SYNTHESIS OF NEW QUATERNARY AMMONIUM SALTS BASED ON MONOCHLOROACETIC ACID ESTERS

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ABSTRACT

In this research, quaternary ammonium salts based on pyridine, 4-butylmorpholine with chloroacetic acid esters: nonyl 2-chloroacetate, benzyl 2-chloroacetate and pentan-2-yl 2-chloroacetate in the presence of ethyl acetate, acetone and ethyl alcohol solvents were synthesized, and then the modified synthesis methodology was first reported. The molecular structures of these salts were confirmed by IR and ¹H NMR spectroscopic techniques. It was found that the ethanol is productively a good solvent for the syntheses of new quaternary ammonium salts with over than 91% yield. The values of theoretical molecular descriptors and thermodynamic parameters of new synthesized quaternary ammonium salts were measured by DFT method. The obtained results indicate that the energy distinctions between the LUMO and HOMO of these salts are less than 0.3 eV, suggesting that new synthesized quaternary ammonium salt molecules are less stable and more reactive. The heat capacity and entropy of these organic compounds could be ranged as: (103)1 > (85)3 > (77)4 > (61)2 > (59)6 > (56)5, and it could be deduced that I was a higher heat capacity and more entropy molecule than the others.

KEYWORDS: Quaternary Ammonium Salts, N-Butylmorpholine, Pyridine, Esters & Molecular Descriptors

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1. INTRODUCTION

In modern times, in the chemical industry, the synthesis of new types of quaternary ammonium salts is key of the more important aspects because; they are used as valuable surfactants, herbicides, disinfectants, deodorants, antistatic agents, dispersants, demulsifiers, softeners and catalysts [1-4].

Quaternary ammonium salts can be synthesized from tertiary amines and chloroacetic acid esters. They are good water-soluble organic chemicals with many biological properties. Nitrogen atoms in the quaternary ammonium salts make them more water-soluble due to the presence of polarized centers. Thus, dipoles present in these salts make them more water-soluble. Another important aspect of the quaternary ammonium salts is that they have several biological active centers, which make the molecule have antimicrobial and anti-bactericidal properties. Therefore, the syntheses of quaternary ammonium salts are important to creating new biologically active drugs. However, herein quaternary ammonium salts (Breasted acidic ionic liquids) were synthesized from imidazole, pyridine, and benzyl chloride, which were used as effective catalysts for the syntheses of carboxylic esters [5-8].

In this research work, the synthesis of new quaternary ammonium salts based on tertiary amines and chloroacetic acid esters is reported. The synthesis methodology of the new organic compounds are based on pyridine, 4-butylmorpholine with chloroacetic acid esters: nonyl 2-chloroacetate, benzyl 2-chloroacetate and pentan-2-yl 2-chloroacetate in the presence of ethyl acetate, acetone, and ethyl alcohol solvents; these synthesized salts structure was proven by IR and ^1H NMR spectroscopic methods; FMO analyses measured the molecular descriptors and thermodynamic parameters of synthesized salts. These new quaternary ammonium salts and their derivatives have a wide range of chemical, physicochemical, pharmaceutical, antimicrobial, emulsifying, anti-corrosion, and anti-bactericidal properties. Besides, they may be used as cleaning materials, paints, emulsifiers, and moisturizers [9-12].

In addition to this, surfactants based on quaternary ammonium salts are used in the gas and oil industry as anti-corrosion inhibitors. Quaternary ammonium salts can influence the cathodic and anodic reactions on the metal surface and thus reduce all corrosion processes in a corrosive environment. Because nitrogen atoms in these organic compounds cover and neutralize the metal surface, to form a thin protective layer[13-23].

2. MATERIALS AND METHODS

2.1 Structural Analysis Method

The IR and ^1H NMR were applied to confirm the structures of the studied organic molecules. ^1H NMR experiments were conducted using a Varian Unity 400 (+) JNM-4H-100 instrument. IR spectroscopic analysis was performed on SPECORD-75 or Avator 360 spectrometers.

