INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com

Research Article

THE ROLE OF 5-(4-ALKOXYBENZYLIDENE)-2-THIOXO-4-OXO-1, 3-THIAZOLIDINE AS ANTIOXIDANTS FOR EGYPTIAN LUBE OIL BASE STOCK

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Abstract

This work presents a study to the oxidation stability of local base stock, delivered from Co-operative Petroleum Company, in the presence of two prepared Rhodanine derivatives, namely 5-(4-hexyloxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine, (I) and 5-(4-octyloxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine, (II). The structures of the prepared compounds were elucidated using the traditional tools analyses including elemental analysis, I.R., ^{1}H-NMR and electron ionization mass spectroscopy (EI-MS). The oxidation reaction was tested using the change in total acid number (TAN) and viscosity. The data showed that compound (II) is more efficient than compound (I). The quantum chemical parameters such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels, the energy gap (E_{HOMO}-E_{LUMO}) and the dipole moment were calculated. The quantum chemical calculations were on the same line with the experimental results.

Keywords: Base stocks, antioxidant, oxidation stability, total acid number, viscosity and quantum chemical calculations.

1.Introduction

Mineral lubricating oils are usually used in presence of air whereby oxidative Chemical reactions can take place. The rate of these oxidative processes varies greatly with the nature of oils, the extent of processing in refining, the temperature, and the presence of a metallic catalyst [1,2]. Such oxidations have a drawback on the oil, thus leading to failures in lubrication that accompanied by damage of engines. Large degree of damage is due to the formation of viscous, solid bodies, or jelly-like emulsions which interfere with the regular distribution of the lubricant. Antioxidants can generally be considered as free radical inhibitors of peroxide decomposers, and may vary in their chemical structures. Three types of additives have been proved to be successful in controlling the oxidation of lubricating oils; radical scavengers, and hydro peroxides decomposers, as well as synergistic mixtures of both of them. Thus, various classes of compounds have been used as antioxidant additives, such as phenols [3-9], amines [10-12] and heterocyclic compounds [13-16] as well as synergistic mixtures of them [17-22].

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity. Recently, antioxidant publications contain substantial chemical calculations [23 - 24]. Such calculations are usually used to explore the relationship between the antioxidants molecular properties and their inhibition efficiency. In the present work, two rhodanine derivatives have been synthesized, characterized and evaluated as antioxidants for local base oil. Also we discussed the relationship between quantum chemical calculations and experimental results of the two synthesized antioxidants by determining the quantum chemical parameters such as the energies of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference E (E_{HOMO}-E_{LUMO}) and the dipole moment.

2. Experimental part

2. 1. Raw material

Base Stock Oil: Hydro finished base stock oil (HBS) sample was obtained from Co-operative Petroleum Company, Cairo, Egypt.

2. 2. Reagents

All reagents purchased from Merck, Aldrich and Fluka chemical companies. They were of analytical grade and used without further purification.

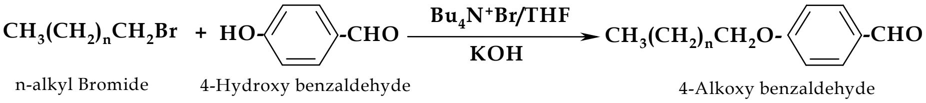
2. 3. Analysis

The chemical structures of the synthesized compounds were well established by elemental analysis [using CHNS-932 (LECO) Vario Elemental Analyzers], Infra-Red, [using a Perkin-Elmer FT-IR type 1650 spectro-photometer; Model "Vector 22"], ^{1}H-NMR [using ^{1}H-NMR (type varian 300 MHz - with the TMS as internal standard zero compound] and Mass spectroscopy [using direct inlet unit (DI Analysis) of SHIMADZU GC/MS-QP-2010].

2. 4. Preparation of antioxidants (I and II)

2. 4.1. Synthesis of alkoxybenzaldehydes:

A solution of 4-hydroxybenzaldehyde (12.29 mmol) in dry tetrahydrofuran (20ml), tetrabutylammonium bromide (0.93 mmol), powdered potassium hydroxide (8.9mmol) and n-alkyl bromide (n-hexyl bromide and n-octyl bromide) (12.02mmol) was added and stirred at room temperature for 6h. The mixture was then filtered and washed with 10% cold sodium hydroxide (2 x 25ml) to remove traces of unreacted 4-hydroxybenzaldehyde. The solvent was dried over anhydrous sodium sulphate and evaporated under reduced pressure to give solid 4-n-alkoxybenzaldehyde in 83% yield [15].

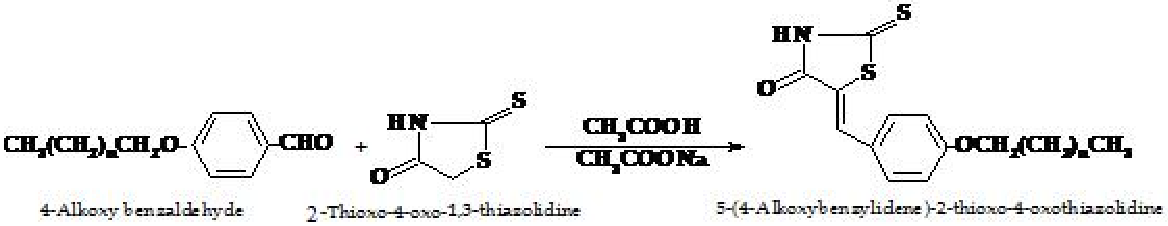


(Where n = 4, 6)

Scheme 1: Preparation of 4-n-alkoxybenzaldehyde.

2. 4.2. Synthesis of Rhodanine derivatives:

4-n-alkoxybenzaldehyde (0.010 mole) is added to a solution of 2-thioxo-4-oxo-1,3-thiazolidine (0.010 mole) in presence of anhydrous sodium acetate (0.015 mole) and glacial acetic acid (20 ml). The whole mixture is refluxed for 2 or 3 hours, allowed to stand at room temperature and the precipitated product is filtered off, washed several times with cold water and recrystallized from glacial acetic acid with ethanol [16].



