82]
420	2.294	–	τ (C–C–C–C) [69]
461	2.880	–	τ (H–C–C–H) [62]
517	23.54	–	τ (O=C–O–H) [78]
593	92.99	590	w (O–H) [79]
670	32.09	665	τ (C=C–C=O) [88]
699	6.273	695	β (C–C–H) [63]
704	1.177	–	β (C–C–C) [52] + β (C–C–H) [25]
735	1.962	–	β (C–C–H) [62]
749	0.735	–	twist (CH ₃) [78]
785	0.645	–	twist (CH ₂) [72]
804	55.19	805	β (C–C–C) [49] + β (C–C=O) [31]
837	2.855	–	twist (CH ₃) [65]
845	6.280	–	β (C–C–C) [58] + β (C–C=O) [32]
884	6.812	885	twist (CH ₂) [72]
917	0.810	–	twist (CH ₃) [69]
959	4.132	–	β (C–C–C) [46] + β (C–C–H) [25]
978	1.750	–	β (C–C–C) [43] + β (C–C–H) [29]
981	6.383	–	β (C–C–C) [42] + β (C–C–H) [27]
998	1.958	1005	β (C–C–C) [49] + β (C–C–H) [23]
1009	0.843	–	β (C–C–C) [48] + β (C–C–H) [31]
1018	0.307	–	β (C–C–C) [43] + β (C–C–H) [26]
1057	6.390	–	twist (CH ₂) [56]
1080	51.63	–	β (C–C–C) [46] + β (C–C–H) [26]
1088	233.2	–	β (C–O–H) [39] + β (C–C=O) [29]
1119	206.6	1125	β (C–O–H) [46] + β (C–C=O) [28]
1149	17.55	1150	β (C–C–H) [59]
1190	0.667	–	β (C–C–H) [48]
1215	1.122	–	twist (CH ₂) [52]
1224	3.572	1225	β (C–C–H) [49]

Table 3
(Continued)

B3LYP (Calculated)	IR (Int.)	IR (Exp.)	Vibrational assignments [P.E.D.]
1247	1.768	–	β (C–C–H) [54]
1258	0.654	–	twist (CH ₂) [62]
1272	6.040	–	β (C–O–H) [49] + β (C–C–H) [19]
1278	4.268	–	β (C–C–H) [54] + β (C–O–H) [26]
1283	2.717	–	twist (CH ₂) [59]
1288	5.396	–	β (C–C–H) [48] + β (C–O–H) [29]
1324	0.597	–	twist (CH ₂) [49]
1327	1.904	–	twist (CH ₂) [58]
1332	4.931	–	β (C–C–H) [45]
1343	1.659	–	twist (CH ₂) [59]
1361	4.224	–	β (CH ₃) [64]
1397	33.71	1390	β (C=C–H) [61] + β (C–O–H) [24]
1426	2.903	–	β (H–C–H) [79]
1428	5.290	–	β (CH ₂) [69]
1430	0.616	–	β (CH ₂) [75]
1432	1.876	–	S (CH ₂) [88]
1438	0.909	–	β (CH ₂) [69]
1444	12.99	–	β (H–C–H) [72]
1451	10.69	1450	S (CH ₂) [82]
1455	6.590	–	β (CH ₂) [78]
1626	118.0	1625	ν (C=C) [96]
1722	229.1	1790	ν (C=O) [94]
2875	11.06	2850	ν (C–H) [91]
2878	1.493	–	ν (C–H) [93]
2880	4.755	–	ν (C–H) [94]
2882	13.40	–	ν (C–H) [95]
2884	27.89	–	ν (C–H) [95]
2888	57.80	–	ν (C–H) [96]
2901	23.90	–	ν (C–H) [91]
2907	22.32	–	ν (C–H) [90]
2916	34.56	–	ν (C–H) [96]
2918	36.88	–	ν (C–H) [95]
2922	75.21	2925	ν (C–H) [93]
2946	80.46	2940	ν (C–H) [92]
2958	45.54	–	ν (C–H) [99]
2969	54.80	–	ν (C–H) [99]
2985	8.556	–	ν (C–H) [93]
3007	10.75	–	ν (C–H) [95]
3057	6.990	–	ν (C–H) [99]
3615	75.42	3595	ν (O–H) [100]

Notes: ν – stretching, β – bending; S – scissoring; w – wagging; τ – torsion; F.C. – force constant.