2.2 Computational Methods

The synthesized organic compounds were theoretically investigated using the modern quantum calculation method of DFT. In modern quantum calculation analysis, DFT is suitable for large organic molecules. The B3LYP method is used in DFT calculations of synthesized quaternary ammonium salts because the quaternary ammonium salts are large molecules and require large integral equations. The basis sets of 6-311G (d,p) were utilized in DFT calculations of the synthesized quaternary ammonium salts. Theoretically, thermodynamic parameters were measured at 298.150 K temperature [24-27].

3. EXPERIMENTAL PART

3.1 Synthesis of 4-butyl-4-(2-(nonyloxy)-2-oxoethyl) morpholin-4-ium chloride (1)

5.72 ml (4.29 g, 0.03 mol.) of 4-butylmorpholine was mixed with 6.125 ml (6.615 g, 0.03 mol.) of nonyl 2-chloroacetate in the presence of 10 ml ethyl alcohol solvent. The reaction yield was 91%. $R_f=0.52$ (benzene:acetone 2:1 ratio), $\text{mp}=217\text{ }^\circ\text{C}$, IR-spectra: $\nu_{(\text{R})\text{N}^+}=2440\text{ cm}^{-1}$, $\nu_{\text{C-O-C}}=1045\text{ cm}^{-1}$, $\nu_{\text{O-CH}_3}=1630\text{ cm}^{-1}$, ^1H NMR-spectrum: 1,98(s, C-CH₃), 3,98-

3,86 (t, CH₂-CH₂-N⁺), 4,73-4,75 (t, O-CH₂-CH₂), 2((-CH₂)₈CH₂)₂, 4,17(4H, t, J=6.9Hz, 1.48(s 6H 2CH₃).

3.2 Synthesis of 4-(2-(benzyloxy)-2-oxoethyl)-4-butylmorpholin-4-ium chloride

(2)

5.72 ml (4.29 g, 0.03 mol.) of 4-butylmorpholine was mixed with 5 ml (5.535 g, 0.03 mol.) of benzyl 2-chloroacetate in the presence of 10 ml ethyl alcohol solvent. The reaction yield was 92 %. $R_f=0.55$ (benzene : acetone 2:1 ratio), mp=225 °C, IR-spectra: $\nu_{\text{N}^+}=2442\text{ cm}^{-1}$, $\nu_{\text{C-O-C}}=1336\text{ cm}^{-1}$, $\nu_{\text{C}_6\text{H}_5}=1452\text{ cm}^{-1}$, ^1H NMR-spectrum: 1.39 (s, 4H, CH₃), 2.10 (br s, 4H(CH₂)₂), 3.56 (br s, 2H N-CH₂), 3.88 (br s, 2H N-CH₂), 4.77 (s 2H Ar CH₂), 5.26 (d J=7.0 Hz, 1H, 5H), 7.29-7.35 (m 4H, ArH), 7.95 (d J=7.0Hz, 1H, 6H).

3.3 Synthesis of 4-butyl-4-(2-oxo-2-(pentan-2-yloxy)ethyl)morpholin-4-ium chloride

(3)

5.72 ml (4.29 g, 0.03 mol.) of 4-butylmorpholine was mixed with 5 ml (5.535 g, 0.03 mol.) of 1-pentan-2-yl 2-chloroacetate in the presence of 10 ml ethyl alcohol solvent. The reaction yield was 92 %. $R_f=0.57$ (benzene : acetone 2:1 ratio), mp=227 °C, IR-spectra: $\nu_{\text{C-O-C}}=1050\text{ cm}^{-1}$, $\nu_{\text{C=O}}=1740\text{ cm}^{-1}$, $\nu_{(\text{R})\text{N}^+}=2450\text{ cm}^{-1}$, ^1H NMR-spectrum: 1.22 (s, 4H, CH₃), 1.92-1.98 (m, 4H (CH₂)₂), 2.95 (s, 2H, 3H), 3.53-3.56 (m, 2H N-CH₂), 3.66-3.70 (m, 2H N-CH₂), 5.28 (d J=7.6 Hz 1H, 5H), 7.36 (dd, J=8.4, 1.8 Hz, 1H, 3CH₂).

