

# DENSITY FUNCTIONAL THEORY (DFT) SIMULATION FOR COMPARATIVE DETERMINATION OF CHEMICAL REACTIVITY AND STABILITY OF CAPRIC ACID AND STEARIC ACID MOLECULES

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## ABSTRACT

The molecular structures of capric acid and stearic acid were simulated using density functional theory (DFT) at the B3LYP/6-31G\* basis set level with a view to investigating their chemical reactivity and stability based on some theoretical calculated parameters. The calculated parameters were HOMO-LUMO gap energy,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , total energy, dipole moment, global hardness, and global softness. The calculated values of total energy (absolute values), HOMO-LUMO band gap energy,  $E_{\text{HOMO}}$  and global hardness values for stearic acid were found to be higher than those of capric acid while  $E_{\text{LUMO}}$ , dipole moment, and global softness values of capric acid were higher than those of stearic acid. The results investigated show that capric acid would have higher reactivity and lower stability than stearic acid.

**KEYWORDS:** Chemical Reactivity, Stability, DFT, Capric Acid, And Stearic Acid.

## INTRODUCTION

Capric acid is a saturated fatty acid. It is also known as decanoic acid, its formula is  $\text{CH}_3(\text{CH}_2)_8\text{COOH}$  with general formula  $\text{C}_n\text{H}_{2n+1}\text{COOH}$ . The salts and esters of decanoic acid are called decanoates or "caprates".

The term capric acid is derived from the latin "caper" (goat) because the sweaty, unpleasant smell of the compound is reminiscent of goats [1].

Stearic acid also called octadecanoic acid with a

chemical formula of  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ . It is one of the many useful types of saturated fatty acids that come from many animal and vegetable fats and oils. It is waxy solid that melts at around  $70^\circ\text{C}$ . Its name comes from Greek word, stear, which means tallow. The salts and esters of stearic acid are called stearates [2]. The structure of capric acid and stearic acid were shown in figure 1 and the summary of the physical properties of capric acid and stearic acid are presented in table 1 for perusal.

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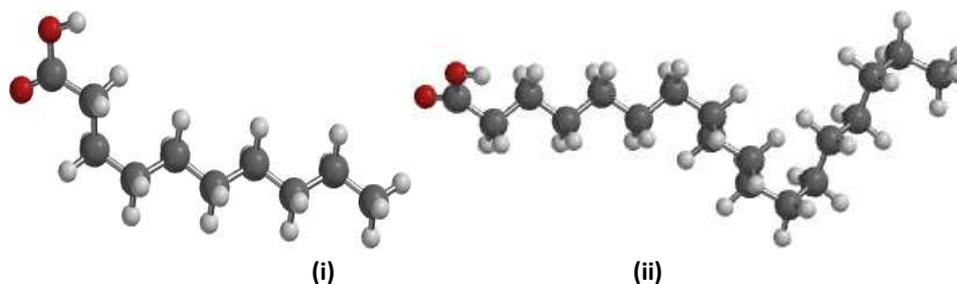


Figure 2. Optimized structure of (i) capric acid (ii) stearic acid using DFT at the B3LYP/6-31G\* basis set level

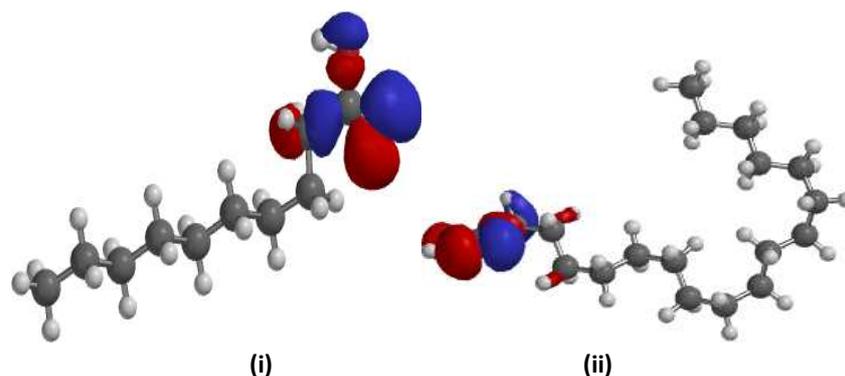


Figure 3. The highest occupied molecular orbital (HOMO) density of (i) capric acid and (ii) stearic acid using DFT at the B3LYP/6-31G\* basis set level

