Novel Heterocyclic Compounds as Antioxidants for Egyptian Base Stock

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Abstract: The oxidation stability of local base stock, delivered from Co-operative Petroleum Company, in the presence of two prepared Rhodanine derivatives, namely 5-(4-butoxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine, (I) and 5-(4-decyloxy-benzylidene) -2-thioxo-4-oxo-1,3-thiazolidine, (II), was studied. The structure 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.

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Key words: Rhodanine derivatives, base stocks, oxidation stability, total acid number, viscosity and quantum chemical calculations

1. Introduction

A lubricant is a substance introduced between two moving surfaces to primarily reduce friction, improve efficiency, and reduce wear [1]. A lubricant may also serve as a function of dissolving or transporting foreign particles, carrying away contaminations and debris, preventing corrosion or rust, sealing clearances, and dissipating heat [1-3]. Base oils are the major components of lubricants, representing usually 85% or more of the formulation. These base oils are in general of mineral origin. They are produced from petroleum crude oil by various processing steps [4].

Mineral lubricating oils are used in presence of air whereby oxidative chemical reactions can take place, so additives are necessary to enhance aspects of base oils performance and replace compounds which may have been lost in the refining of oil. Additives packages are typically present at around10% (w/w) of final application.

Lubricating oil additives are used to reduce the oxidative or thermal degradation of an oil, to lessen the deposition of harmful deposits on lubricated parts, to minimize rust and corrosion, to control frictional properties, to reduce wear, and to prevent destructive metal to metal contact [5-7]. Although additives of many divers types have been developed to meet special lubrication needs, their principal functions are relatively few in number [8].

Oxidation is one of the most important processes causing degradation of engine oils during service. Oil oxidation leads to formation of acidic products, insoluble materials, and sludge, depletion of additives, loss of dispersancy, increase of viscosity, etc. All of these undesirable changes are affected by other concurrent processes occurring in an operating engine such as thermal degradation, mechanochemical reactions, and metal catalysis [9]. Hence, antioxidant additives became highly required to decrease oil oxidation, with secondary effect of reducing corrosion of certain types of sensitive bearing materials [4]. Antioxidants act in two different ways: by radical scavengers, and by inhibition of peroxides [6]. Three types of additives have been proved to be successful in controlling the degradation of lubricating oils; radical scavengers, and hydro peroxide decomposers, as well as synergistic mixtures of both of them. Thus, various classes of compounds have been used as antioxidant-additives, such as phenols [10], amines [11], and heterocyclic compounds [12-13] as well as synergistic mixtures of them and also azo compounds [14-15]. In the present work, new two rhodanine derivatives have been synthesized, characterized and evaluated as antioxidants for a lubricating oil.

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. Such calculations are usually used to explore the relationship between the antioxidants molecular properties and their inhibition efficiency [16-17]. The aim of this paper is extended to discuss the relationship between quantum chemical calculations and experimental inhibition efficiencies 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 values ( ).

2. Experimental

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.

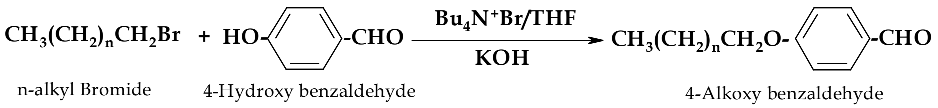
2. 3. Analysis

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 alkoxyaldehydes:

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-butyl bromide and n-decyl 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 75% yield [18].

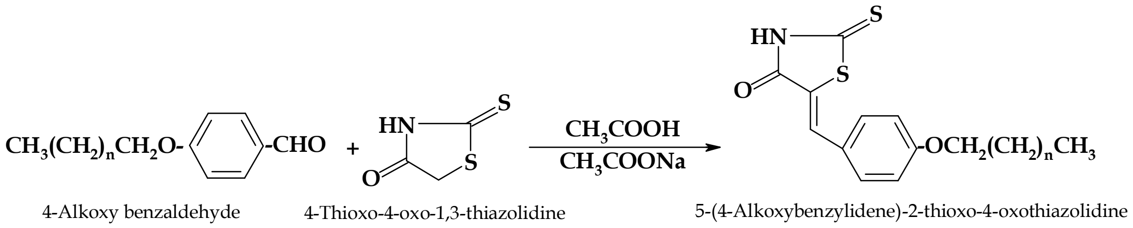


(Where n = 2, 8)

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 [19].



Where n = 2 (I) 5-(4-butoxybenzylidine)-2-thioxo-4-oxathiazalidine
n = 8 (II) 5-(4-decyloxybenzylidine)-2-thioxo-4-oxathiazalidine

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	174 -176	80
II	120 -124	85

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-664 and D- 445, respectively.