3.4 Synthesis of 1-(2-(nonyloxy)-2-oxoethyl) pyridin-1-ium chloride

(4)

2.4 ml (2.37 g, 0.03mol.) of pyridine was mixed with 6.125 ml (6.615 g, 0.03mol.) of nonyl 2-chloroacetate in the presence of 10 ml ethyl alcohol solvent. The final product was dried in a desiccator for one day. The reaction yield was 92 %. $R_f=0.55$ (benzene : acetone 2:1 ratio), $mp=233^{\circ}\text{C}$, IR-spectra: $\nu_{(\text{R})4\text{N}^+}=2365$, $\nu_{\text{C}_6\text{H}_5}=1358$, $\nu_{\text{C-O-C}}=1380\text{ cm}^{-1}$, ^1H NMR-spectrum: 4.83-4.93 (4H m, O-CH₂), 0.86[6H, t, $J=5.7\text{ Hz}$, 2(CH₃)], 1.25-1.40 (18H m), 1.66-1.79 (4H m, O-CH₂-CH₂).

3.5 Synthesis of 1-(2-(benzyloxy)-2-oxoethyl) pyridin-1-ium chloride

(5)

4 ml (3.95 g, 0.05 mol.) of pyridine was mixed with 8.3 ml (9.225 g, 0.05 mol.) of benzyl 2-chloroacetate in the presence of 15 ml ethyl alcohol solvent. The final product was dried in a desiccator for 1 day. $R_f=0.63$ (benzene : acetone 2:1 ratio), $mp=218^{\circ}\text{C}$, IR-spectra: $\nu_{(\text{R})3\text{N}^+}=2445\text{ cm}^{-1}$, $\nu_{\text{C=O}}=1730\text{ cm}^{-1}$, $\nu_{\text{C-O-C}}=1080\text{ cm}^{-1}$, ^1H NMR-spectrum: 1.22 (s, 6H, 2CH₃), 1.93-1.96 (m, 4H, (CH₂)₂), 3.51-3.54 (m, 2H, N-CH₂), 4.76 (s, 2H, Ar-CH₂), 5.25 (d, $J=7.0\text{ Hz}$, 1H, 5H), 7.20-7.24 (m, 2H, Ar-H), 7.38-7.42 (m, 2H, ArH), 7.82(d, $J=7.0\text{ Hz}$, 1H, 6H).

3.6 Synthesis of 1-(2-oxo-2-(pentan-2-yloxy) ethyl)pyridin-1-ium chloride

(6)

4 ml (3.95 g, 0.05mol.) of pyridine was mixed with 7.45 ml (8.225 g, 0.05mol.) of pentan-2-yl 2-chloroacetate in the presence of 15 ml ethyl alcohol solvent. The final product was dried in a desiccator for 1 day. $R_f=0.55$ (benzene : acetone 2:1 ratio), mp=220°C, IR-spectra: $\nu_{C-O-C}=1120\text{ cm}^{-1}$, $\nu_{C=O}=1640\text{ cm}^{-1}$, $\nu_{(R)_4N^+}=2380\text{ cm}^{-1}$, ^1H NMR-spectrum: 1.27 (s, 5H, CH_3), 1.94-1.99 (m, 4H, $(\text{CH}_2)_2$), 3.03 (s, 2H, 3H), 3.55(brt, $J=6.2\text{ Hz}$, 2H, N-CH_2), 3.70(br t, $J=6.0\text{ Hz}$, 2H N-CH_2).