Where n = 4 (I) 5-(4-hexyloxybenzylidine)-2-thioxo-4-oxo-1,3-thiazalidine
n = 6 (II) 5-(4-octyloxybenzylidine)-2-thioxo-4-oxo-1,3-thiazalidine

Scheme 2 : Preparation of additives (I and II)

Table 1: Melting point and Yield % of the synthesized antioxidants

Compound	Melting point (^{o}C)	Yield (%)
I	160 -164	75
II	130 -133	78

2. 5. Oxidation stability study

The oxidation test was carried out according to ASTMD-943 standard method. The oxidation cell in the static mode contained 200 ml base stock, and copper and iron wires as catalysts. The base stock sample was subjected to oxidation at 120 ^{o}C with pure oxygen (99.95%) at a flow rate of 0.1 liter/hour for maximum 96 hours. The characterized compounds (I and II) were added with different concentrations (100, 200 and 300 ppm). The oil samples were examined (after 24, 48, 72 and 96 hours respectively) through the change of viscosity and total acid number (TAN). The latter two parameters were carried out for the oxidized samples according to ASTM standard test methods D- 445 and D- 664, respectively.

2. 6. Quantum chemical calculations

Quantum mechanical program Chem Bio draw Ultra 12 [17] , was used for the molecular modeling. The calculations were based on Ab initio (HF/3-21G) and semiempirical gas phase AM1 (Austin Model 1).

Results and Discussion

3.1. Physicochemical properties of the Base Stock

The physicochemical properties of the delivered base stock were carried out according to ASTM standard test methods. The results were tabulated in **Table 2**.

Table 2: physicochemical properties of the Base Stock

Test	Result	Standard Test Method
Density at 15.56 ^{O}C, g / cm^{3}	0.8817	ASTM D - 1298
Pour Point, ^{O}C	-6	ASTM D - 97
Viscosity at 40 ^{O}C at 100 ^{O}C	52.34 7.41	ASTM D – 445
Viscosity Index (VI)	92	ASTM D – 2270
Total Acid Number (TAN)	0.067	ASTM D – 664
Sulfur Content, wt %	0.34	ASTM D – 4294
Color	2.5	ASTM D – 1500
Ash Content, wt %	0.003	ASTM D – 482
Copper Corrosion	1 a	ASTM D – 130
Flash Point, ^{o}C	220	ASTM D – 92
Aniline Point	100.5	ASTM D – 611
Molecular Weight	468.9	——

3.2. Confirmation of antioxidants I and II structures

The chemical structure of compounds I and II were elucidated using the following analyses tools:

3.2.1. Elemental analysis

Table 3: Elemental analysis of I&II structures*

Compound	Element							
	C%		H%		N%		S%	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
I	59.81	60.35	5.92	6.65	4.36	4.32	19.94	19.97
II	61.89	61.74	6.59	6.04	4.01	4.24	18.34	18.38

*The observed results were in good compatibility with the calculated values.

3.2.2. Infrared spectroscopy

Table 4: IR spectra of I and II

Compound	STREACHING OF, (¬ , cm^{-1})						
	NH (broad)	CH $_{aliphatic}$	C=C $_{aromatic}$	C-O-C	C=C $_{aliphatic}$	C=O*	Aromatic zone (banding vibration)
I	3453	2952-2914	1509	1242	1583	1686	825
II	3453	2922-2850	1509	1256	1588	1687	826

* The infrared spectra of prepared compounds show($¬_{C=O}$) at some lower wave numbers as compared with the respective saturated analogues which is consistent with the existence of an α-β unsaturated carbonyl group system.

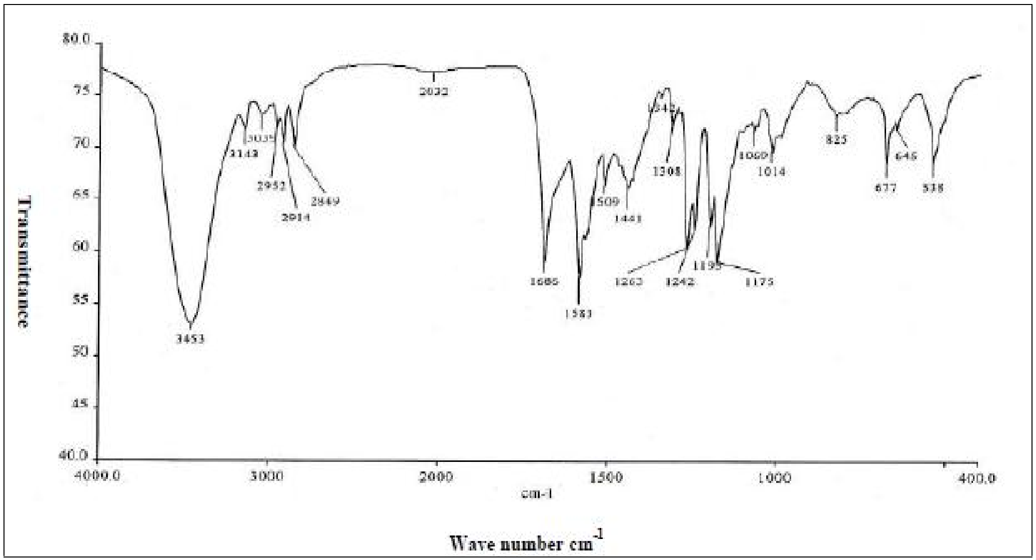


Figure 1 : Infrared spectrum of the prepared compound (I)

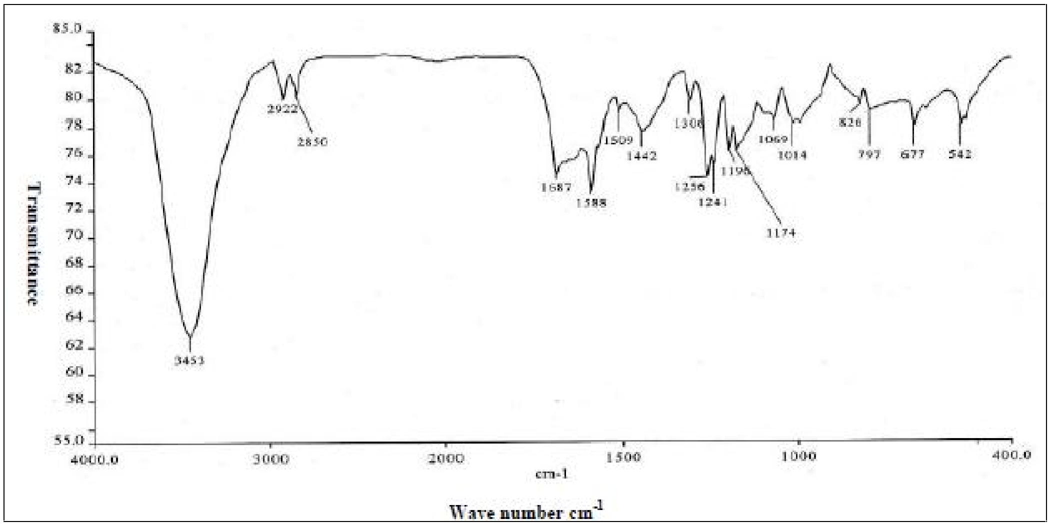


Figure 2 : Infrared spectrum of the prepared compound (II)