2. 6. Quantum chemical calculations

Quantum mechanical program Chem Bio draw Ultra 12 [20], was used for the molecular modeling. The calculations were based on Ab initio (HF/3-21G) and semiempirical gas phase AM1 (Austin Model 1).

3. 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 @ 15.5 ^{O}C, g / cm^3	0.8817	ASTM D - 1298
Pour Point, ^{O}C	-6	ASTM D - 97
Viscosity @ 40 ^{O}C @100 ^{O}C	52.34 7.41	ASTM D – 445 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	I 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	57.34	56.96	5.12	4.72	4.78	4.89	21.84	20.44
II	63.66	63.82	7.16	6.94	3.71	4.32	16.98	16.29

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

3.2.2. Infrared spectroscopy

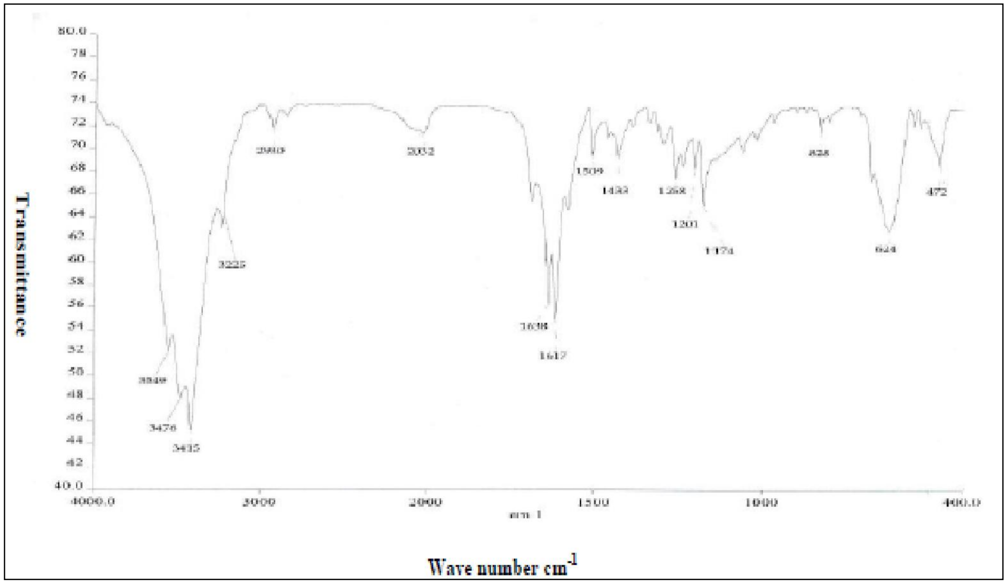


Figure 1: Infrared spectrum of the prepared compound (I)

Table 4: IR spectra of I and II

Compound	STREACHING OF, (ν , cm^{-1})						
	NH (broad)	$CH_{aliphatic}$	$C=C_{aromatic}$	C-O-C	$C=C_{aliphatic}$	$C=O^*$	Aromatic zone (banding vibration)
I	3476-3415	2930	1509	1258	1638-1617	1685	828
II	3415	2921-2849	1509	1256	1589	1689	823

* The infrared spectra of prepared compounds show($\nu_{C=O}$) 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.

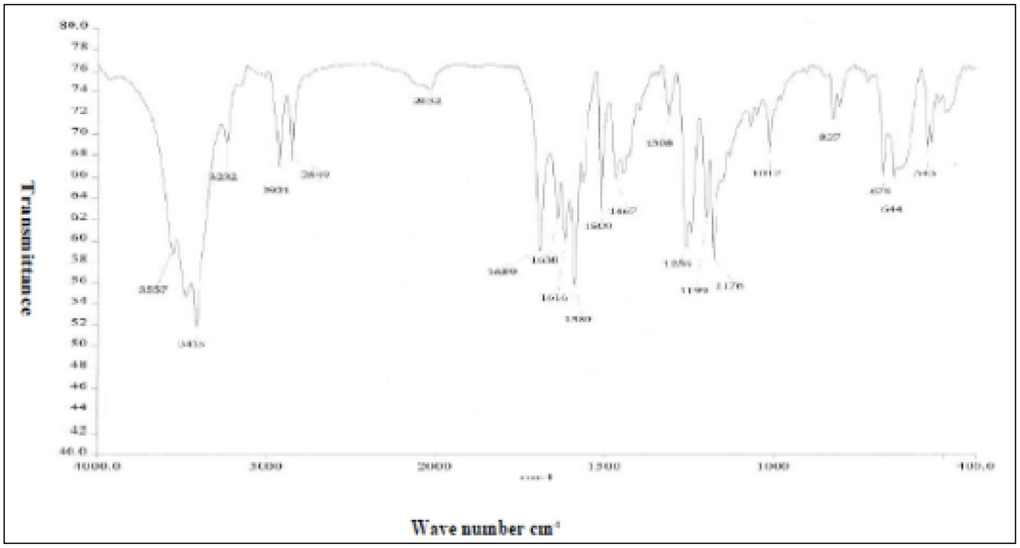


Figure 2: Infrared spectrum of the prepared compound (II)

