

Computational (DFT) simulations for comparative prediction of chemical reactivity and stability of linoleic and stearic acid molecules

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Abstract: The frontier molecular orbitals (HOMO and LUMO) of stearic and linoleic acids were simulated using density functional theory (DFT) at the B3LYP/6-31G*basis set level with the use of Spartan '10 wave function software with a view to comparing their reactivity and stability based on some theoretically calculated parameters. The total energy (absolute values), energy gap between the HOMO and LUMO, E_{HOMO} , total energy and global hardness values of stearic acids were found to be higher than those of linoleic acid while values of E_{LUMO} , dipole moment and global softness calculated were higher for linoleic acid than stearic acid. Results show that linoleic acid would have higher reactivity and lower stability than stearic acid due to its relative softness. Spectroscopic investigation gives similar spectral positions with an additional infra-red vibrational frequency at around 3000 cm^{-1} for linoleic acid.

Keywords: Chemical Reactivity, DFT, Frontier Orbitals, Linoleic Acid, Stability, Stearic Acid

1. Introduction

Linoleic acid (LA) is an unsaturated omega-6 fatty acid with molecular formula $\text{C}_{18}\text{H}_{31}\text{COOH}$. It is a colorless liquid at room temperature. In physiological literature, it has a lipid number of 18:2 cis, cis-9,12. Chemically, linoleic acid is a carboxylic acid with an 18-carbon chain and two *cis* double bonds; the first double bond is located at the sixth carbon from the methyl end, hence the name omega-6. Linoleic acid belongs to one of the two families of essential fatty acids. The body cannot synthesize linoleic acid from other food components. Stearic acid is a saturated fatty acid with an 18-carbon chain and has the IUPAC name octadecanoic acid. It is a waxy solid having the chemical formula $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$. Salts or esters of stearic acid are called stearates [1]. Figure 1 shows the structure of stearic and linoleic acids while a summary of some physical properties of stearic and linoleic acids are shown in table 1 for easy distinction.

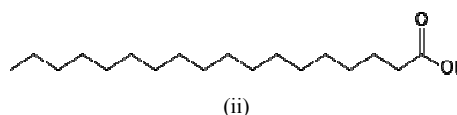
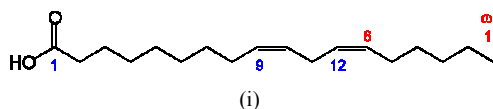


Figure 1. Molecular structures of (i) linoleic acid (ii) stearic acid.

Table 1. Summary of some physical properties of stearic acid and linoleic acid.

Properties	Stearic acid	Linoleic acid
Molecular mass (g/mol)	284.48	280.45
Appearance	White solid	Colourless oil
Density	0.847 g/L at 343 K	0.99 g/cm ³
Melting point (K)	343	261-268
Boiling point(K)	652	503
Solubility in water	3.0 g/L	0.139 mg/L

2. Computational Method

Density functional theory (DFT) is a popular quantum mechanical calculation tool for probe into structures and reactivity of chemical molecules. In this study, DFT at the B3LYP/6-31G*basis set level is used to calculate the

frontier molecular orbitals energies, optimized geometric structures, dipole moments, total energies, energy gaps, global hardness and softness, absorption and vibrational spectroscopic properties of stearic acid and linoleic acid. These parameters are calculated using Spartan '10 wavefunction software [10]. The calculated values were correlated with the reactivity and stability of the fatty acids and the results obtained were used as a basis for comparison.

3. Results and Discussion

3.1. Dipole Moment

An important 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 1). 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 linoleic acid ($\mu=1.78$ Debye) would be more reactive than stearic acid ($\mu=1.26$ Debye), which would imply that stearic acid would be more stable than linoleic acid..

$$\mu = /Q/r \quad (1)$$

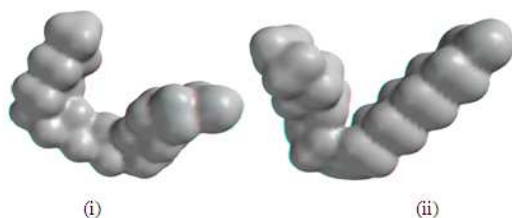


Figure 2. The density of (i) stearic acid and (ii) linoleic acid using DFT at the B3LYP/6-31G*basis set level.