Table 4

Comparison of the observed and calculated vibrational spectra of 10-Hydroxy 2-Decenoic acid with B3LYP/6-311 G (d, p)

B3LYP (Calculated)	IR (Int.)	Force constant (FC)	Vibrational assignments [P.E.D.]
15	0.902	0.0007	τ (C–C–C) [77]
18	0.300	0.0011	(whole molecule bend from center)
41	1.589	0.0104	τ (whole molecule)
52	0.272	0.0058	τ (whole molecule)
67	2.340	0.0065	τ (whole molecule)
89	1.260	0.0101	twist (CH ₂ –OH) [75]
110	2.123	0.0248	twist (CH ₂ –OH) [85]
120	0.369	0.0224	τ (C–C–C) [72]
141	0.584	0.0332	twist (CH ₂) [69]
196	0.260	0.1000	τ (whole molecule)
240	3.032	0.1184	τ (C–C–C) [56] + τ (C–C–C–O) [24]
241	7.026	0.0765	τ (C–C–C) [76]
273	2.219	0.1497	τ (whole molecule)
307	93.40	0.0757	w (OH) [92]
322	0.570	0.2085	τ (whole molecule)
366	12.29	0.2332	τ (whole molecule)
397	9.213	0.3583	τ (C–C–C) [59] + τ (C–C–O–H) [29]
444	1.465	0.3442	τ (whole molecule)
477	2.886	0.3169	τ (C–C–C) [82]
529	19.72	0.8700	τ (C=C–C=O) [78]
585	87.55	0.2679	w (OH) [88]
652	31.36	0.6981	β (C–O–H) [62] + β (C–C–C) [21]
693	1.340	0.6557	β (C–C–H) [52] + β (C–O–H) [29]
704	2.287	0.3557	β (C–C–C) [46] + β (C–C–H) [25]
740	1.178	0.4580	twist whole molecule
769	1.107	0.4846	twist whole molecule
779	7.140	0.6873	twist whole molecule
809	27.76	1.4235	β (C–C–C) [58] + β (C–O–H) [29]
827	45.87	1.3349	β (C–C–C) [59] + β (C–C–H) [24]
872	2.652	0.8770	β (C–C–C) [49] + β (C–C–H) [28]
894	6.852	0.9588	twist CH ₂ [72]
928	2.027	1.4345	β (C–C–C) [56] + β (C–C–H) [21]
953	6.069	1.3218	β (C–C–C) [52] + β (C–C–H) [29]
973	9.737	1.4573	β (C–C–H) [49] + β (C–O–H) [26]
996	0.040	0.9142	β (C–C–H) [82]
1002	25.09	1.4928	twist whole molecule
1007	50.99	1.3629	twist whole molecule
1019	48.51	2.1748	twist (CH ₂ –OH) [78]
1047	8.840	1.8341	β (C–C–C) [48] + β (C–C–H) [31]
1052	4.587	1.5430	β (C–O–H) [58] + β (C–C–H) [29]
1081	56.82	1.2369	twist (OH) [65] + twist (CH ₂) [25]
1102	6.255	1.0193	twist (OH) [62] + twist (CH ₂) [19]
1144	112.0	1.4216	β (C–C–H) [52] + β (C–O–H) [23]
1165	45.20	1.2796	β (C–C–H) [56] + β (C–O–H) [21]

Table 4
(Continued)