3.2.3. ^{1}H-NMR spectroscopy:

Table 5: Chemical structures of compounds I, II

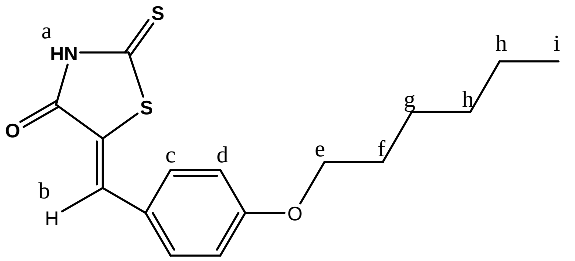
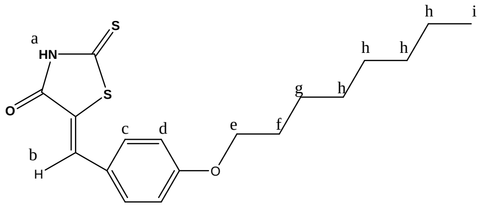
I	II
	

Table 6: Chemical shifts (ppm) of compounds I & II

Type of $^{+}$H	a	b	c	d	e	f	g	H	i
Compound I									
Chemical shift	9.743	7.652 7.269	7.445	6.995	4.034	1.819	1.482	1.353	0.924
No. of $^{+}$H & spin multiplicity	1(s)	1(s)	2(d)	2(d)	2(t)	2(m)	2(m)	4(m)	3(t)
Compound II									
Chemical shift	9.950	7.656 7.270	7.440	6.992	4.031	1.804	1.484	1.328	0.917
No. of $^{+}$H & spin multiplicity	1(s)	1(s)	2(d)	2(d)	2(t)	2(m)	2(m)	8(m)	3(t)

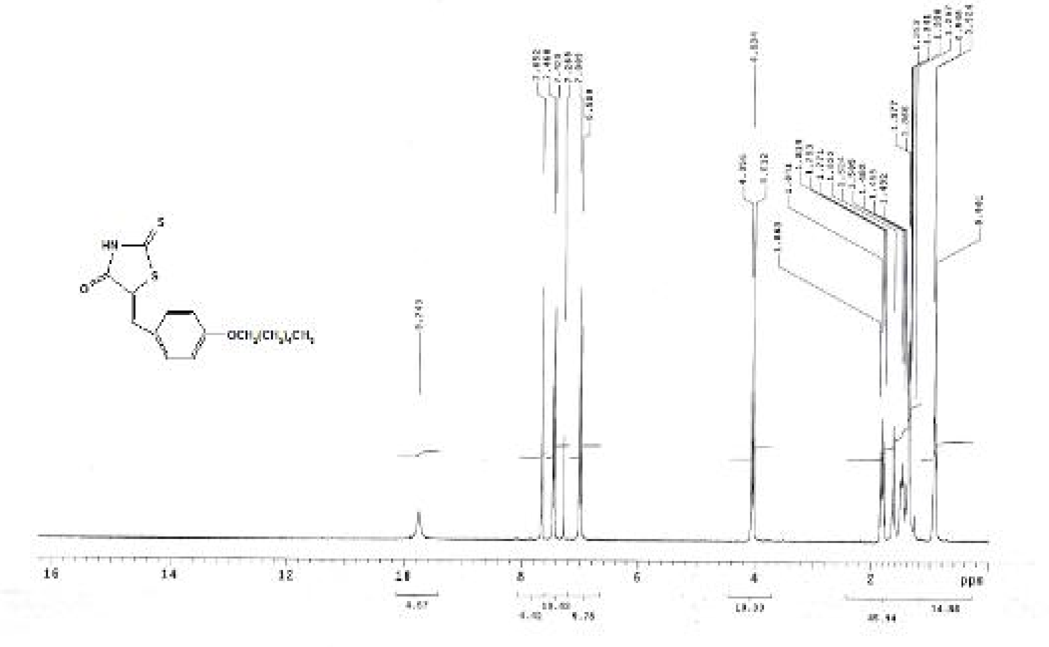


Figure 3: ^{1}HNMR of the prepared compound (I)

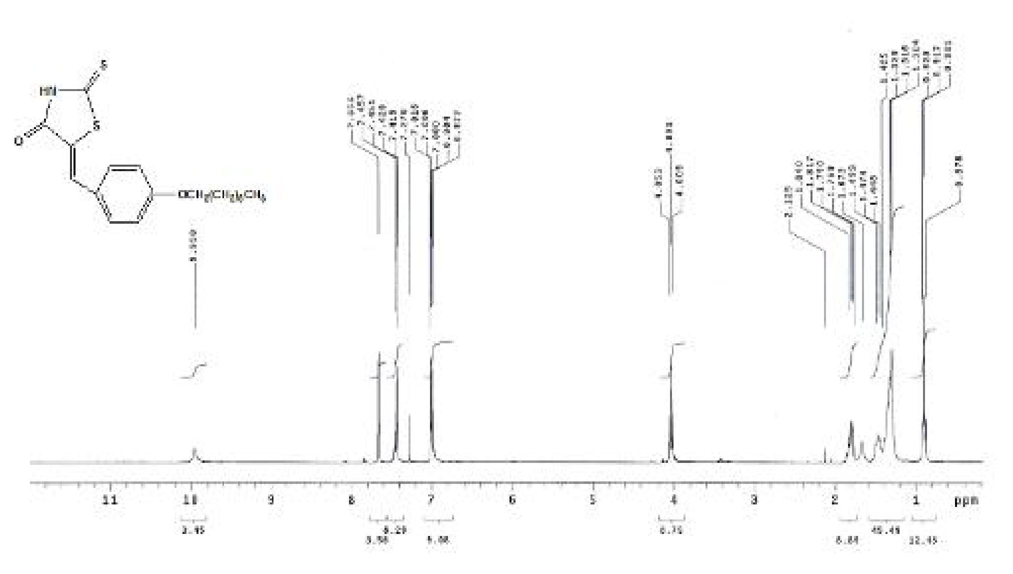


Figure 4: ^{1}HNMR of the prepared compound (II)