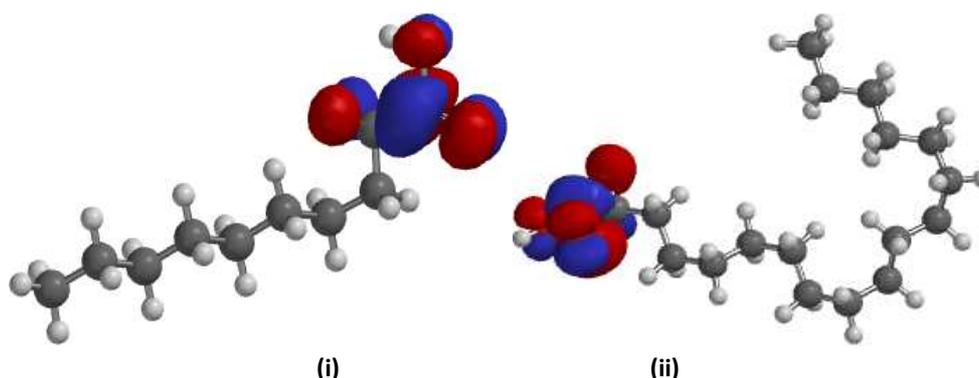


Figure 4. The lowest unoccupied molecular orbital (LUMO) density of (i) capric acid and (ii) stearic acid using at the B3LYP/6-31G- basis set level

### DIPOLE MOMENT

Dipole moment is an important parameter that helps to know the in depth understanding of interaction between atoms in the same or different molecules. It is a measure of the net molecular polarity, which is usually quantitatively expressed as the magnitude of charge ( $/Q/$ ) at the either ends of the molecular dipole time the distance between the charges.

$$\mu = \frac{Qr}{r} \quad (1)$$

Dipole moment increases with increase in electronegativity of atoms [6].

Hence, chemical reactivity usually increases with increase in dipole moment. In our theoretical study suggests that capric acid ( $\mu= 4.24$ debye) would be more chemical reactivity than stearic acid ( $\mu=1,25$ debye). This implies that stearic acid would be more stable than capric acid. The density (solid) of capric acid and stearic acid simulated using DFT at the B3LYP/6-31G\* basis set level presented in figure 5.

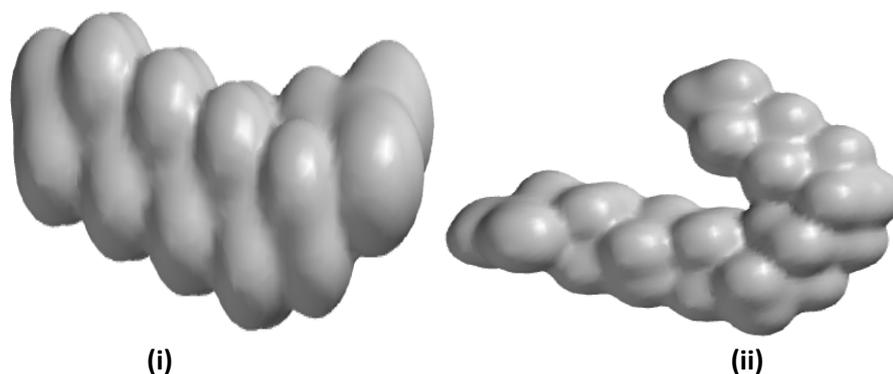


Figure 5. The density (solid) of (i) capric acid and (ii) stearic acid using DFT at the B3LYP/6-31G\* basis set level

### TOTAL ENERGY

The total energy calculated by quantum mechanical method is also an important parameter. The total energy determined the occurrence or non-occurrence of chemical reactions and stereospecific paths intra- and intermolecular processes [7]. The total energy of a system is composed of the internal potential and kinetic energy. Hohenberg and Kohn [8] 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 is 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. Our theoretical results, it may be seen that the total energy (absolute values) calculated (table 2) using DFT at the B3LYP/6-31G\* basis set level for capric acid and stearic acid. The atomic charges (Mullikens) were also calculated per atom for each of the molecules (Table 3 AND 4) as well as their bond order (Mullikens) presented (Table 5 and 6). thermodynamically, large energy implies higher reactivity and lower stability. Our results using DFT at the B3LYP/6-31G\* basis set level suggests that capric acid is more reactive than stearic acid. This implies that stearic acid is more stable relative to capric acid.

### 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 ( $\eta$ ) and global softness ( $\epsilon$ ). 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].

Chemical hardness ( $\eta$ ) measures the resistance of an atom to a charge transfer [9], it is estimated by using the equation:  $\eta = -\frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}})$ .