B3LYP (Calculated)	IR (Int.)	Force constant (FC)	Vibrational assignments [P.E.D.]
1194	0.546	1.1719	twist (CH ₂) [69]
1222	7.949	1.2115	rock (CH ₂) [86]
1228	1.620	1.2008	rock (CH ₂) [79]
1245	5.961	1.2468	β (C–C–H) [86]
1264	5.318	1.2365	twist (CH ₂) [49] + twist (OH) [26]
1279	0.282	1.1782	twist (CH ₂) [76]
1284	3.130	1.2516	twist (CH ₂) [72]
1286	1.202	1.2153	β (C–C–H) [65]
1301	0.056	1.2757	β (C–C–H) [59]
1311	27.56	1.9547	β (C–O–H) [56] + β (C–C–H) [25]
1324	9.337	1.5340	β (C–C–H) [79]
1327	7.746	1.5805	twist (CH ₂) [89]
1341	8.838	1.6954	twist (CH ₂) [82]
1346	9.023	1.5281	β (C–C–H) [75]
1370	27.84	1.5769	β (C–C–H) [79]
1378	19.36	1.9814	β (C–C–H) [76]
1425	2.119	1.4045	β (H–C–H) [81]
1430	0.379	1.4168	S (CH ₂) [59]
1432	5.217	1.4145	rock (CH ₂) [69]
1435	3.976	1.4383	rock (CH ₂) [76]
1439	0.244	1.4591	S (CH ₂) [73]
1451	8.452	1.4838	S (CH ₂) [69]
1459	0.807	1.4799	S (CH ₂) [79]
1622	15.30	11.378	ν (C=C) [82]
1727	474.9	16.971	ν (C=O) [88]
2870	66.13	5.6472	ν (C–H) [92]
2873	26.81	5.6162	ν (C–H) [98]
2880	4.497	5.6382	ν (C–H) [93]
2885	1.502	5.6614	ν (C–H) [99]
2888	22.44	5.6732	ν (C–H) [99]
2892	36.19	5.7017	ν (C–H) [98]
2897	32.64	5.7658	ν (C–H) [90]
2911	36.40	5.9225	ν (C–H) [99]
2924	19.16	5.9700	ν (C–H) [93]
2925	18.43	5.9890	ν (C–H) [99]
2929	63.59	5.9879	ν (C–H) [96]
2945	59.84	6.1007	ν (C–H) [99]
2951	75.78	6.1246	ν (C–H) [97]
2988	3.708	6.2025	ν (C–H) [99]
3005	19.99	6.3003	ν (C–H) [98]
3057	5.478	6.5216	ν (C–H) [99]
3608	65.50	8.8561	ν (O–H) [100]
3671	18.72	9.1877	ν (O–H) [100]

Notes: ν – stretching; β – bending; S – scissoring; w – wagging; τ – torsion; F.C.: force constant.

For 10-HDA, intense bands due to O–H stretching vibrations are calculated at 3608 and 3671 cm^{-1} with PED of 100% for both and for C–H stretching vibrations, intense bands are calculated at 2870, 2929, 2945 and 2951 cm^{-1} with PED of 92, 96, 99 and 97%, respectively.

4.2.2. Spectral region 1800–1000 cm^{-1}

For 2-DA, an intense band due to C=O stretching vibration is calculated at 1722 cm^{-1} with a PED of 94% is far away matches with experimental frequency 1790 cm^{-1} and for C=C stretching vibration, intense band is calculated at 1626 cm^{-1} with PED of 96% is in good agreement with experimental one, i.e. 1625 cm^{-1} . An intense band due to scissoring of CH_2 group is calculated at 1451 cm^{-1} with a PED of 82% matches well with 1450 cm^{-1} in experimental spectrum and for (C–O–H) bending vibrations, intense band is calculated at 1119 cm^{-1} with PED of 46% is in good agreement with 1125 cm^{-1} in experimental spectrum. An band due to (C–C–C) bending vibration is calculated at 998 cm^{-1} in with a PED of 46% matches well with the 1005 cm^{-1} in the experimental spectrum.

