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Molecular structure, chemical reactivity, stability and vibrational spectroscopic investigation of stearic and palmitic acid using density functional theory

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Abstract: *The molecular structures of stearic acid and palmitic acid were simulated using density functional theory (DFT) at the B3LYP/6-31G*basis set level with a view to compare their reactivity and stability based on some theoretically calculated parameters. The energy gap between the HOMO and LUMO of both fatty acids were found to be similar (7.76 eV) and independent of alkyl residue. The total energy (absolute values) of stearic acid was found to be higher than that of palmitic acid. Values of global hardness and softness indicate significant chemical reactivity and stability of both molecules. Spectroscopic investigation gives similar spectral positions while slight differences in dipole moment values suggests higher reactivity of palmitic acid than stearic acid.*

Keywords: *Chemical reactivity, DFT, palmitic acid, stability, stearic acid.*

I. Introduction

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 $CH_3(CH_2)_{16}CO_2H$. Salts or esters of stearic acid are called stearates [1]. Palmitic acid, or hexadecanoic acid in IUPAC nomenclature, is the most common fatty acid (saturated) found in animals, plants and microorganisms [1]. Its molecular formula is $CH_3(CH_2)_{14}CO_2H$. As its name indicates, it is a major component of the oil from palm trees (palm oil, palm kernel, and palm kernel oil), but can also be found in meats, cheeses, butter, and dairy products. Palmitate is a term for the salts and esters of palmitic acid. The palmitate anion is the observed form of palmitic acid at basic pH. Both fatty acids are commonly used in manufacture of soaps, cosmetics and release agents. Table 1 below shows a summary of physical properties of stearic and palmitic acids for easy comparison.

Table 1: Some physical properties of stearic acid and palmitic acid.

Properties	**Stearic acid**	**Palmitic acid**
Molecular mass (g/mol)	284.48	256.42
Appearance	White solid	White crystal
Density (g/L)	0.847 at 343 K	0,.835 at 335 K
Melting point (K)	343	335
Boiling point(K)	652	624-625
Solubility in water (g/L at 313 K)	3.0	Insoluble

II. Computational Method

Density functional theory (DFT) is the most popular of the quantum mechanical calculation approaches for probe into structures and reactivity of chemical molecules. In this study, DFT at the B3LYP/6-31G*basis set level is used to investigate and compare the molecular structure, chemical reactivity, stability, electronic and vibrational spectroscopic properties of stearic acid and palmitic acid.

III. Results and discussion

3.1 Effects of HOMO-LUMO energy gap

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 chemical and thermodynamic stabilities of molecules. 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, while E_{HOMO} of stearic acid (-7.47 eV) is greater than that of palmitic acid (-7.46 eV) by 0.01 eV, the E_{LUMO} of stearic acid (0.29 eV) is less than that of palmitic acid (0.30 eV) by the same amount. This suggests than stearic acid and palmitic acid are of same reactivity and stability. This can be further seen in their equal amount of ΔE (7.76) value.

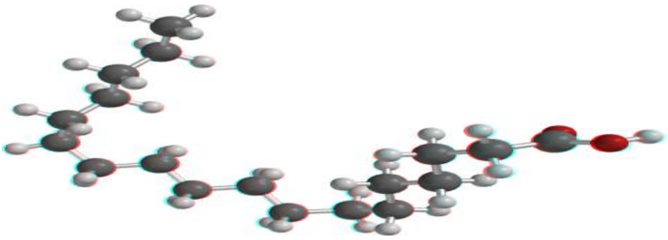

Figure 1 (a): Optimized stearic acid structure using DFT at the B3LYP/6-31G*basis set level.

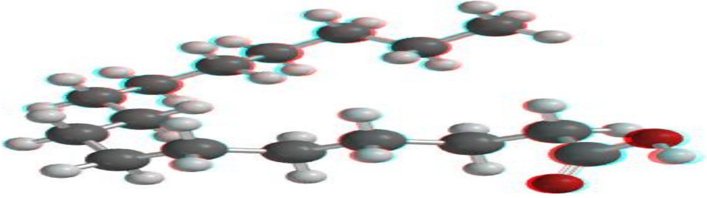

Figure 1(b): Optimized palmitic acid structure using DFT at the B3LYP/6-31G*basis set level.