The data of **compound I** (**Table 6**) reveals that:

- Proton (a), which has singlet peak and chemical shift δ value of 9.743 ppm is attributed to NH proton of thiazolidine.
- Proton b (β – olefinic proton) has two singlet peaks at 7.652 and 7.269 ppm .That indicates the presence of compound (I) in two isomeric forms, Z and E respectively [18]. This is the result of the highly deshielded Z proton more than E one, whereas the ratio of Z to E isomer is 8:2 respectively.
- The four aromatic protons of both types c & d appear with the doublet splitting at 7.445 and 6.995 ppm, respectively.
- The two protons of type (e) exhibit a triplet peak at 4.034 ppm. This is attributed to the attachment of these protons to the aromatic ring.
- The two protons of type (f) appear as multiplet in their multiplicity at 1.819 ppm
- The two protons of type (g) appear as multiplet in their multiplicity at 1.482 ppm
- The four protons of type (h) appear at 1.353 ppm with multiplet multiplicity.
- The three protons of type (i) appear at 0.924 ppm with triplet multiplicity.

The data of **compound II (Table 6)** discloses that:

- Proton (a), which has singlet peak and chemical shift δ value of 9.950 ppm is attributed to NH proton of thiazolidine.
- Proton b (β – olefinic proton) has two singlet peaks at 7.656 and 7.270 ppm .That indicates the presence of compound (II) in two isomeric forms , Z and E respectively [18]. This is the result of the highly deshielded Z proton more than E one, whereas the ratio of Z to E isomer is 8:2 respectively.
- The four aromatic protons of both types c & d appear with the doublet splitting at 7.440 and 6.992 ppm respectively.
- The two protons of type (e) exhibit a triplet peak at 4.031 ppm. This is attributed to the attachment of these protons to the aromatic ring.
- The two protons of type (f) appear as multiplet in their multiplicity at 1.804 ppm.
- The two protons of type (g) appear as multiplet in their multiplicity at 1.484 ppm.
- The eight protons of type (h) appear as multiplet in their multiplicity at 1.328ppm.
- The three protons of type (i) appear at 0.917 ppm with triplet multiplicity.

3.2.4 Mass Spectroscopy

Table 7: Mass spectroscopy of compounds I & II

I (m/z 321 ($C_{16}H_{19}NO_2S_2$)			II (m/z 349 ($C_{18}H_{23}NO_2S_2$)		
Molecular formula	**m/z**	**Intensity**	**Molecular formula**	**m/z**	**Intensity**
$C_{16}H_{19}NO_2S_2]^{+\cdot}$	321	22.14	**$C_{18}H_{23}NO_2S_2]^{+\cdot}$**	349	45.62
$C_{14}H_{18}OS]^{+\cdot}$	234.05	21.96	**$C_{16}H_{22}OS]^{+\cdot}$**	262	32.10
$C_8H_6OS]^{+\cdot}$	150	100	**$C_8H_6OS]^{+\cdot}$**	150.05	100
$C_8H_5S]^{+\cdot}$	133	0.65	**$C_8H_5S]^{+\cdot}$**	133	38.73
$C_6H_5]^{+\cdot}$	77	14.99	**$C_6H_5]^{+\cdot}$**	77	27.32

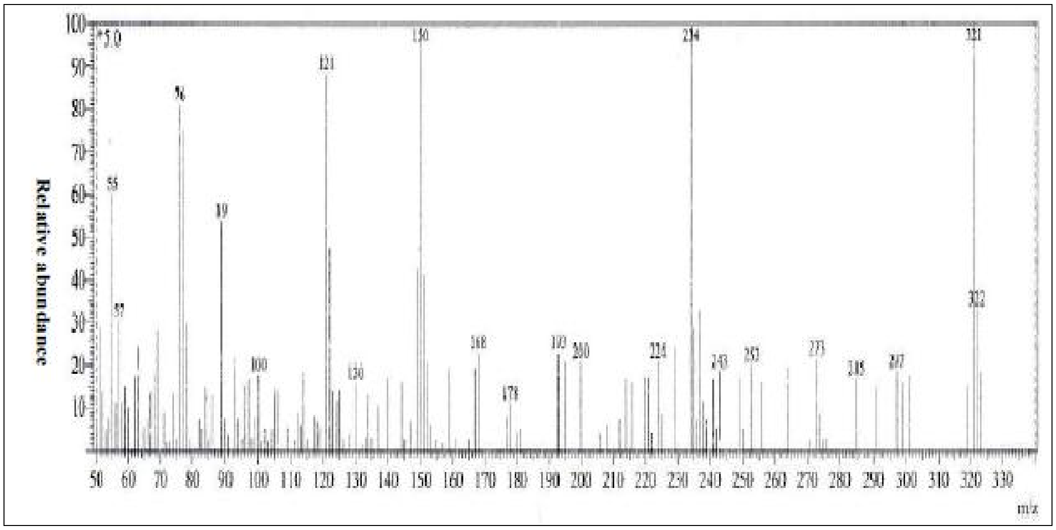


Figure 5 : Mass spectra of the prepared compound (I)