For 10-HDA, an intense band due to C=O stretching vibration is at 1727 cm^{-1} with PED of 88% and for C=C stretching vibration, intense band is calculated at 1622 cm^{-1} with PED of 82%. An intense band due to Scissoring of CH_2 group is at 1451 cm^{-1} with PED of 69% and for (C–O–H) bending vibration; intense band is calculated at 1311 cm^{-1} with PED of 56%. Intense bands due to (C–C–H) bending vibrations are at 1165 and 1370 cm^{-1} with PED of 56 and 79% in calculated spectrum.

4.2.3. Spectral region 1000–450 cm^{-1}

As expected, the ring torsion modes along with wagging modes appear in the low frequency range. The ring torsion and wagging appear in the 1000–450 cm^{-1} frequency range. For 2-DA, an intense band due to O–H wagging vibration is calculated at 593 cm^{-1} with PED of 79% is in good agreement with 590 cm^{-1} in experimental spectrum and an intense band due to torsion of C=C–C=O is at 670 cm^{-1} with PED of 88% in calculated spectrum matches well with experimental one, i.e. 665 cm^{-1} . For 10-HDA, an intense band due to O–H wagging vibration is at 585 cm^{-1} with PED of 88% and an intense band due to torsion of C=C–C=O is at 529 cm^{-1} with PED of 78% in calculated spectrum.

4.2.4. Spectral region below 450 cm^{-1}

For 2-DA, there are some frequencies in lower region due to the torsion modes like 339, 388 and 420 cm^{-1} with PED of 69, 82 and 69% respectively and for 10-HDA, modes are 241, 307, 366 and 397 cm^{-1} having appreciable IR intensity with PED of 76, 92 and 59%, respectively. Furthermore, the study of low frequency vibrations is of great significance, because it gives information on weak intermolecular interactions, which takes place in enzyme reactions [5]. Knowledge of low frequency mode is also essential for the interpretation of the effect of electromagnetic radiation on biological systems [11]. Although no experimental FTIR spectrum is available in the present case so the whole frequency assignments including lower region has been discussed throughout the calculated spectra. The aim of this paper is to obtain direct information on lower and higher frequency vibrations of such biological contents of royal jelly.

In the absence of experimental vibrational spectra of the title compounds, the theoretically calculated spectra should provide an important path for experimentalists. The measurements were made for the gas phase.

4.3. Electronic properties

In addition to the above studies there are a number of other descriptors that may be compared for a further insight into the structural behavior of the molecules. The basic electronic parameters related