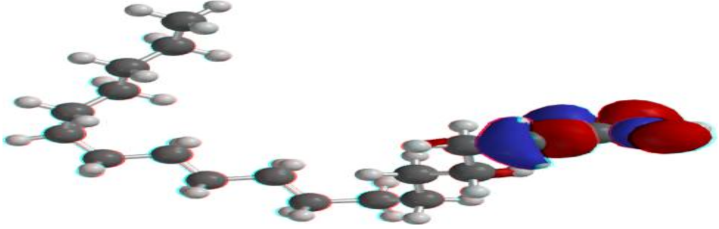

Figure 2 (a): The highest occupied molecular orbital (HOMO) density of stearic acid using DFT at the B3LYP/6-31G*basis set level.

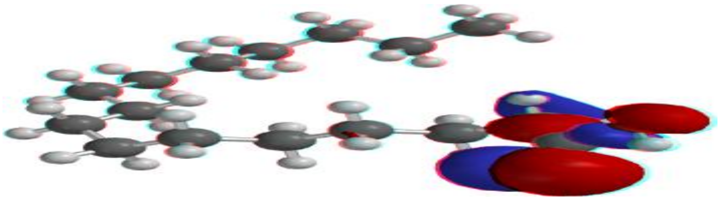

Figure 2 (b): The highest occupied molecular orbital (HOMO) density of palmitic acid using DFT at the B3LYP/6-31G*basis set level.

Figure 3 (a): The Lowest unoccupied molecular orbital (LUMO) density of stearic acid using DFT at the B3LYP/6-31G*basis set level.

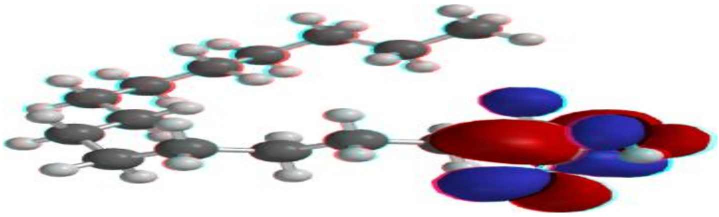

Figure 3(b): The Lowest unoccupied molecular orbital (LUMO) density of PALMITIC ACID using DFT at the B3LYP/6-31G*basis set level.

3.2 Total Energy

The total energy calculated by quantum mechanical method is also a beneficial parameter. 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. From our study, the total energy (absolute values) of stearic acid is higher than that of palmitic acid.

3.3 Global hardness and global softness

According to the HSAB principle of pearson, [5], within the framework of density functional theory, chemical reactivity and stability of a molecule is associated with its global hardness (α) and global softness (β) calculated using 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 palmitic acid are similar indicating similar reactivity.

$$\alpha = {}^{\Delta E}/_{2} \qquad (1)$$

$$\beta = {}^{1}/_{\alpha} \qquad (2)$$

3.4 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. 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 palmitic acid (μ=1.28 Debye) is more reactive than stearic acid (μ=1.26 Debye).

3.5 Spectroscopic investigation

Results obtained from theoretical calculation of electronic absorption wavelength and vibrational frequencies of stearic acid and palmitic acid are shown in figures 5-8. From the above figures, it may be inferred that the spectroscopic characteristics of palmitic and stearic acid are similar considering the fact that they produce similar peaks and exhibit similar spectral positions. Thus, it may be inferred that stearic acid and palmitic acid exhibit similar responses to an approaching electromagnetic field.

