Frontier Molecular Orbital Simulations for Comparative Prediction of Reactivity and Stability of Stearic Acidand Oleicacid using Density Functional Theory

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ABSTRACT: The frontiermolecular orbitals (HOMO and LUMO) of stearic acid and oleic acid were simulated based on their chemical structures using density functional theory (DFT) at the B3LYP/6-31G*basis set level using Spartan '10 wavefunction software to facilitate comparative prediction of their reactivity and stability based on some theoretically calculated parameters. The total energy (absolute values),energy gap (ÄE) between the E_{HOMO} and E_{LUMO} and global hardness values of stearic acids were found to be higher than those of oleic acid. Values of global hardness and softness indicate significant differences in the chemical reactivity and stability of both molecules. Spectroscopic investigation afforded similar spectral positions with an additional infra-red vibration frequency at around 3000-3100 cm^{-1} for oleic acid. Dipole moment value of oleic acid was found to be greater than that of stearic acid suggesting higher reactivity of oleic acid than stearic acid. However, oleic acid was found to be of higher global softness than stearic acid indicating higher reactivity and lower stability.

Keywords: Chemical reactivity, DFT, frontier orbitals, oleic acid, stability, stearic acid.

INTRODUCTION

Stearic acid is a saturated fatty acid with 18-carbon with themolecular formula $CH_3(CH_2)_{16}CO_2H$. It is assigned a lipid number of C 18:0. It is one of the most common saturated fatty acids found in nature and may be prepared by treating triglycerides with water at a high pressure and temperature (above 200 °C) and distilling the resulting mixture. [1, 12]. It is chemically less reactive and is used in the production of soaps, cosmetics, detergents, lubricants, softening agents and release agents. Oleic acid is an unsaturated fatty acid with the molecular formula $C_{17}H_{33}C00H$. It contains 17 carbon atoms in the hydrophobic hydrocarbon residue with a double bond at the 9-position which introduces some level of unsaturation onto the molecule, thus suggesting relatively higher reactivity than stearic acid [2]. It occurs naturally in various animals and vegetable fats and oils. It is odourless and colourless, although commercial samples may be coloured. Classified as monounsaturated omega-9 fatty acid, it is often abbreviated with a lipid number of 18:1 cis-9. It is soluble in aqueous base to give soaps called oleates. Addition reaction can occur across the double bond in the presence of substances like iodine and hydrogen. Addition of hydrogen (reduction) leads to the formation of the saturated counterpart-stearic acid [10]. Oxidation at the double bond occurs slowly in air, a process called rancidification in foodstuffs or drying in coatings. Reduction of the carboxylic acid group yields oleyl alcohol. Oxonolysis of oleic acid is an important route to azelaic acid with nonanoic acid as the co-product [10].

The structure of stearic and oleic acids determined by X-ray crystallography[13] is shown in figure 1 below.A summary of some physical properties of stearic and oleic acids is shown in table 1 for easy distinction.
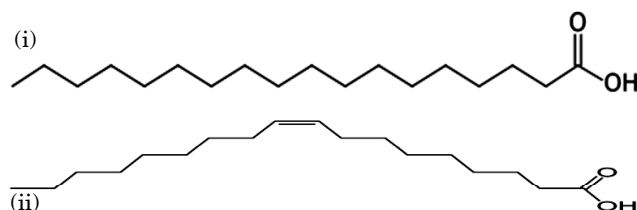

Figure 1: X-ray crystallographic molecular structure of (i) stearic acid and (ii) oleic acid

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Table 1
Summary of Some Physical Properties of Stearic Acid and Oleic Acid

Properties	Stearic acid	Oleic acid
Molecular mass (g/mol)	284.48	282.46
Appearance	White solid	Pale yellow or brownish yellow oily liquid
Density	0.847 g/L at 343 K	0.895 g/mL at 286-287 K
Melting point (K)	343	286-287
Boiling point(K)	652	633
Solubility in water (g/L at 313 K)	3.0	Insoluble, soluble in EtOH

COMPUTATIONAL METHOD

Density functional theory (DFT) is a popular quantum mechanical calculation toolfor probe into structures and reactivity of chemical molecules. Theoretically calculated parameters using Density Functional Theory at the B3LYP/6-31G*basis set level were used to investigate and compare the frontier orbitals energies (E_{HOMO} and E_{HUMO}), orbital energy gap (ΔE), total energy density, dipole moment, global softness and global hardness and hence correlated to reactivity and stability of stearic acid and oleic acid molecules. The software used was Spartan '10 wavefunction software.