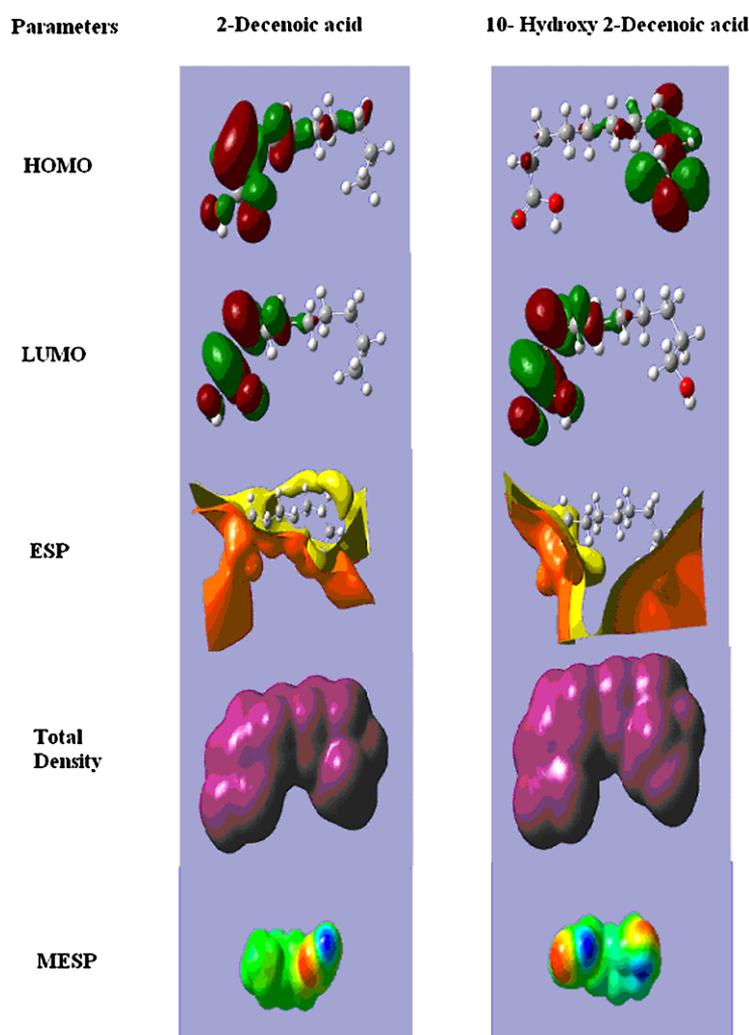


Fig. 7. Frontier orbitals and surfaces of 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

to the orbital in a molecule are the HOMO and LUMO and the difference between them, resulting in an energy gap. These orbitals not only determine the way the molecule interacts with other species, but their energy gap (frontier orbital gap) helps to characterize the chemical reactivity and kinetic stability of the molecule. The plots of the HOMO, LUMO, total electron density (TED) and electrostatic potential for both the molecules are shown in Fig. 7. For 2-DA, the HOMO is found to be concentrated over the whole atom except $\text{CH}_2\text{-CH}_3$ atoms, but the LUMO lies mainly over the left half of the molecule. This clearly indicates that the reactive part of this molecule lies over half left side at which LUMO is situated. For 10-HDA, the HOMO is found to be concentrated mainly over right half side, but the LUMO lies to the other left half of the molecule. Reactive part of the both the molecules lie in the same region. The calculated values of the frontier orbital energy gap, for 2-DA and 10-HDA are 5.84 and 0.7 eV, respectively (Table 6). The low frontier orbital gap is also associated with a high chemical reactivity and

Table 5
Atomic charges in gas phase

2-Decenoic acid atom	Charges	10-Hydroxy 2-Decenoic acid atom	Charges
C1	0.361623	C1	0.357005
C2	-0.174006	C2	-0.169351
O3	-0.349131	O3	-0.342379
O4	-0.332732	O4	-0.340696
H5	0.247990	H5	0.249770
C6	-0.060551	C6	-0.064774
C7	-0.206169	C7	-0.206234
C8	-0.218054	C8	-0.206507
C9	-0.206182	C9	-0.207801
C10	-0.209745	C10	-0.209914
C11	-0.212871	C11	-0.222981
C12	-0.220843	C12	-0.244536
C13	-0.297922	C13	0.015597
H14	0.118338	H14	0.124208
H15	0.109730	H15	0.112676
H16	0.118206	H16	0.115816
H17	0.149602	H17	0.138259
H18	0.117860	H18	0.118860
H19	0.101354	H19	0.105140
H20	0.102270	H20	0.105313
H21	0.116215	H21	0.105725
H22	0.103807	H22	0.102690
H23	0.103958	H23	0.107593
H24	0.101298	H24	0.105616
H25	0.107083	H25	0.112680
H26	0.103799	H26	0.090813
H27	0.106121	H27	0.116313
H28	0.106802	H28	0.102621
H29	0.102471	H29	0.096101
H30	0.109681	O30	-0.394869
-	-	H31	0.227245

low kinetic stability due to the hydrogen replaced by OH group and hence an increase in the polar part in case of 10-HDA [8].