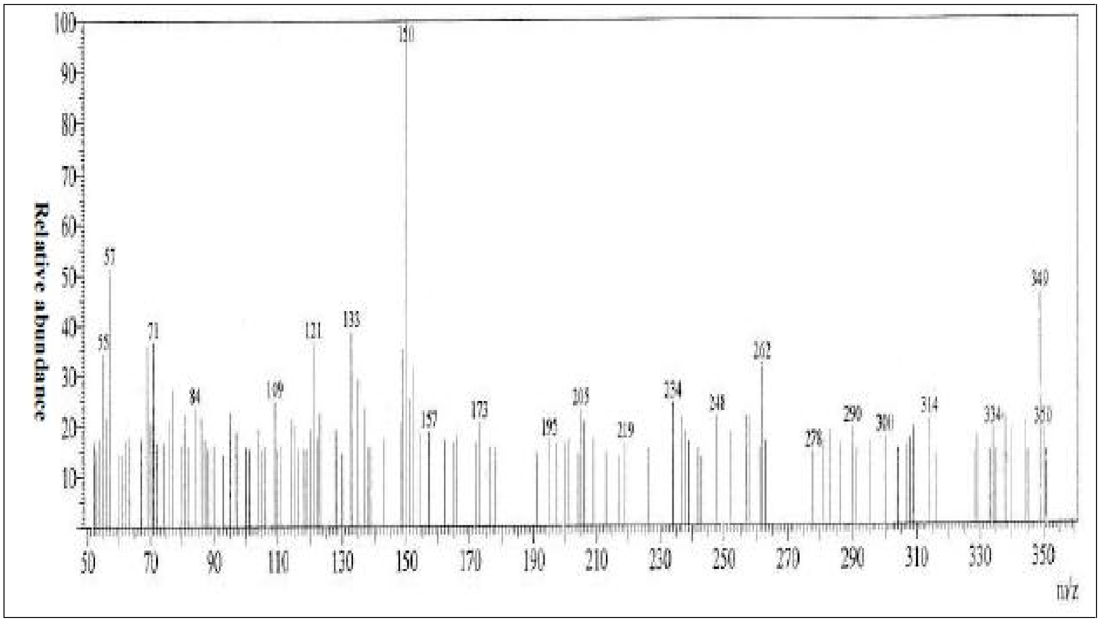
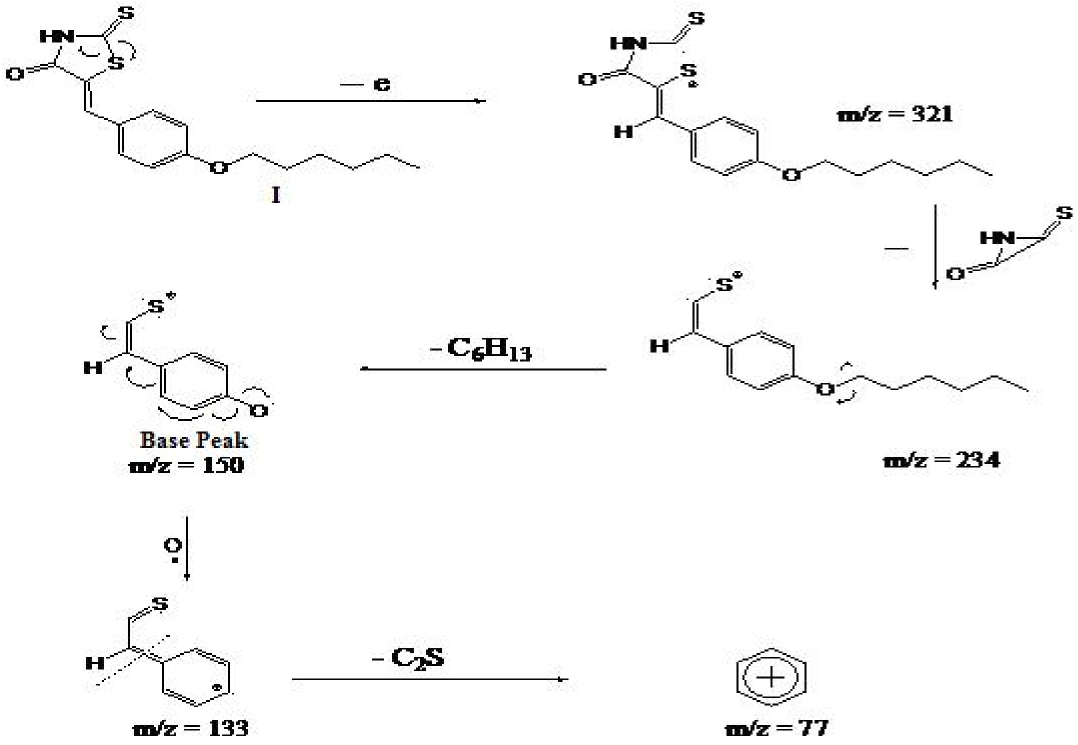


Figure 6 : Mass spectra of the prepared compound (II)

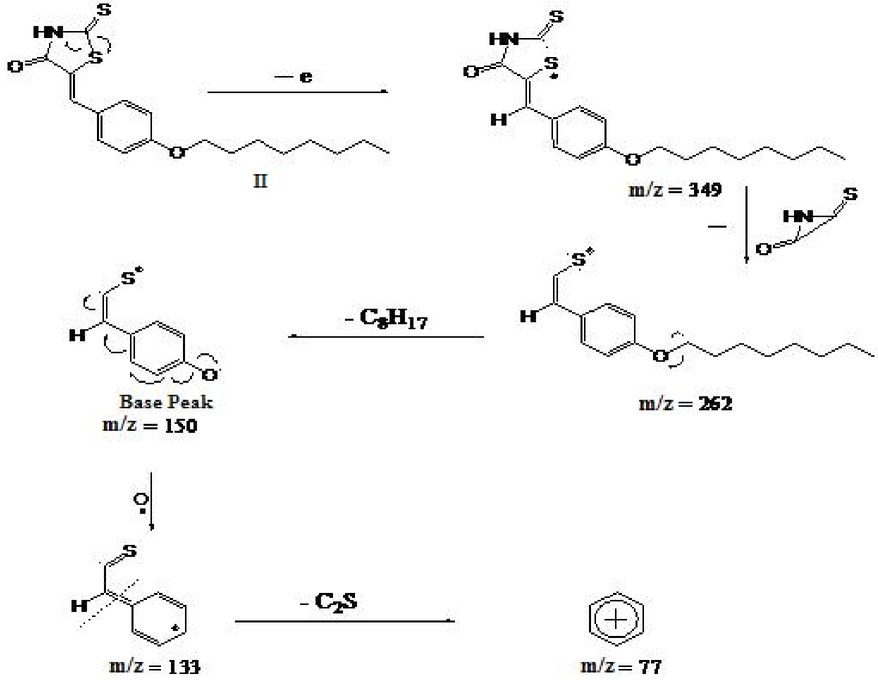
The schematic fragmentation of compounds I and II are illustrated as follows:

Route of fragmentation of compound (I):



Scheme 3 : Schematic fragmentation of compound (I)

Route of fragmentation of compound (II):