RESULTS AND DISCUSSION

Effects of HOMO-LUMO Energy Gap

The study of energies of pairs of frontier orbitals, namely HOMO and LUMO energies of molecules provide reliable and quantitative data for straightforward prediction and comparative study of stabilities of molecules both from chemical and thermodynamic viewpoints [14]. It has been reported earlier that HOMO-LUMO energy gap (ΔE) is an important stability index [2]. A large energy gap implies higher stability and lower chemical reactivity, and vice versa. From the calculations made using DFT at the B3LYP/6-31G* basis set level, E_{HOMO} of stearic acid (-7.47 eV) is greater than that of oleic acid (-6.43) eV by 1.04 eV. Also, the E_{LUMO} of stearic acid (0.29 eV) is less than that of oleic acid (0.24 eV). A the name implies, the highest occupied molecular orbital (HOMO) would be of high energy, therefore, electrons would likely be interactive at the lowest

unoccupied molecular orbital (LUMO). Since the latter is greater for oleic acid than for stearic acid, thermodynamically, high reactivity would be expected to be associated with oleic acid than stearic acid in order to decrease the energy. This suggests than oleic acid would be of higher reactivity than stearic acid. In other words, a higher reactivity of oleic acid indicates lower stability. This could be further seen in their calculated amount of ΔE values: stearic acid has higher band gap energy than oleic acid. However, thermodynamically, a lower energy is representative of higher stability of molecules and low reactivity. It is worth recalling that a molecule may be thermodynamically stable but kinetically unstable. Therefore, the proposed higher stability of stearic acid may be ascribed to kinetic stability due to saturation of the hydrophobic moiety compared to the unsaturation of that of oleic acid [15]. An experimental verification would probably help to provide more explanations these discrepancies.Figure 2 shows the optimized structures of both acids while figures 3 and 4 show the HOMO and LUMO densities of both acids using DFT at the B3LYP/6-31G*basis set level with Spartan '10 software.

Figure 2(a): Optimized stearic acid structure using DFT at the B3LYP/6-31G*basis set level

Figure 2(b): Optimized oleic acid structure using DFT at the B3LYP/6-31G*basis set level

Figure 3(a): The highest occupied molecular orbital (HOMO) density of stearic acid using DFT at the B3LYP/6-31G*basis set level

Figure 3(b): The highest occupied molecular orbital (HOMO) density of oleic acid using DFT at the B3LYP/6-31G*basis set level

Figure 4(a): The Lowest unoccupied molecular orbital (LUMO) density of stearic acid using DFT at the B3LYP/6-31G*basis set level
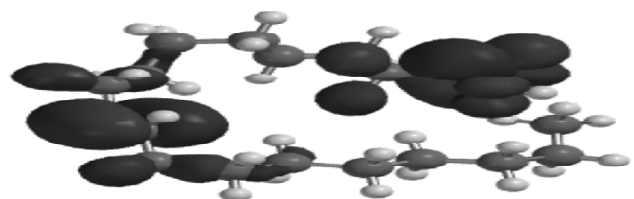

Figure 4(b): The Lowest unoccupied molecular orbital (LUMO) density of oleic acid using DFT at the B3LYP/6-31G*basis set level.

Total Energy

The total energy determines the occurrence or non-occurrence of chemical reactions and stereospecific paths in intra- and intermolecular processes [3]. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn [4] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy. This makes the total energy calculated by quantum mechanical method is also a beneficial parameter. From our study, the total energy (absolute values) calculated using DFT at the B3LYP/6-31G*basis set level for stearic acid is higher than that of oleic acid. This energy has been, for the first time, been attributed to excess kinetic energy due to C-H bond mobility in stearic acid than in oleic acid due to more saturation.A higher

electron density at carbon-9of the oleic acid could also have resulted in this energy discrepancy. However, since oleic acid undergoes addition reaction like hydrogenation and oxonolysis as earlier mentioned, its reactivity is predicted, based on results of our studies, to be kinetic in nature.