MESP have been shown to correlate well with experimentally based quantities such a pK_a and other donor and acceptor values [22]. The MESP is an important factor by which we can confirm the electrostatic potential region distribution of size and shape of molecules as well as the total physiology of the molecules. We have plotted electrostatic potential contour plots of both the compounds as shown in Fig. 8. In the case of 2-DA, the electro negative region (red) is towards the outer part near the oxygen but close to the oxygen, positive region (blue) is located which shows that the lone pair of electron lies at oxygen atom. The energy equal to the shielded potential energy surface is required for any substitution reaction near the oxygen. The electronegative lines (in between -0.04 and -0.02 a.u.) form a closed contour which clearly indicates that the total flux passing in between these curves is not equal to zero.

Table 6

Lowest energy, HOMO–LUMO gap (frontier orbital energy gap) and dipole moment of 2-Decenoic acid (2-DA) and 10-Hydroxy 2-Decenoic acid (10-HDA) by (B3LYP)/6-311 G (d, p) methods

Parameters	2-Decenoic acid (2-DA)	10-Hydroxy 2-Decenoic acid (10-HDA)
Energy (in a.u.)	−542.5145	−617.7446
HOMO (in eV)	−7.37	−3.68
LUMO (in eV)	−1.53	−2.98
Frontier orbital energy gap (in eV)	5.84	0.7
Dipole moment (in Debye)	1.26	2.66

It generates a negative electric field region near the oxygen atom which opposes the electrophilic substitution. This shows that any electrophilic substitution reaction can take place by giving energy equal to the shielded potential surface. The molecule acts as a dipole in which the area near the oxygen atom acts as the negative pole (better site for nucleophilic substitution reaction) however, remaining part of the molecule is suitable for electrophilic substitution reaction. An interesting thing is that the oxygen of hydroxyl group has a positive potential. This may be due to the fact that electropositive carbon where hydroxyl group is attached attracts the electron from the oxygen which produces a positive potential over oxygen (0.8 a.u.). In the case of 10-HDA, the electronegative region is present near left and right side of oxygen in molecule and also a closed contour near oxygen of hydroxyl group on the left side. The remaining portion is electropositive. For any nucleophilic substitution reaction near oxygen (closed contour area), an amount of energy equal to shielded potential energy surface is required however remaining part of molecule is suitable for electrophilic substitution reaction. Thus it can be asserted that MESP values have been shown to be well related to biological properties [4,16,18].

4.4. Dipole moment, polarizability, hyper polarizability and thermodynamic properties

Dipole moment (μ), polarizability (α) and total first static hyperpolarizability β [15,24] are also calculated (Table 7) by using density functional theory. They can be expressed in terms of x , y , z components and are given by following Eqs (1)–(3):

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}, \quad (1)$$

$$\langle \alpha \rangle = 1/3[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}], \quad (2)$$

$$\begin{aligned} \beta_{\text{Total}} &= (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \\ &= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}. \end{aligned} \quad (3)$$

The β components of Gaussian output are reported in atomic units, where (1 a.u. = 8.3693×10^{-33} e.s.u.). For 2-DA and 10-HDA, the calculated dipole moment values are 1.27 and 2.66 Debye. Having higher dipole moment, 10-HDA can be used as better solvent. Comparison of the calculated dipole moment of 10-HDA with water shows that it is slightly higher than water (dipole moment values for water is 2.16 Debye, at the same level of calculations, i.e., B3LYP/6-311 G (d, p)).