Chemical softness ( $\epsilon$ ) is the measure of the capacity of an atom or group of atoms to receive electrons [9], it is estimated by using the equation:  $\epsilon = -2 / (E_{\text{HOMO}} - E_{\text{LUMO}})$

Values of global hardness and global softness calculated (table 2) using DFT at the B3LYP/6-31G\* basis set level suggests that capric acid is more reactive than stearic acid. This implies that stearic acid is more stable relative to capric acid.

Table 2. Some molecular properties of Capric acid and Stearic acid calculated using DFT at the B3LYP/6-31G\* basis set level

Parameter	Capric acid	Stearic acid
ELUMO (eV)	0.34	0.3
EHOMO (eV)	-7.35	-7.46
$\Delta E$ (eV)	7.69	7.76
Total Energy (eV)	-14790.9	-23348.7
Dipole Moment (Debye)	4.24	1.25
Global Softness	3.84	3.88
Global Hardness	0.26	0.2577

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

Atom	C9	H18	H19	C10	H20	H22	C11	H21	H23	C12
Charge	-0.246	0.126	0.128	-0.253	0.125	0.128	-0.253	0.127	0.130	0.256
Atom	H24	H26	C13	H25	H27	C14	H29	H30	C15	H28
Charge	0.124	0.131	-0.263	0.126	0.137	-0.249	0.158	0.152	-0.406	0.163
Atom	H32	C16	O1	O2	H31	C1	H2	H3	C2	H1
Charge	0.165	0.607	-0.436	-0.569	0.407	-0.247	0.129	0.131	-0.441	0.141
Atom	H4	H5								
Charge	0.142	0.142								

Table 3 (b). Mulliken 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	0.578	-0.464	-0.568	0.407	-0.353	0.171	0.177	-0.254	0.154	0.136
Atom	C4	H3	H7	C5	H8	H9	C6	H10	H12	C7
Charge	-0.262	0.122	0.150	-0.259	0.134	0.132	-0.258	0.124	0.130	-0.256
Atom	H13	H14	C8	H11	H15	C9	H16	H17	C10	H18
Charge	0.127	0.134	-0.258	0.125	0.133	-0.260	0.128	0.128	-0.254	0.127
Atom	H19	C11	H20	H22	C12	H21	H23	C13	H25	H26
Charge	0.127	-0.128	0.148	0.127	-0.254	0.126	0.127	-0.260	0.128	0.127
Atom	C14	H24	H27	C15	H29	H30	C16	H28	H31	C17
Charge	-0.255	0.126	0.126	-0.254	0.127	0.134	-0.246	0.126	0.126	-0.247
Atom	H33	H34	C18	H32	H35	H36				
Charge	0.130	0.128	-0.441	0.141	0.141	0.140				

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

Bond order	C9H18	C9H19	C9H10	C9C10	C10H22	C10C11	C11H21	C11H21	C11H23	C11C12
Mulliken	0.939	0.939	1.008	1.01	0.939	0.939	1.006	0.939	0.938	1.006
Bond order	C12H24	C12H26	C12C13	C13H25	C13H27	C13C14	C14H29	C14H30	C14C15	C15H28
Mulliken	0.937	0.938	1.005	0.938	0.939	0.993	0.936	0.937	1	0.92
Bond order	C15H32	C15C16	C16O1	C16O2	O1O2	O2H31	C1H2	C1H3	C1C2	C2H1
Mulliken	0.917	0.95	1.922	1.037	0.07	0.769	0.943	0.942	1.016	0.952
Bond order	C2H4	C2H5								
Mulliken	0.952	0.952								

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

<b>Bond order</b>	C1O1	C1O2	C1C2	O1O2	O1H2	O2H2	C2H1	C2H4	C2C3	C3H5	C3H6
Mulliken	1.865	1.069	0.939	0,065	0.037	0.760	0.921	0.920	0.993	0.931	0.932
<b>Bond order</b>	C3C4	C4H3	C4H1	C4C5	C5H8	C5H9	C5V6	C6H1	C6H1	C6C7	C7H1
Mulliken	1.013	0.937	0.932	1.007	0.935	0.937	1.013	0.938	0.937	0.998	0.937
<b>Bond order</b>	C7H1	C7C8	C8H1	C8H1	C8C9	C9H1	C9H1	C9C1	C10H	C10H	C10C
Mulliken	0.933	1.016	0.938	0.934	1.014	0.943	0.938	0.990	0.939	0.943	1.010
<b>Bond order</b>	C11H	C11H	C11C	C12H	C12H	C12C	C13H	C13H	C13C	C14H	C14H
Mulliken	0.925	0.938	1.011	0.937	0.942	0.992	0.943	0.938	1.014	0.938	0.939
<b>Bond order</b>	C14C	C15H	C15H	C15C	C16H	C16H	C16C	C17H	C17H	C17C	C18H
Mulliken	1.011	0.938	0.932	1.005	0.939	0.939	1.011	0.943	0.942	1.015	0.953
<b>Bond order</b>	C18H	C18H									
Mulliken	0.952	0.953									

### SPECTROSCOPIC INVESTIGATION

Results obtained from theoretical calculation at DFT at the B3LYP/6-31G\* basis set level, of

electronic absorption wavelength and vibrational frequencies of capric acid and Stearic acid are shown in figures 4-7.