3.2.3. ¹H-NMR spectroscopy

Table 5: Chemical structures of compounds I, II

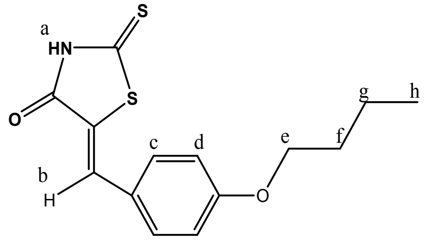
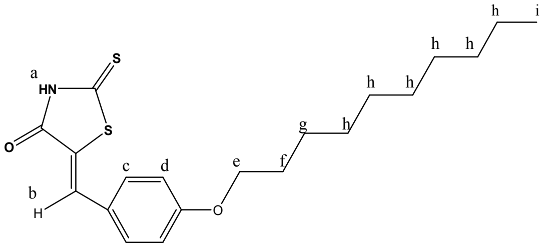
I	II
	

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	9.579	7.643 7.271	7.355	6.997	4.045	1.823	1.516	0.999	
No. of ^+H & spin multiplicity	1(s)	1(s)	2(d)	2(d)	2(t)	2(m)	2(m)	3(t)	
Compound II									
Chemical shift	9.579	7.843 7.269	7.444	6.995	4.033	1.813	1.448	1.287	0.894
No. of ^+H & spin multiplicity	1(s)	1(s)	2(d)	2(d)	2(t)	2(m)	2(m)	12(m)	3(t)

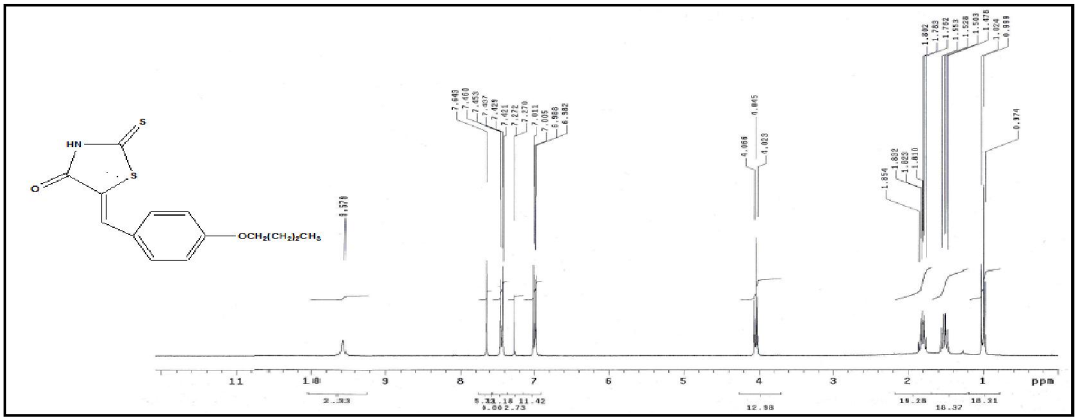


Figure 3: ^{1}HNMR of the prepared compound (I)

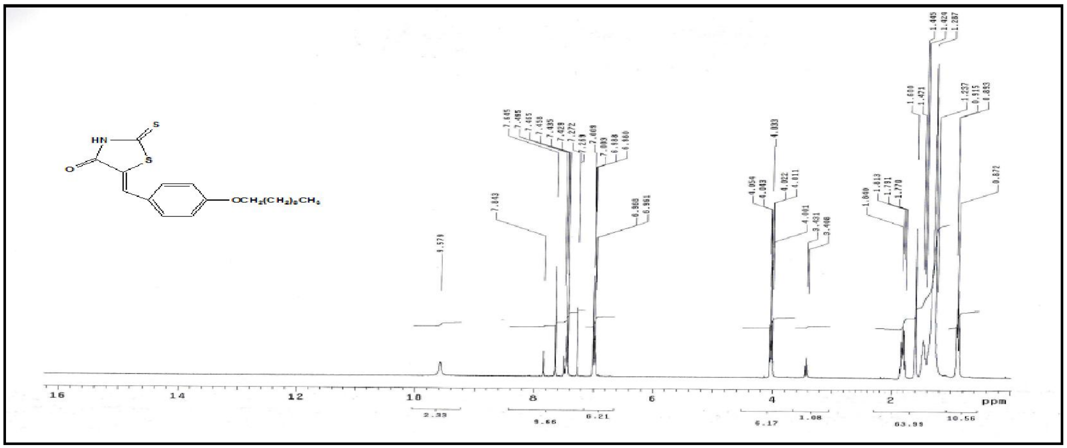


Figure 4: ^{1}HNMR of the prepared compound (II)