As we see a greater contribution of α_{xx} in both the molecules which shows that molecules are elongated more towards X direction and more contracted in the Z direction. Perpendicular part contributes less part of polarizability of both molecules. β_{xxx} , β_{xyy} contribute larger part of hyperpolarizability in both the molecule. This shows that XY plane and X-axis are more optically active in this direction. It can be

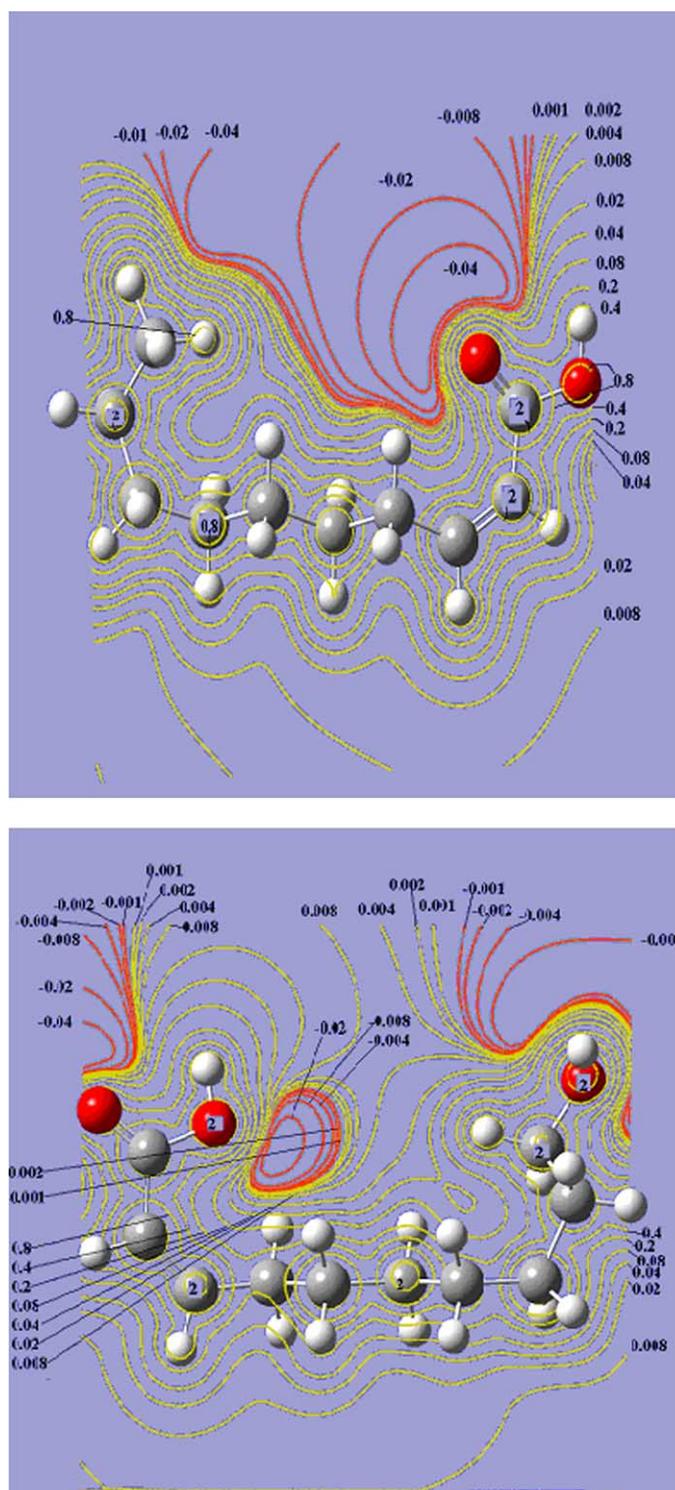


Fig. 8. Electrostatic potential contour plots of 2-Decenoic acid and 10-Hydroxy 2-Decenoic acid. (Colors are visible in the online version of the article; <http://dx.doi.org/10.3233/SPE-2012-0562>.)