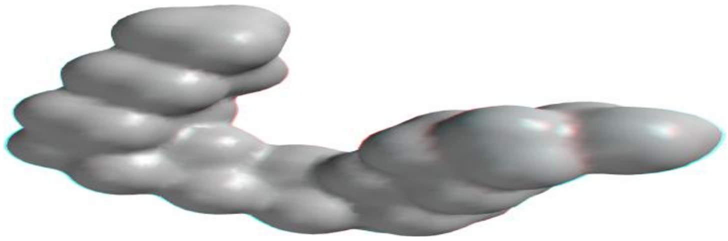

Figure 4 (a): The density of stearic acid using DFT at the B3LYP/6-31G*basis set level.

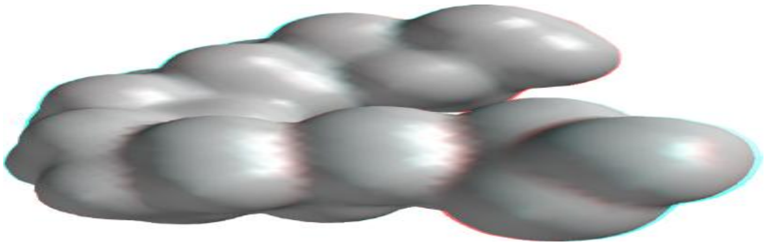

Figure 4 (b): The density of PALMITIC ACID using DFT at the B3LYP/6-31G*basis set level.

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

Parameter	Stearic acid	Palmitic acid
EHOMO (eV)	-7.47	-7.46
ELUMO (eV)	0.29	0.30
ΔE (eV)	7.76	7.76
Total energy	-23348.68936	-21209.30056
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 palmitic 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	-0.568	+0.407	-0.354	+0.170	+0.177	-0.252	+0.155	+0.131
ATOM	C4	H3	H7	C5	H9	H10	C6	H8	H11	C7
CHARGE	-0.261	+0.122	+0.151	-0.261	+0.133	+0.133	-0.255	+0.126	+0.132	-0.260
ATOM	H12	H13	C8	H14	H15	C9	H16	H18	C10	H17
CHARGE	+0.129	+0.128	-0.255	+0.126	+0.126	-0.255	+0.141	+0.125	-0.255	+0.126
ATOM	H19	C11	H21	H22	C12	H20	H24	C13	H25	H26
CHARGE	+0.127	-0.254	+0.126	+0.126	-0.256	+0.124	+0.137	-0.255	+0.127	+0.126
ATOM	C14	H23	H27	C15	H28	H30	C16	H29	H31	H32
CHARGE	-0.247	+0.125	+0.126	-0.247	+0.133	+0.129	-0.441	+0.141	+0.142	+0.139

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 palmitic 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	1.865	1.070	0.967	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	0.930	1.009	0.938	0.931	1.012	0.939	0.942
BOND ORDER	C6C7	C7H12	C7H13	C7C8	C8H14	C8H15	C8C9	C9H16	C9H18	C9C10
MULLIKAN	0.990	0.943	0.938	1.013	0.938	0.939	1.012	0.927	0.938	1.006
BOND ORDER	C10H17	C10H19	C10C11	C11H21	C11H22	C11C12	C12H20	C12H24	C12C13	C13H25
MULLIKAN	0.938	0.939	1.003	0.939	0.938	1.009	0.939	0.930	1.009	0.940
BOND ORDER	C13H26	C13C14	C14H23	C14H27	C14C15	C15H28	C15H30	C15C16	C15H29	C16H31
MULLIKAN	0.938	1.004	0.938	0.940	1.015	0.939	0.943	1.015	0.952	0.952

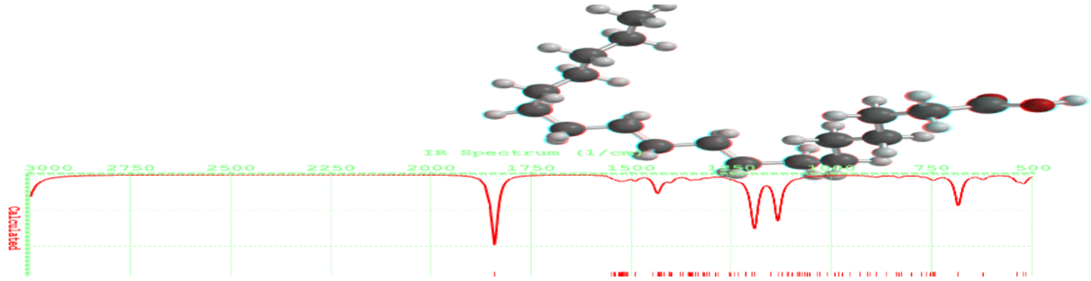

Figure 5 (a): Infra-red spectra of stearic acid using DFT at the B3LYP/6-31G* basis set level.