4. RESULTS AND DISCUSSIONS

4.1 Syntheses Methodology

In this study, new types of quaternary ammonium salts were synthesized based on pyridine and 4-butylmorpholine along with chloroacetic acid esters, i.e., nonyl 2-chloroacetate, benzyl 2-chloroacetate, and pentan-2-yl 2-chloroacetate.

At the first step of syntheses, chloroacetic acid esters, i.e., nonyl 2-chloroacetate, benzyl 2-chloroacetate, and pentan-2-yl 2-chloroacetate were synthesized by the following reaction scheme:

Where R= C_9H_{19} -, i - C_5H_{11} -, $\text{C}_6\text{H}_5\text{CH}_2$ -.

In this reaction scheme, chloroacetic acid was reacted with nonyl alcohol, benzyl alcohol and isopentyl alcohol in the concentrated sulfuric acid (H_2SO_4) medium. H_2SO_4 is an effective catalyst in this reaction. In the final step, the reaction products of nonyl 2-chloroacetate, benzyl 2-chloroacetate, and pentan-2-yl 2-chloroacetate were formed. The reaction conditions are given in table 1. Concentrated sulfuric acid was used as the acid catalyst. The dependence of reaction productivity on the molar ratio of chloroacetic acid and alcohol was researched, and the observed data are depicted in table 1. The reaction between chloroacetic acid and both alcohols (i.e., nonyl alcohol and isopentyl alcohol) is over 75% productive at a 1:2 molar ratio. However, it can be seen from table 1 that the reaction yield is lower in the case of benzyl alcohol.

Table 1: Dependence of Reaction Productivity on the Molar Ratio of Chloroacetic Acid and Alcohols

Alcohol	The Molar Ratio Chloroacetic Acid:Alcohol	Reaction Yield (%)
Nonyl alcohol	1:1	65
	1:2	76
Benzyl alcohol	1:1	55
	1:2	58
Isopentyl alcohol	1:1	74
	1:2	78

It is clear from Table 1 that the reaction yield is more in the 1:2 molar ratio may be because many alcohol molecules increase the number of collisions in the esterification reaction. The reaction of nonyl alcohol and isopentyl alcohol with chloroacetic acid was more productive, relatively 76%, and 78%. Because nonyl and isopentyl radicals have positive induction effects. In contrast, the benzyl alcohol reaction with chloroacetic acid is less productive, 58 %, because benzyl radicals have negative inductive and mesomeric effects, which can decrease oxygen electron affinity.

The next part of this research is the synthesis of new quaternary ammonium salts based on pyridine. The chloroacetic

acid esters, i.e., nonyl 2-chloroacetate, benzyl 2-chloroacetate, and pentan-2-yl 2-chloroacetate reacted with pyridine and 4-butylmorpholine. All reactions were carried out in ethyl acetate, acetone, and ethyl alcohol solvents at reflux temperature.

Pyridine reacted with chloroacetic acid esters: nonyl 2-chloroacetate, benzyl 2-chloroacetate and pentan-2-yl 2-chloroacetate related to the following reaction scheme:

Where $\text{R} = \text{C}_9\text{H}_{19}-$, $i\text{-C}_5\text{H}_{11}-$, $\text{C}_6\text{H}_5\text{CH}_2-$.

To conduct the above reaction, the first pyridine was mixed with chloroacetic acid esters in a solvent, and then this mixture heated for 3 hours. Finally, the yellow light solution formed, and then this solution was recrystallized in ethanol, and white crystals formed. The reaction conditions are illustrated in Table 2.

The following part of the investigation is the synthesis of new quaternary ammonium salts based on 4-butylmorpholine. First, morpholine was alkylated with butyl bromide, and then 4-butylmorpholine was formed. The reaction was done related to the following scheme:

Morpholine was added to butyl bromide and heated at 120°C in the presence of dimethyl formamide. When a solid mass was formed, it was cooled, and 20% NaOH was added. Because NaOH can react with morpholine hydrobromide in the final solution. Finally, the solid 4-butylmorpholine was filtered through a filtration funnel. The reaction yield was 54%. The reaction conditions are illustrated in table 2.