Global Hardness and Global Softness

Based on the assumptions of the HSAB principle of Pearson [5], within the framework of density functional theory, chemical reactivity and stability of a molecule may be associated with its global hardness (α) and global softness (β) calculated according to equation 1 and 2. Increase in hardness increases movement of the system towards a more stable configuration-equilibrium configuration. When a molecule moves away from its equilibrium configuration its hardness value decreases. Greater hardness therefore implies high stability and low reactivity. Global softness has an inverse relationship with hardness: soft molecules undergo changes in electron density more easily than the hard molecules and are more reactive than the hard molecules [7]. Values of global hardness and global softness calculated for stearic acid and oleic acid shows that stearic acid would be harder than oleic acid. In other words, oleic acid would be a softermolecule than stearic acid. This is in agreement with the higher reactivity and lower stability of oleic acid than stearic acid earlier proposed from our theoretical inference.

$$\alpha = \frac{\Delta E}{2} \qquad (1)$$

$$\beta = \frac{1}{\alpha} \qquad (2)$$

Dipole Moment

Another parameter that helps in the understanding of interaction between atoms in the same or different molecules is the dipole moment. It is a measure of the net molecular polarity, which is the magnitude of charge (/Q/) at the either ends of the molecular dipole time the distance between the charges (equation 3). Dipole moment increases with increase in electronegativity of atoms [8]. Chemical reactivity usually increases with increase in dipole moment. The use of dipole moment to probe chemical reactivity according to our theoretical study suggests that oleic acid (μ=1.40 Debye) is more reactive than stearic acid (μ=1.26 Debye) which agrees with the trend earlier proposed.

$$\mu = /Q/r \qquad (3)$$

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Figure 5(a): The density of stearic acid using DFT at the B3LYP/6-31G*basis set level
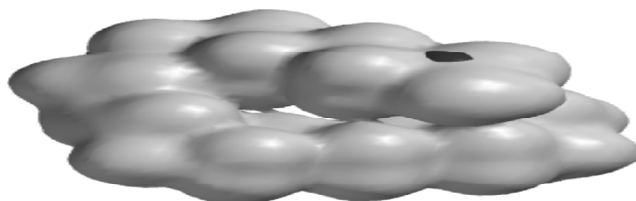

Figure 5(b): The density of oleic acid using DFT at the B3LYP/6-31G*basis set level

Tables 2
Some molecular properties of stearic acid and oleic acid calculated using DFT at the B3LYP/6-31G* basis set level.

Parameter	Stearic acid	Oleic acid
EHOMO (eV)	-7.47	-6.43
ELUMO (eV)	0.29	0.24
ΔE (eV)	7.76	6.67
Total energy	-23348.69	-23316.34
Dipole moment (Debye)	1.26	1.28
Global hardness	3.88	3.88
Global softness	0.2577	0.2577

Table 3 (a)
Mullikan charge distribution of stearic acid calculated using DFT at the B3LYP/6-31G * basis set level

ATOM	C1	O1	O2	H2	C2	H1	H4	C3	H5	H6
CHARGE	+0.579	-0.464	-0.569	+0.407	-0.354	+0.171	+0.177	-0.252	+0.154	+0.130
ATOM	C4	H3	H7	C5	H9	H10	C6	H8	H11	C7
CHARGE	-0.262	+0.122	+0.152	-0.254	+0.133	+0.132	-0.255	+0.125	+0.129	-0.260
ATOM	H12	H13	C8	H14	H15	C9	H16	H18	C10	H17
CHARGE	+0.128	+0.128	-0.253	+0.125	+0.127	-0.259	+0.135	+0.127	-0.254	+0.125
ATOM	H19	C11	H20	H22	C12	H21	H23	C13	H25	H26
CHARGE	+0.126	-0.253	+0.133	+0.127	-0.255	+0.126	+0.126	-0.260	+0.128	+0.128
ATOM	C14	H24	H27	C15	H29	H30	C16	H28	H31	C17
CHARGE	-0.254	+0.127	+0.127	-0.260	+0.126	+0.137	-0.246	+0.125	+0.125	-0.247
ATOM	H32	H34	C18	H33	H35	H36				
CHARGE	+0.130	+0.130	-0.441	+0.140	+0.141	+0.141				

Table 3 (b)
Mullikan charge distribution of oleic acid calculated using DFT at the B3LYP/6-31G * basis set level

ATOM	C1	O1	O2	H2	C2	H3	H4	C3	H1	H5
CHARGE	+0.587	-0.463	-0.572	+0.408	-0.384	+0.175	+0.182	-0.251	+0.151	+0.150
ATOM	C4	H7	H8	C5	H6	H9	C6	H10	H11	C7
CHARGE	-0.270	+0.126	+0.148	-0.258	+0.131	+0.130	+0.263	+0.132	+0.131	-0.263
ATOM	H12	H14	C8	H13	H15	C9	H16	C10	H20	C11
CHARGE	+0.133	+0.140	-0.261	+0.130	+0.127	-0.256	+0.139	+0.126	-0.259	+0.127
ATOM	H28	C15	H26	H29	C16	H31	H32	C17	H33	H34
CHARGE	+0.132	-0.254	+0.130	+0.126	-0.251	+0.125	+0.122	-0.248	+0.127	+0.127
ATOM	C18	H30	H35	H36						
CHARGE	-0.454	+0.143	+0.139	+0.158						

Table 4 (a)
Bond order of stearic acid calculated using DFT at the B3LYP/6-31G* basis set level.