3.2. Total Energy

The minimum value of the total energy functional is the ground state energy of a system [3]. 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 a beneficial parameter. The total energy determines the occurrence or non-occurrence of chemical reactions and stereospecific paths in intra- and intermolecular processes. 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. Figure 2 shows the density of stearic acid and palmitic acid. 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 (see table 2).

3.3. HOMO-LUMO Energy Gap

It is common knowledge that similar to the way electrons occupy the atomic orbitals, electrons occupy the molecular orbitals surrounding the molecule. The formations of molecular orbitals are from the linear combination of atomic orbitals or more specific, from the wave interaction of atomic orbitals. The study of energies of pairs of frontier orbitals, namely HOMO and LUMO of molecules provide reliable and quantitative data for straightforward prediction and comparative study of stabilities of molecules both from chemical and thermodynamic viewpoints. 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 linoleic acid (-6.30 eV). Also, the E_{LUMO} of stearic acid (0.29 eV) is less than that of linoleic acid (0.24 eV). This suggests that linoleic acid would be of higher reactivity than stearic acid. The higher reactivity of linoleic acid would indicate a lower stability relative to stearic acid.

It could further be seen from the calculated amount of ΔE values (table 2) that stearic acid has higher band gap energy than oleic acid. Thermodynamically, a lower energy is representative of higher stability of molecules and low reactivity. However, 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 linoleic acid. The two double bonds at positions 9 and 12 from the hydrophobic component in addition to the hydrophilic carboxylic group of linoleic acid would probably convey enhanced reactivity on the molecule. An experimental verification would probably help to provide more explanations these discrepancies.

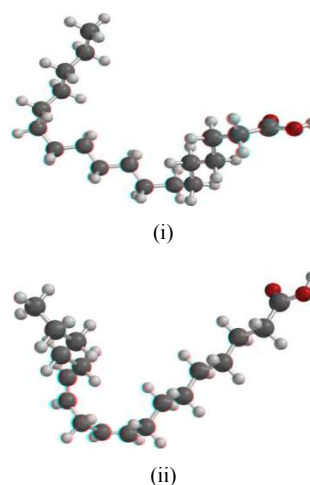


Figure 3. Optimized structure of (i) stearic acid and (ii) linoleic acid using DFT at the B3LYP/6-31G*basis set level.

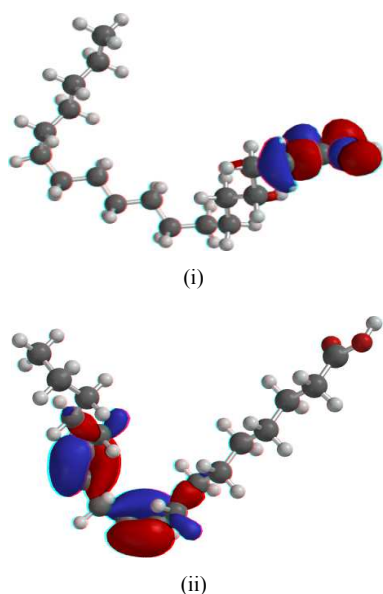


Figure 4. The highest occupied molecular orbital (HOMO) density of (i) stearic acid and (ii) linoleic acid using DFT at the B3LYP/6-31G* basis set level.