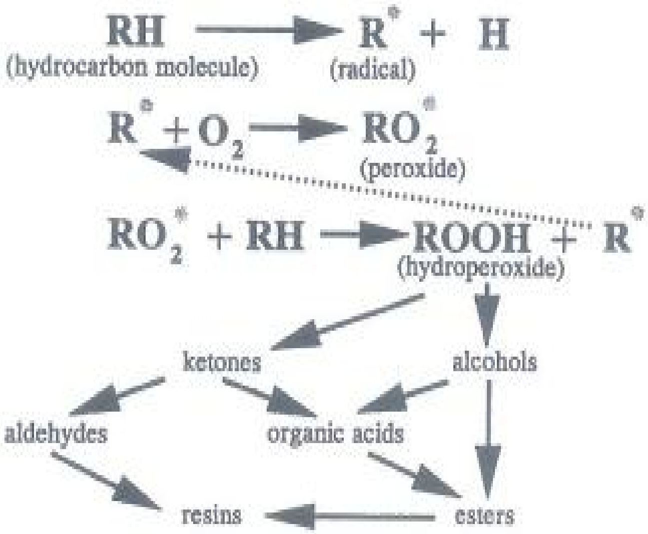


Scheme 4: Schematic fragmentation of compound (II)

3.3 Evaluation of the synthesized compounds as antioxidants for base stock:

3.3.1 Total Acid Number (TAN):

The synthesized antioxidants were added to the delivered base stock. The blends obtained were subjected to severe oxidation conditions at 120 °C. Samples were taken at specific time intervals (24, 48, 72 and 96 hours) of oxidation. Usually the total acid number (TAN) of the oil increases by increasing the oxidation time. The increment of TAN values is due to the oxidation processes which produce peroxides. These peroxides undergo further reaction to form a variety of oxygenated compounds such as alcohols, aldehydes and ketones. The TAN is affected by the formation of carboxylic acids after prolonged oxidation and increases with increasing carbonyl formation which deteriorates the lubrication ability of the oil.



Scheme 5: Schematic representation of oxidation of mineral oil

In case of the base oil (Table 8), the TAN values increase from 0.067 mg KOH/g sample at room temperature to 2.01 mg KOH/g sample when thermally oxidized to 96 hours.

Table 8: Total acid numbers (TANs) and viscosities of the base stock at different times without additives'

Oxidation time interval (hrs)									
Total acid numbers, mg KOH /g Sample ×10^2					Viscosity, cst at 40 °C×10^2				
Zero	24 hrs	48 hrs	72 hrs	96 hrs	zero	24 hrs	48 hrs	72 hrs	96 hrs
6.7	94	102	120	201	5234	5938	6433	6849	7770

Effect of substituted alkyl additives

Results of the TAN in presence of the antioxidants **I** and **II**, having short and long alkyl chain lengths, respectively, after thermal oxidation of the base oil up to 96 hours, are given in Table 9. First of all, the TANs give more efficient results as long chain increase the efficiency order of these compounds towards decreasing TAN is ranked as follows: II > I> fresh . This may be attributed to the effect of the long chain carbon atom which increases the solubility of the additive in the mineral oil which intern increase antioxidant properties of the additives.

Effect of additives concentration

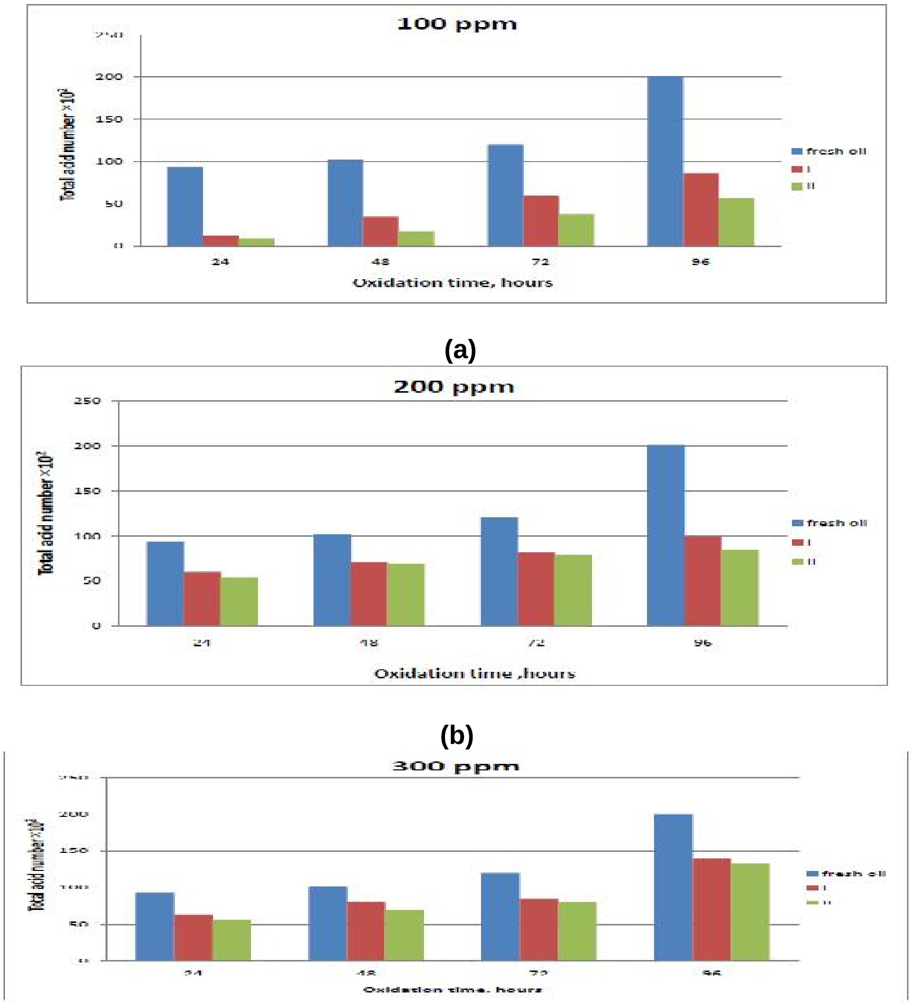
The data depicted in Figures 7a,7b and 7c represented the relation between the TAN and the oxidation periods (24, 48, 72 and 96hrs) when the additive concentrations corresponds to 100, 200 and 300 ppm for compounds **I** and **II** were used, respectively. Figure 7a shows that with the additive concentration correspond to 100 ppm, the order of increasing inhibition efficiency is ranked as follows: II > I > Fresh. Figure 7b discloses that, with the concentration of 200 ppm, the order of increasing inhibition efficiency is ranked as follows: II > I > Fresh. It is evident from Figure 7c that, with 300 ppm of I and II, there is a marked increase in the TAN on using them and the order of inhibition efficiency was as follows: II > I > Fresh sample.