Second, 4-butylmorpholine was reacted with chloroacetic acid esters related to the following reaction scheme:

where R – C₉H₁₉-, C₅H₁₁-, C₆H₅CH₂-.

Table 2: Reaction Conditions of Pyridine with Chloroacetic Acid Esters in Different Solvents

N ^o	Tertiary Amine	Chloroacetic Acid Esters	Solvents	Reaction Time (hour)	Temperature	Yield, %
1	Pyridine	Nonyl 2-chloroacetate	ethyl acetate	3	Reflux	61
			acetone	3	Reflux	58
			ethyl alcohol	3	Reflux	91
2		Benzyl 2-chloroacetate	ethyl acetate	3	Reflux	65
			acetone	3	Reflux	62
			ethyl alcohol	3	Reflux	93
3		Pentan-2-yl 2-chloroacetate	ethyl acetate	3	Reflux	61
			acetone	3	Reflux	58
			ethyl alcohol	3	Reflux	92

Table 3: Reaction Conditions of 4-Butylmorpholine with Chloroacetic Acid Esters in Different Solvents

N ^o	Tertiary Amine	Chloroacetic Acid Esters	Solvents	Reaction Time (Hour)	Temperature	Yield, %
4	4-Butyl-morpholine	Nonyl 2-chloroacetate	ethyl acetate	3	Reflux	52
			acetone	3	Reflux	56
			ethyl alcohol	3	Reflux	91
5		Benzyl 2-chloroacetate	ethyl acetate	3	Reflux	52
			acetone	3	Reflux	54
			ethyl alcohol	3	Reflux	92
6		Pentan-2-yl 2-chloroacetate	ethyl acetate	3	Reflux	54
			acetone	3	Reflux	52
			ethyl alcohol	3	Reflux	91

To conduct the above reaction, first, 4-butylmorpholine was mixed with chloroacetic acid esters in a solvent and refluxed for 3 hours. Finally, the light yellow solution formed was recrystallized in ethanol to obtain white crystals.

Tables 2 and 3 describe that the reaction of pyridine with chloroacetic acid esters was more productive in ethyl alcohol solvent than in ethyl acetate and acetone for several reasons: first, ethyl alcohol solvent is more polar, which easily breaks Cl-CH₂ bonds; second, ethyl acetate and acetone are less polar; third, the reaction product is a polar molecule that can

easily be dissolved in a more polar solvent.

4.2 Frontier Molecular Orbital Analyses

In this research, frontier molecular orbital (FMO) tests were conducted using DFT. The FMO analysis indicates that the global reactivity properties of studied organic compounds, for example, the chemical softness, global electrophilicity index, chemical hardness, electronic chemical potential, and electronegativity of the synthesized researched chemical compounds. The obtained results are presented in Tables 4-10. The optimized molecular HOMO and LUMO are displayed in figures 1-12.

In the FMO theory, the LUMO and HOMO energies are equal to the electronic affinity and ionization potential, respectively. It was shown from Tables 4-9, the electronic affinity of the synthesized quaternary ammonium salts was ranged correspondingly: **2** > **6** > **5** > **1** > **3** > **4**, meaning that **2** and **6** quaternary ammonium salts are more electronic affinity molecules than others. Because the quaternary nitrogen atoms in **2** and **6** molecules are linked with more electronic affinity functional groups, such as $-\text{COOH}$ and $-\text{C}_6\text{H}_5$. These functional groups make molecules more reactive.