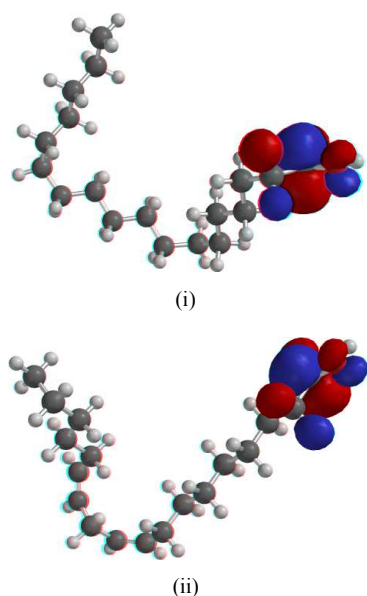


Figure 5. The Lowest unoccupied molecular orbital (LUMO) density of (i) stearic acid and (ii) linoleic acid using DFT at the B3LYP/6-31G* basis set level.

3.4. Global Hardness and Global Softness

On the basis of 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 2 and 3. 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 linoleic acid show that stearic acid would be harder than linoleic acid. In other words, linoleic acid would be a softer molecule than stearic acid. This is in agreement with the higher reactivity and lower stability earlier predicted for linoleic acid than stearic acid.

$$\alpha = \Delta E / 2 \quad (1)$$

$$\beta = 1 / \alpha \quad (2)$$

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

Parameter	Stearic acid	linoleic acid
EHOMO (eV)	-7.47	-6.30
ELUMO (eV)	0.29	0.33
ΔE (eV)	7.76	6.63
Total energy	-23348.69	-23281.75
Dipole moment (Debye)	1.26	1.78
Global hardness	3.88	3.31
Global softness	0.2577	0.3021

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 linoleic acid calculated using DFT at the B3LYP/6-31G* basis set level.

ATOM	C1	O1	O2	H2	C2	H1	H4	C3	H3	H5	C4
CHARGE	+0.577	-0.462	-0.572	+0.407	-0.355	+0.173	+0.174	-0.249	+0.149	+0.150	-0.258
ATOM	H6	H8	C5	H7	H9	C6	H10	H12	C7	H11	H13
CHARGE	+0.128	+0.128	-0.254	+0.131	+0.131	-0.254	+0.127	+0.127	-0.253	+0.130	+0.142
ATOM	C8	H14	H16	C9	H17	C10	H15	C11	H18	H19	C12
CHARGE	-0.302	+0.136	+0.135	-0.103	+0.118	-0.094	+0.119	-0.348	+0.145	+0.149	-0.100
ATOM	H21	C13	H20	C14	H22	H23	C15	H24	H26	C16	H25
CHARGE	+0.119	-0.097	+0.117	-0.304	+0.139	+0.136	-0.253	+0.135	+0.134	-0.249	+0.126
ATOM	H27	C17	H29	H30	C18	H28	H31	H32			
CHARGE	+0.126	-0.248	+0.130	+0.130	-0.433	+0.140	+0.142	+0.147			

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 linoleic 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			

3.5. Spectroscopic Investigation

Results obtained from theoretical calculation of electronic absorption wavelength and vibrational frequencies of stearic acid and linoleic acids are shown in figures 5-8. From the above figures, it may be inferred that the spectroscopic characteristics of linoleic acid and stearic acid are dissimilar. The fingerprint region of infra-red spectrum of linoleic acid showed sharp and intense peaks than stearic acid. The prominent intense peak for linoleic

acid at around 1400 cm^{-1} may be assigned to the cis C=C twin functionality present in its molecular structure. This peak may also be used to justify the higher reactivity of linoleic acid over stearic acid. The peaks at about $1700\text{--}1800\text{ cm}^{-1}$ may be assigned to the carbonyl present in the hydrophilic carboxylic acid ends of both molecules. On the other hand, the ultraviolet spectra of the fatty acids show only very slight differences in their absorption wavelengths.