First of all, the TANs increase by increasing the additive dose from 100 to 300 part per million.

This may be attributed to at a sufficiently high content of sulpher, the concentration of acids in the oxidized oils deponds linearly on the total content of sulpher

Table 9: TAN variation with oxidation time at different additive concentrations

Compound	Total acid number, mg KOH / g Sample ×10^2				
	Concentration (ppm)	Oxidation time (hr)			
		24	48	72	96
I	**100**	13.1	35.5	59.3	86
	200	60	71.1	82	99.2
	300	63	81.2	84.5	140.1
II	**100**	9	17.6	38.5	56.9
	200	53.5	69.2	79	85.3
	300	56.3	70.2	80.3	133.2



(a)

(b)

(c)

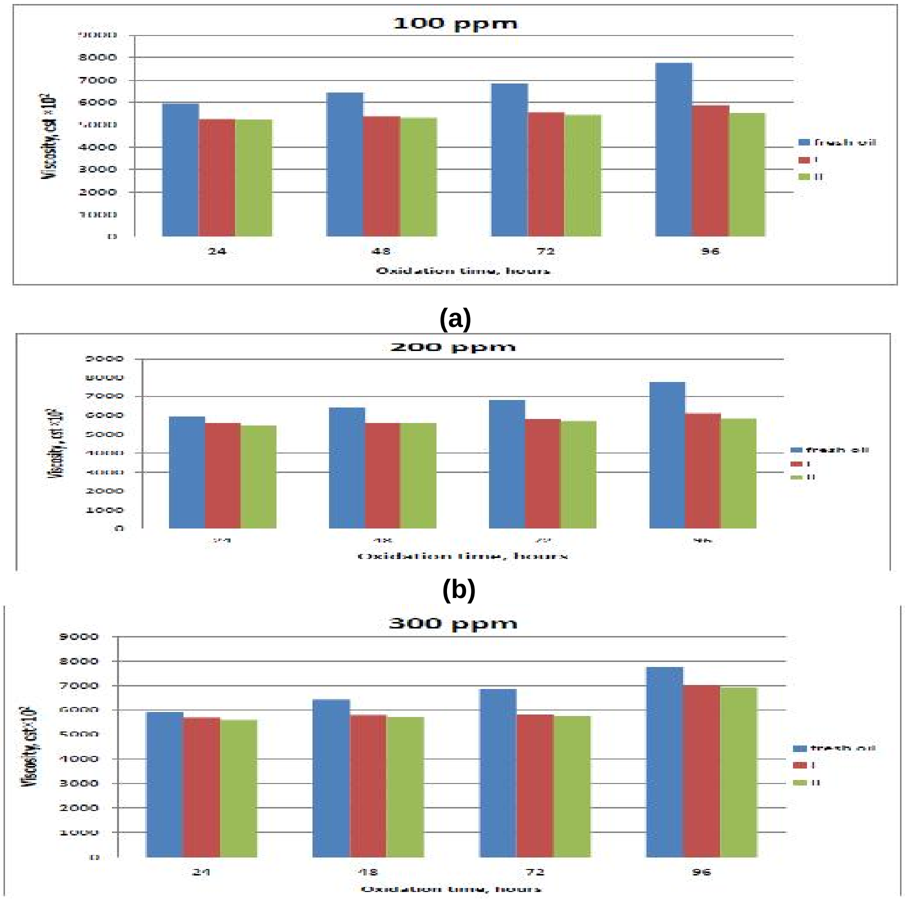
Figure 7: Variation of TAN of the base oil without and with I and II additives of concentration: (a) 100 ppm , (b) 200 ppm , and (c) 300 ppm

3.3.2 Viscosity

Viscosity is one of the most important physical properties for the characterization of lubricants and their transport properties, and it is a measure of internal friction in a fluid. In general, the viscosity of the base oil increases with the operating time of oxidation. The increments in viscosity is due to the polymerization in the molecular structure. That is, during the oxidation, the oil degrades from peroxides to carboxylic acids, which polymerize to a long chain molecular structure. The latter greatly enhances the viscosity and indicating that the heavy lubricant degradation exists. The viscosity is always decreased by the addition of additives to the base oil. The data of the viscosities are tabulated in Table 10 and graphically represented in Figures 8a-c

Table 10 : Viscosity variation with oxidation time and different additive concentrations

Compound	Viscosity, cst at 40 °C× 10^2				
	Concentration (ppm)	Oxidation time (hr)			
		24	48	72	96
I	**100**	5260	5390	5570	5890
	200	5608	5630	5796	6110
	300	5692	5790	5812	7012
II	**100**	5240	5302	5420	5530
	200	5482	5619	5723	5829
	300	5592	5730	5769	6912



(a)

(b)

(c)

Figure 8 : Variation of viscosity of the base oil without and with I and II additives of concentration: (a)100 ppm , (b) 200 ppm , and 300 ppm

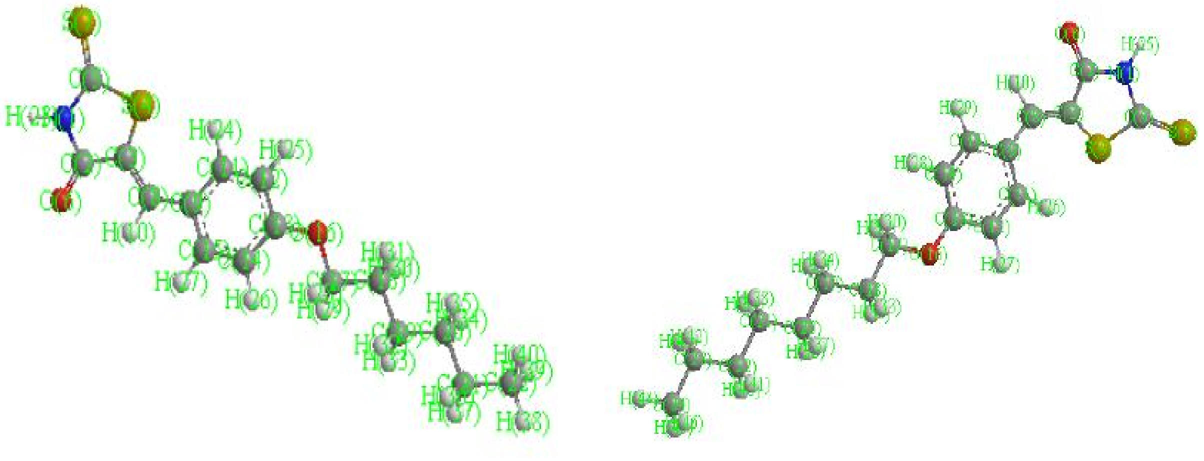
3.3.3 Quantum chemical calculations:

Geometric structures of 5-(4-hexyloxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine (I) and 5-(4-octyloxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine (II) are given in Figures 9(a&b), respectively. The optimized molecular structure of the studied molecules, using Ab initio (HF/3-21G) and semiempirical gas phase AM1 (Austin Model 1) methods, are shown in Figures 10(a&b) and 11(a&b), respectively. The calculated Quantum chemical indices of E_{HOMO}, E_{LUMO}, dipole moment (μ) and the ΔE (E_{HOMO} - E_{LUMO}) energy gap data are given in Table 11.