It is clear from the obtained results that the ionization potential of the synthesized quaternary ammonium salts ranged, respectively; **2** > **1** > **3** > **4** > **6** > **5**, suggesting that **2** and **1** quaternary ammonium salts are more electronic affinity molecules than the other. The reason is that the quaternary nitrogen atoms in **2** and **1** molecules are linked with more ionization radicals like $^*\text{C}_4\text{H}_9$, $^*\text{C}_6\text{H}_5$. These radicals make the molecule more ionized.

In the FMO theory, the energy distinction between the LUMO and HOMO shows molecular stability. This energy distinction is called E_g . If E_g is lower, the molecule is more stable and nonreactive. If E_g is lower, the molecule is nonstable and more reactive. The results in Tables 4-9 indicate that E_g for the researched chemical compounds is lower than 0.3 eV, which means that the researched chemical compounds are lower stable and more reactive. The energy band ranges **2** < **1** < **3** < **5** < **6** < **4**, suggesting that **2**, **1**, and **3** quaternary ammonium salts molecules are more reactive and nonstable than others. Because they have nitrogen atoms which linked with four $^*\text{CH}_2$ radicals. Many electron acceptor functional groups make molecules more negative. **2**, **1**, and **3** researched chemical compounds were formed by the reaction between 4-butylmorpholine and esters, which make molecules more reactive and nonstable.

In the FMO theory, the chemical structural parameters are calculated regarding to Equations (1-5):

$$\text{Chemical hardness, } \eta \text{ (eV)} = \frac{E_{\text{LUMO}}(\text{eV}) - E_{\text{HOMO}}(\text{eV})}{2} \quad (1)$$

$$\text{Electronegativity, } \chi \text{ (eV)} = \frac{-(E_{\text{LUMO}}(\text{eV}) - E_{\text{HOMO}}(\text{eV}))}{2} \quad (2)$$

$$\text{Chemical softness, } s \text{ (eV)} = \frac{1}{2\eta \text{ (eV)}} \quad (3)$$

$$\text{Electronic chemical potential, } \mu \text{ (eV)} = \frac{E_{\text{LUMO}}(\text{eV}) + E_{\text{HOMO}}(\text{eV})}{2} \quad (4)$$

$$\text{Global electrophilicity index, } \omega \text{ (eV)} = \frac{\mu^2 \text{ (eV)}}{2\eta \text{ (eV)}} \quad (5)$$

In this research, the molecular descriptors for the **6** synthesized quaternary ammonium salts were computed by DFT, and results are displayed in Tables 4-9. The obtained FMO analysis results reveal that the molecular descriptor and reactivity

property of the synthesized quaternary ammonium salts. The HOMO can donate the valent electrons to empty orbitals. The LUMO shows that the tendency of organic molecules to accept valent electrons. The green and red colors in the LUMO and HOMO of the researched chemical compounds show correspondingly positive and negative values of the LUMO and HOMO orbitals (figures 1-12), which means that the valence and π electrons covered around the benzene rings and nitrogen atoms in the synthesized quaternary ammonium salts.

The chemical hardness value shows the resistance degree of molecular change and deformation. The chemical softness is negative of the chemical hardness, and it is molecular changeable and deformation able degrees. The chemical hardness and softness values of the researched chemical compounds were computed by DFT quantum analysis, and the observed data have resulted in Tables 4-9. It is clear from the results that all researched chemical compounds are lower chemical hardness and softness organic molecules; results indicate that they are more changeable and reactive organic molecules.

The global electrophilicity index values of the synthesized quaternary ammonium salts were computed by DFT quantum analysis, resulted in Tables 4-10. The global electrophilicity index value is an indicator to calculate the quantity value of Lewis acid. It depends on the molecular structure and physical properties, such as the dipole moment, polarization, and solubility. The global electrophilicity index DFT calculations were performed in the gas phase. The results show that the global electrophilicity index values of the researched chemical compounds were lower at 0.3 eV, suggesting that they are weak Lewis acid. Because the aromatic rings and $^{\bullet}\text{CH}_2$ radicals reduced Lewis acid value in the researched chemical compounds. It was found that the following range of the global electrophilicity index values: **3** > **6** > **5** > **1** > **4** > **2**. **3** and **6** molecules more acidic than others, because the morpholine ring is linked with nitrogen atoms. **5**, **1**, **4** and **2** molecules have more benzene rings, which decrease the molecules' Lewis acid values.