BOND ORDER	C1O1	C1O2	C1C2	O1O2	O1H2	O2H2	C2H1	C2H4	C2C3	C3H5
MULLIKAN	1.866	1.069	0.968	0.065	0.037	0.760	0.921	0.920	0.993	0.931
BOND ORDER	C3H6	C3C4	C4H3	C4H7	C4C5	C5H9	C5H10	C5C6	C6H8	C6H11
MULLIKAN	0.936	1.010	0.938	0.929	1.007	0.929	0.932	1.011	0.938	0.939
BOND ORDER	C6C7	C7H12	C7H13	C7C8	C8H14	C8H15	C8C9	C9H16	C9H18	C9C10
MULLIKAN	1.014	0.942	0.938	0.995	0.939	0.942	1.012	0.930	0.938	1.005
BOND ORDER	C10H17	C10H19	C10C11	C11H20	C11H22	C11C12	C12H21	C12H23	C12C13	C13H25
MULLIKAN	0.939	0.938	1.003	0.933	0.938	1.011	0.938	0.939	1.014	0.943
BOND ORDER	C13H26	C13C14	C14H24	C14H27	C14C15	C15H29	C15H30	C15C16	C16H28	C16H31
MULLIKAN	0.939	0.989	0.939	0.943	1.011	0.938	0.932	1.007	0.939	0.933
BOND ORDER	C16C17	C17H32	C17H34	C17C18	C18H33	C18H35	C18H36			
MULLIKAN	1.011	0.942	0.943	1.016	0.953	0.952	0.952			

Table 4 (b)
Bond order of oleic acid calculated using DFT at the B3LYP/6-31G* basis set level.

BOND ORDER	C1O1	C1O2	C1C2	O1O2	O1H2	O2H2	C2H3	C2H4	C2C3	C3H1
MULLIKAN	1.856	1.056	0.965	0.066	0.037	0.758	0.919	0.915	0.993	0.936
BOND ORDER	C3H5	C3C4	C4H7	C4H8	C4C5	C5H6	C5H9	C5C6	C6H10	C6H11
MULLIKAN	0.938	0.995	0.937	0.924	1.012	0.937	0.939	1.013	0.943	0.939
BOND ORDER	C6C7	C7H12	C7H14	C7C8	C8H13	C8H15	C8C9	C9H16	C9C10	C10H20
MULLIKAN	0.987	0.945	0.941	0.978	0.931	0.936	1.004	0.927	1.930	0.924
BOND ORDER	C10C11	C11H18	C11H21	C11C12	C12H23	C12H24	C12C13	C13H22	C13H25	C13C14
MULLIKAN	1.014	0.937	0.929	0.985	0.940	0.938	1.009	0.927	0.939	1.006
BOND ORDER	C14H27	C14H28	C14C15	C15H26	C15H29	C15C16	C16H31	C16H32	C16C17	C17H33
MULLIKAN	0.939	0.935	1.005	0.935	0.939	1.010	0.941	0.934	1.008	0.942
BOND ORDER	C17H34	C17C18	C18H30	C18H35	C18H36					
MULLIKAN	0.944	1.017	0.950	0.952	0.940					