Table 7
Polarizability and hyperpolarizability of 2-DA and 10-HDA

Polarizability	2-Decenoic acid (2-DA)	10-Hydroxy 2-Decenoic acid (10-HDA)
α_{xx}	155.517	153.980
α_{xy}	8.2686	8.506
α_{yy}	121.0392	128.968
α_{yz}	-7.759	-6.204
α_{zz}	92.431	96.425
α_{zx}	0.594	-5.589
α	122.9957	126.4577
Hyperpolarizability		
β_{xxx}	46.6480	-60.3527
β_{xxy}	26.2387	-64.7817
β_{xyy}	30.9454	18.7447
β_{yyy}	9.3301	25.7923
β_{zzz}	0.8472	0.0745
β_{xxz}	-1.4496	-12.0351
β_{xzz}	7.7494	-4.5578
β_{yzz}	4.2538	10.0711
β_{yyz}	-4.4458	-10.5924
β_{xyz}	-3.1285	24.7770
B_{total}	94.3118	58.9592

seen that in both the molecules polarizability and hyperpolarizability gave opposite trend, i.e. in case of 2-DA polarizability has a lower value than 10-HDA, but hyperpolarizability gave reverse result. The values of hyperpolarizability indicate a possible use of these compounds in electro-optical applications.

Standard thermodynamic functions such as free energy, constant volume heat capacity CV , and entropy S have also been calculated for both [2-Decenoic acid (2-DA) and 10-Hydroxy 2-Decenoic acid (10-HDA)] and are given in Table 2. These functions can provide helpful information for further study of the title compounds. The atomic charges of each atom in the gas phase have also been calculated as listed in Table 5.

5. Conclusion

This paper reports a comprehensive computational structural study on the constituents of Royal Jelly. The frequency assignments for 2-Decenoic acid (2-DA) and 10-Hydroxy 2-Decenoic acid (10-HDA) have been done for the first time by employing Density functional theory (DFT) with 6-311 G (d, p) as the basis set. Normal modes analysis provides detailed description of the vibrational spectra of the molecules in question. The values of hyperpolarizability indicate a possible use of these compounds in electro-optical applications. The lower value of frontier orbital energy gap and a higher dipole moment in case of 10-HDA suggests a more reactive nature as compared to 2-DA.

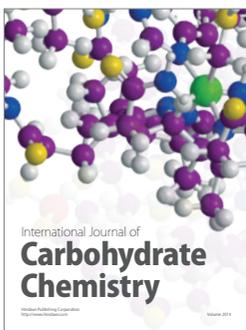
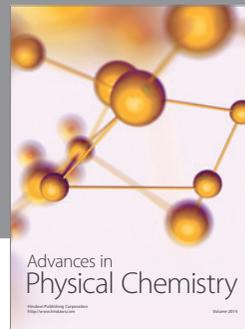
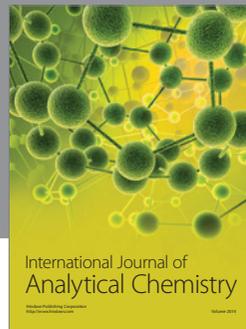
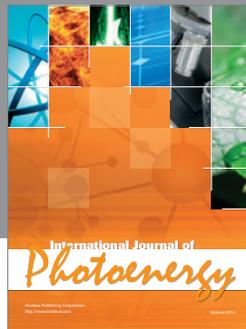
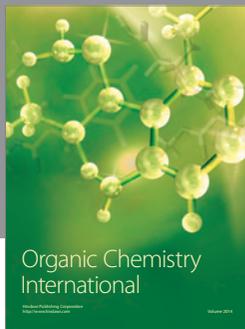
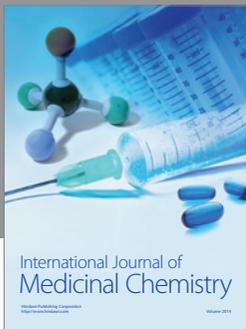
The present work might encourage the need for an extensive study by the experimentalists interested in the vibrational spectra and the structure of these compounds. The results reported in the present paper can help guide future experimental investigations on the origin of the biological activity of these molecules.

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