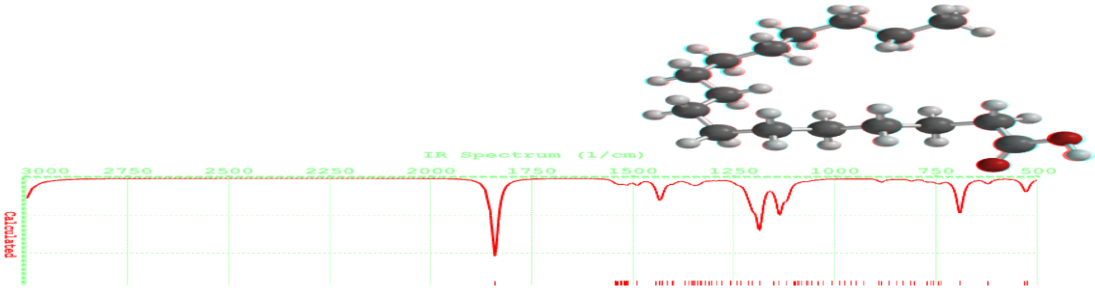

Figure 5 (b): Infra-red spectra of palmitic acid using DFT at the B3LYP/6-31G* basis set level.

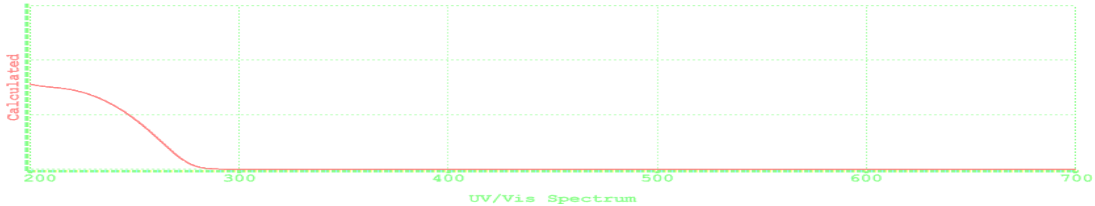

Figure 6 (a): Ultra-violet spectra of stearic acid using DFT at the B3LYP/6-31G* basis set level.

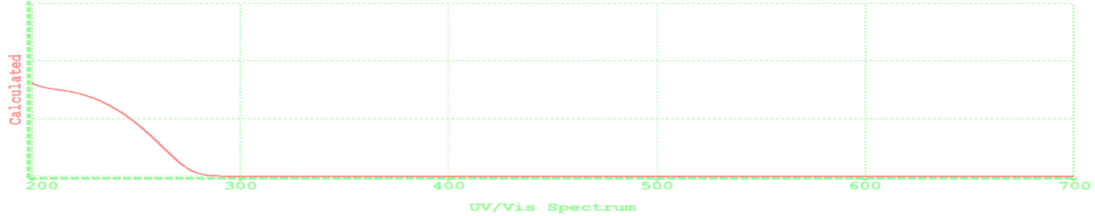

Figure 6 (b): Ultra-violet spectra of palmitic acid using DFT at the B3LYP/6-31G* basis set level

IV. Conclusions

On the basis of this study, it has been concluded that stearic acid and palmitic acid have similar spectral positions, similar global hardness and global softness hence similar chemical reactivity and stability. Energy gap of frontier orbitals of both fatty acids are also similar. However, slight differences in dipole moment suggests possibility of higher reactivity of palmitic acid than stearic acid.

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