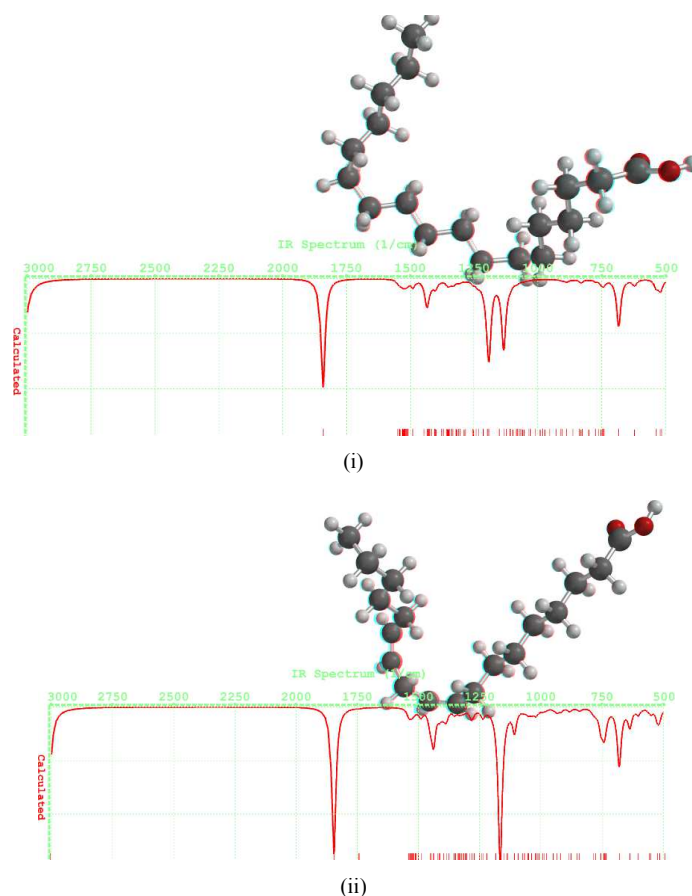


Figure 6. Infra-red spectra of (i) stearic acid and (ii) linoleic acid using DFT at the B3LYP/6-31G* basis set level.

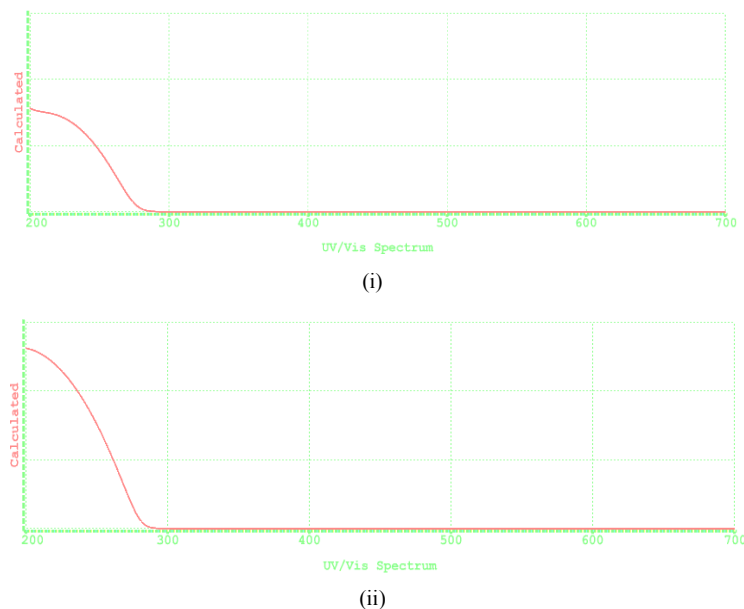


Figure 7. Ultra-violet spectra of (i) stearic acid and (ii) linoleic acid using DFT at the B3LYP/6-31G* basis set level.

4. Conclusions

On the basis of this study, it has been concluded that linoleic 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 softness values and spectral bands and peaks. It has also been concluded that linoleic acid is a soft molecule compared to stearic acid. Our study has also shown that stearic acid would be more stable than oleic acid. However, experimental verification would be needed to further ascertain adherence to these predictions.

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