In this research, it was computed the theoretical thermodynamic values of the researched chemical compounds by DFT quantum analysis. All theoretical thermodynamic DFT experiments were conducted at 298.150 K temperature and gas phase. The theoretical dipole moment, polarizability, entropy, heat capacity, and thermal energy of the researched chemical compounds were computed; the results are given in Tables 4-9. The dipole moment and polarizability values indicate the inductive interaction between dipole and ions in the organic molecule. The results show that all synthesized quaternary ammonium are more polarized molecules in gas phases. From the DFT analysis, it was calculated the following variation: 6.8 (**2**) > 3.8 (**4**) > 3.7 (**5**) > 3.4 (**6**) > 2.5 (**3**) > 2.3 (**1**). The molecule of **2** is more polarized than others because it has an aromatic ring and aliphatic rings, which make it more polarized. The heat capacity and entropy of the synthesized quaternary ammonium salts ranged: (103)**1** > (85)**3** > (77)**4** > (61)**2** > (59)**6** > (56)**5**. 4-Butyl-4-(2-(nonyloxy)-2-oxoethyl)morpholin-4-ium chloride quaternary ammonium salt has a high heat capacity and is more entropy molecule than others because it has the aromatic ring, $-\text{C}_4\text{H}_9$ radical and aliphatic ring, which make the molecule more heat capacity molecule.

Table 4: Energy Values of the Global Reactivity and Thermodynamic Parameters for 1 (298.150 K)

Parameters, eV	1
E_{HOMO}	-0.19
E_{LUMO}	-0.12
E_{g}	0.07
Electronic affinity	-0.12
Ionization potential	-0.19

η	0.035
χ	-0.035
ω	0.343
μ	-0.155
Table 1: Contd.,	
s	14.285
Dipole moment, Debye	2.331
Polarizability (α), a.u.	217.009
E(UB3LYP), Hartree	-1026.989
E (Thermal), kcal/mol	368.358
Entropy (S), cal/mol-kelvin	206.171
Heat capacity (Cv), cal/mol-kelvin	103.726

Figure 1: LUMO Orbitals of 1.

Figure 2: HOMO Orbitals of 1.

Table 5: Energy Values of the Global Reactivity and Thermodynamic Parameters for 2 (298.150 K)

Parameters, eV	2
E_{LUMO}	0.023
E_{HOMO}	-0.040
E_g	0.063
Electronic affinity	0.023
Ionization potential	-0.040
η	0.0315
χ	-0.0315
ω	0.00114
μ	-0.0085
s	15.873
Dipole moment, Debye	6.844
Polarizability (α), a.u.	256.624
E(UB3LYP), Hartree	-943.056

E (Thermal), kcal/mol	260.100
Entropy (S), cal/mol-kelvin	122.084
Heat capacity (Cv), cal/mol-kelvin	61.915

Figure 3: LUMO Orbitals of 2.

Figure 4: HOMO Orbitals of 2.

Table 6: Energy Values of the Global Reactivity and Thermodynamic Parameters for 3 (298.150 K)

Parameters, eV	3
E_{LUMO}	-0.115
E_{HOMO}	-0.195
E_g	0.08
Electronic affinity	-0.115
Ionization potential	-0.195
η	0.04
χ	-0.04
ω	0.3
μ	-0.155
s	12.5
Dipole moment, Debye	2.528
Polarizability (α), a.u.	173.706
$E(\text{UB3LYP})$, Hartree	-869.772
E (Thermal), kcal/mol	292.364

Entropy (S), cal/mol-kelvin	178.488
Heat capacity (Cv), cal/mol-kelvin	85.510

Figure 5: LUMO orbitals of 3.