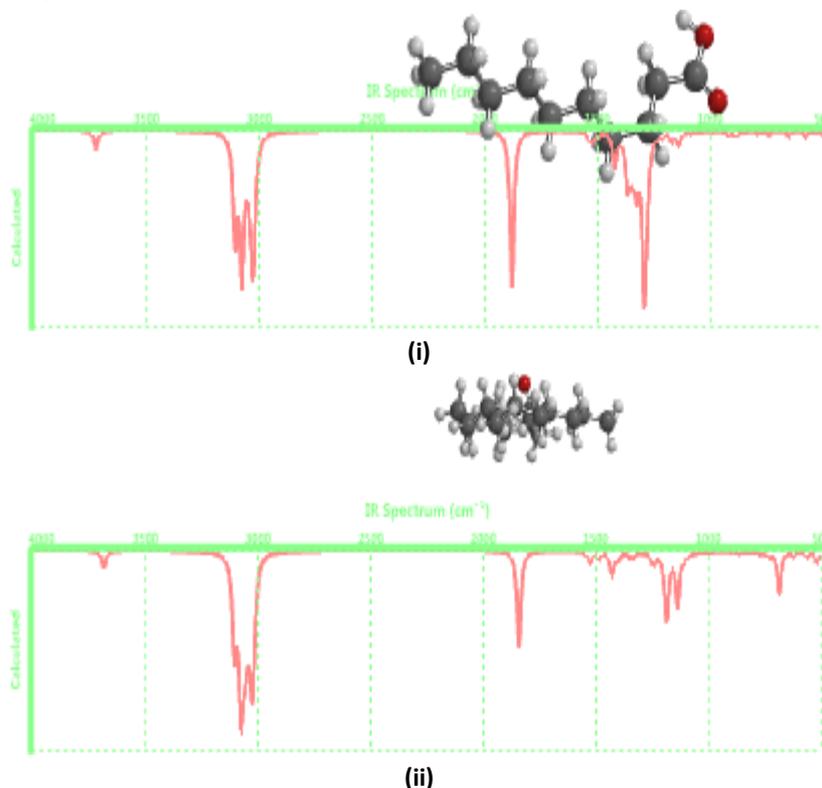


Figure 6. Infra-red spectra of (i) capric acid and (ii) stearic acid using DFT at the B3LYP/6-31G\* basis set level

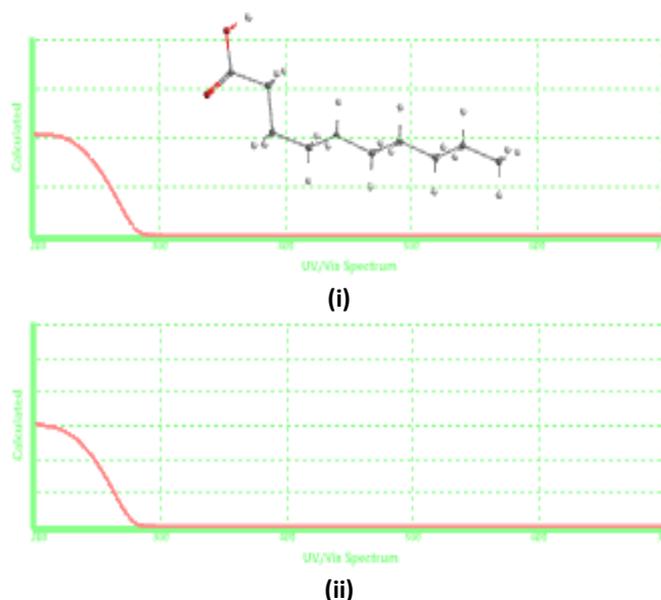


Figure 7. Ultra-violet spectra of (i) capric acid and (ii) stearic acid using DFT at the B3LYP/6-31G\* basis set level

## CONCLUSION

In this study, it has been concluded that the capric acid would show higher chemical reactivity than stearic acid judged from the values of their band gap energy differences, total energies, global hardness, global softness and dipole moments. Our study has also shown that stearic acid would be more stable than capric acid. However experimental verification would be needed to further ascertain adherence to this predictions.

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