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between HOMO and LUMO orbitals of reacting species [19]. Thus, the treatment of the frontier orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reaction. HOMO is often associated with the electron donating ability of a molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital [20]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of E_{LUMO}, the more probable it is that the molecules to accept electrons. Increasing values of the E_{HOMO} facilitate adsorption and therefore inhibition by influencing the transported process through the adsorbed layer [21]. Low absolute values of the energy gap (ΔE) gives good inhibition efficiencies because the energy required to remove an electron from the last occupied orbital will be low [22],which facilitate oxidation inhibition process.

Table 11: Quantum Chemical Parameters

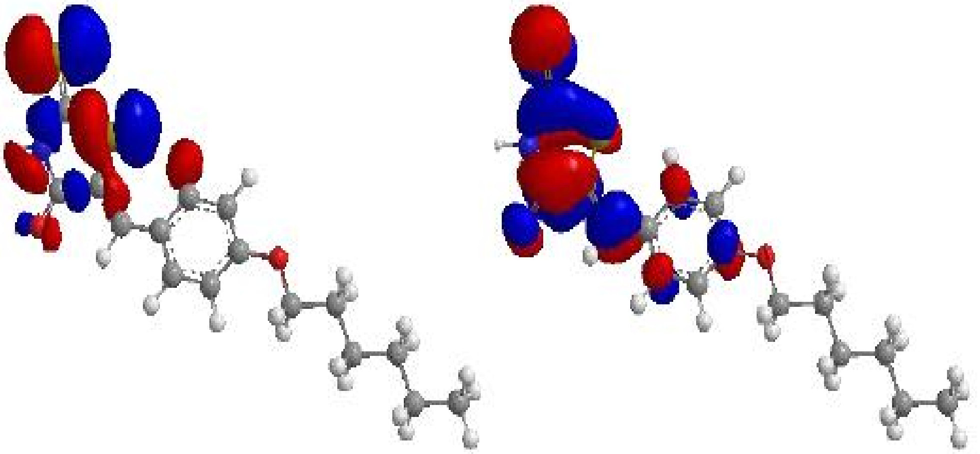
Compound	**Quantum Parameters**				
	Dipole Moment (Debye)	**Dipole/Dipole (Kcal/mole)**	**E_{LUMO} eV**	**E_{HOMO} eV**	**ΔE eV E_{LUMO} - E_{HOMO}**
Ab Initio HF/3-21G					
I	6.2259	2.7429	- 4.043	-7.797	3.754
II	6.269	2.7426	- 4.143	-7.799	3.656
Semiempirical AM1					
I	6.438	2.8973	- 4.044	-7.795	3.751
II	6.334	2.8949	- 4.143	-7.794	3.651



Structure (I)
(a)

Structure (II)
(b)

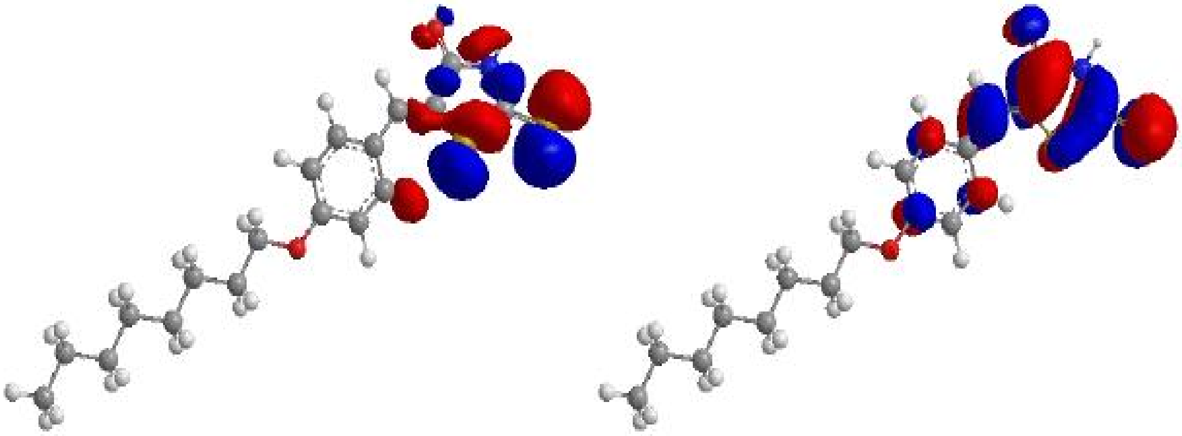
Figure 9: Optimized structures of (I) and (II)



HOMO **(a)**

LUMO **(b)**

Figure 10: The frontier molecule orbital density distributions of (I)



HOMO **(a)**

LUMO **(b)**

Figure 11: The frontier molecule orbital density distributions of (II)

From the data given in Table 11, it is obvious that the higher value of calculated energy gap (ΔE) obtained by (I), while the lower energy gap value (ΔE) was that of (II). That gives good evidence on the obtained efficiency of the studied antioxidant to inhibit the oxidation process. So the inhibition efficiency of II is greater than that of I which is in good compatibility with the experimental results shown in the change of viscosity and total acid numbers.

Conclusion

The results obtained in this paper, indicate the following:

- ✓ Increasing the oxidation time, always increase both of the total acid number and the viscosity of the base stock.
- ✓ The synthesized antioxidants (I and II) proved to be successful in controlling the oxidation stability of the base stock.
- ✓ We noticed for compound (II), with long hydrophobic part, has more efficiency than compound (I).
- ✓ The data reveals that the most effective concentration is (100 ppm).
- ✓ Quantum chemical calculations were found to give good reasonable correlation with the results obtained by total acid number (TAN) and viscosity.

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