Spectroscopic Investigation

Results obtained from our theoretical calculation of electronic absorption wavelength and vibration frequencies of stearic acid and oleic acid are shown in figures 6-7. From the above figures, it may be inferred that the spectroscopic characteristics of oleic and stearic acid are similar considering the fact that they produce similar signals at their fingerprint regions. However, there is an extra and prominent peak at about 3000-3100 cm^{-1} in the infra-red spectrum of oleic acid which may be ascribed to aliphatic carbon-carbon double bond. This peak may also be used to justify the higher reactivity of oleic acid over stearic acid. The peaks at about 1700-1800 cm^{-1} may be assigned to the carbonyl present in the hydrophilic carboxylic acid ends of both molecules. This extra peak supports the higher reactivity of oleic acid relative to stearic acid. In addition, the ultraviolet spectra of the fatty acids show slight differences in their absorption wavelengths.
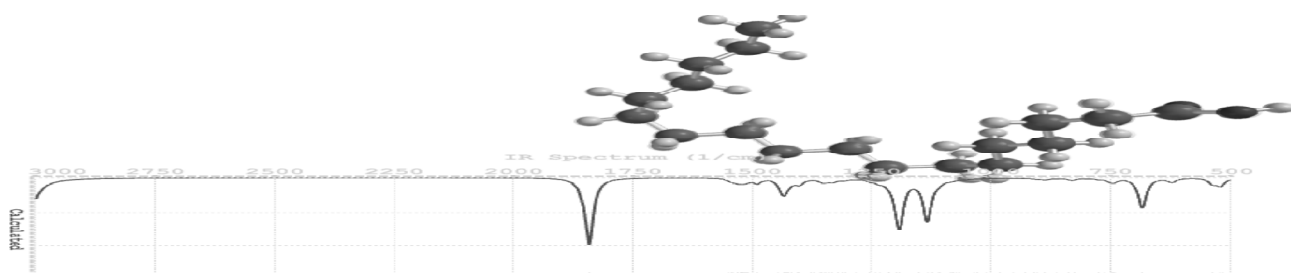

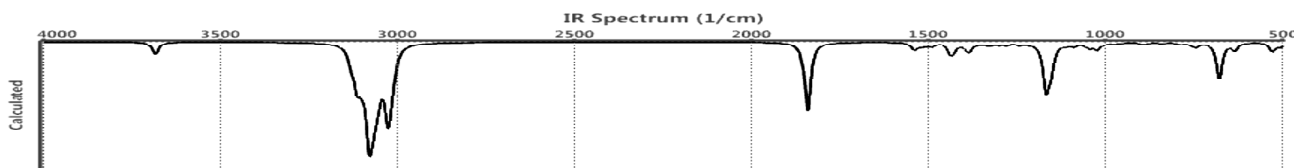**Figure 6(a):** Infra-red spectra of stearic acid using DFT at the B3LYP/6-31G* basis set level

Figure 6(b): Infra-red spectra of oleic acid using DFT at the B3LYP/6-31G* basis set level
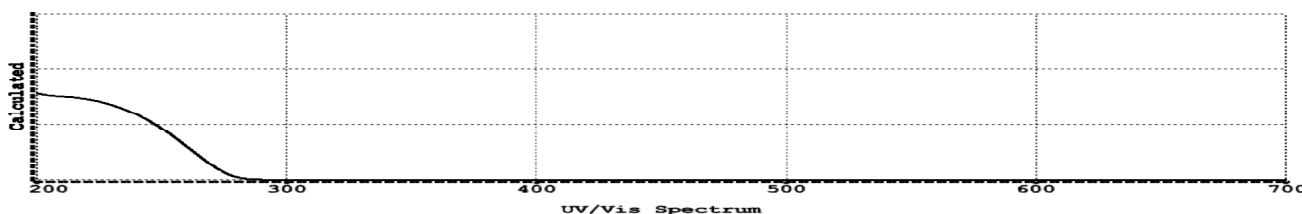

Figure 7(a): Ultra-violet spectra of stearic acid using DFT at the B3LYP/6-31G* basis set level
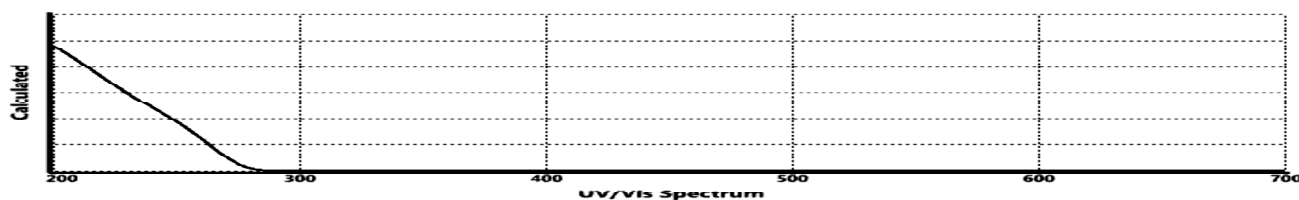

Figure 7(b): Ultra-violet spectra of palmitic acid using DFT at the B3LYP/6-31G* basis set level

CONCLUSIONS

On the basis of this study, it has been concluded that oleic acid would show higher chemical reactivity than stearic acid judged from the values of their band gap energy differences, total energies, dipole moments, global hardness and softnessvalues and spectral bands and peaks. It has also been concluded that oleic acid is a soft molecule compared to stearic acid, implying that stearic acid would be more stable than oleic acid.

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