Figure 6: HOMO Orbitals of 3.

Table 7: Energy Values of the Global Reactivity and Thermodynamic Parameters for 4 (298.150 K)

Parameters, eV	4
E_{LUMO}	-0.134
E_{HOMO}	-0.243
E_g	0.377
Electronic affinity	-0.134
Ionization potential	-0.243
η	0.188
χ	-0.054
ω	0.094
μ	-0.188
s	2.652
Dipole moment, Debye	3.683
Polarizability (α), a.u.	180.533
E(UB3LYP), Hartree	-830.303

E (Thermal), kcal/mol	264.389
Entropy (S), cal/mol-kelvin	167.919
Heat capacity (Cv), cal/mol-kelvin	77.357

Figure 7: LUMO Orbitals of 4.

Figure 8: HOMO Orbitals of 4.

Table 8: Energy Values of the Global Reactivity and Thermodynamic Parameters for 5 (298.150 K)

Parameters	5
E_{LUMO}	-0.022
E_{HOMO}	-0.244
E_g	0.222
Electronic affinity	-0.022
Ionization potential	-0.244
η	0.111
χ	-0.111
ω	0.16
μ	-0.133
s	4.5
Dipole moment, Debye	3.7
Polarizability (α), a.u.	154.83
$E(\text{UB3LYP})$, Hartree	-746.866
E (Thermal), kcal/mol	167.636

Entropy (S), cal/mol-kelvin	138.503
Heat capacity (Cv), cal/mol-kelvin	56.803

Figure 9: LUMO Orbitals of 5.

Figure 10: HOMO Orbitals of 5.

Table 9: Energy Values of the Global Reactivity and Thermodynamic Parameters for 6 (298.150 K)

Parameters, eV	6
E_{LUMO}	-0.013
E_{HOMO}	-0.243
E_g	0.230
Electronic affinity	-0.013
Ionization potential,	-0.243
η	0.115
χ	-0.115
ω	0.285
μ	-0.256
s	4.347
Dipole moment, Debye	3.432
Polarizability (α), a.u.	134.878

E(UB3LYP), Hartree	-673.092
E (Thermal), kcal/mol	188.553-
Entropy (S), cal/mol-kelvin	137.442
Heat capacity (Cv), cal/mol-kelvin	58.999

Figure 11: LUMO Orbitals of 6.

Figure 12: HOMO Orbitals of 6.

5. CONCLUSIONS

To sum up, the **6** types of new quaternary ammonium salts of pyridine and N-butylmorpholine with nonyl, isoamyl, and benzyl esters of chloroacetic acid in the presence of ethyl acetate, acetone and ethanol solvents were synthesized, and their synthesis methodology was first reported. Their molecular structure was confirmed by IR and ^1H NMR experimental spectroscopic methods, and theoretical molecular descriptors and thermodynamic parameters were analyzed by (frontier molecular orbital (FMO) analyses) DFT methods with B3LYP at 6-311G (d,p) basis sets, and the concluded following opinions:

- The reaction between the chloroacetic acid esters and alcohols (nonyl alcohol, isoamyl alcohol, and benzyl alcohol) yield was over 75% at 1:2 molar ratios.
- It was found that the syntheses reactions of new quaternary ammonium salts are productive when it was

conducted in an ethanol solvent with over 91% yield.

- The ionization potential of the synthesized organic compounds ranged, respectively, , suggesting that 2 and 1 have more electronic affinity.
- The energy gap between LUMO and HOMO for the synthesized organic compounds is lower than 0.3 eV, suggesting that they have low stability and more reactivity.
- The global electrophilicity index values are in the following variation: showing that 3 and 6 are more acidic than others.
- The heat capacity and entropy of the synthesized organic compounds ranged in the order: which indicates that was high heat capacity and more entropy molecule.

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