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

- Proton (a), which has singlet peak and chemical shift δ value of 9.579 ppm is attributed to NH proton of thiazolidine.
- Proton b (β – olefinic proton) has two singlet peaks at 7.643 and 7.271 ppm. That indicates the presence of compound (I) in two isomeric forms, Z and E respectively [21]. 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 7.335 and 6.997 ppm, respectively.
- The two protons of type (e) exhibit a triplet peak at 4.045 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 1.823 ppm.
- The two protons of type (g) appear as multiplet in their multiplicity at 1.516 ppm.
- The three protons of the type (h) appear at 0.999 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 9.579 ppm is attributed to NH proton of thiazolidine.
- Proton b (β – olefinic proton) has two singlet peaks at 7.843 and 7.269 ppm.That indicates the presence of compound (I) in two isomeric forms, Z and E respectively [21]. 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 7.444 and 6.995 ppm respectively.
- The two protons of type (e) exhibit a triplet peak at 4.033 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 1.813 ppm.
- The two protons of type (g) appear as multiplet in their multiplicity at 1.448 ppm.
- The twelve protons of type (h) appear as multiplet in their multiplicity at 1.287ppm.
- The three protons of the type (i) appear at 0.894 ppm with triplet multiplicity.

3.2.4 Mass spectroscopy

Table 7: Mass spectroscopy of compounds I & II

I **(m/z 293 ($C_{14}H_{15}NO_2S_2$)**			**II** **(m/z 377 ($C_{20}H_{27}NO_2S_2$)**		
Molecular formula	**m/z**	**Intensity**	**Molecular formula**	**m/z**	**Intensity**
$C_{14}H_{15}NO_2S_2]^{+\cdot}$	293	36.06	$C_{20}H_{27}NO_2S_2]^{+\cdot}$	377.20	17.57
$C_{12}H_{14}OS]^{+\cdot}$	206	41.29	$C_{18}H_{26}OS]^{+\cdot}$	290.02	17.59
$C_8H_6OS]^{+\cdot}$	150	100	$C_8H_6OS]^{+\cdot}$	150	100
$C_8H_5S]^{+\cdot}$	133	9.71	$C_8H_5S]^{+\cdot}$	133.05	3.32
$C_6H_5]^{+\cdot}$	77	18.80	$C_6H_5]^{+\cdot}$	77.05	9.36

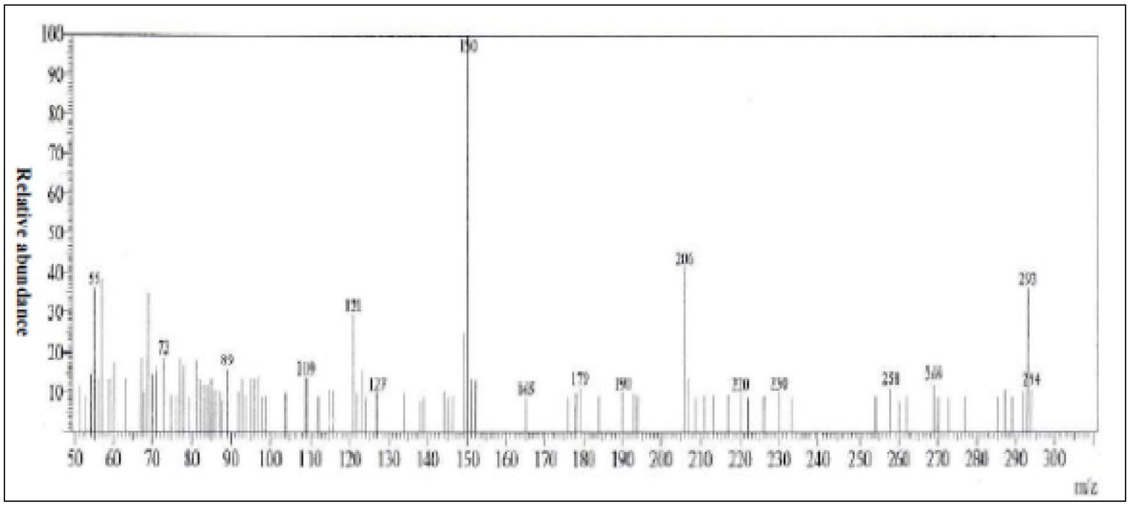


Figure 5: Mass spectra of the prepared compound (I)

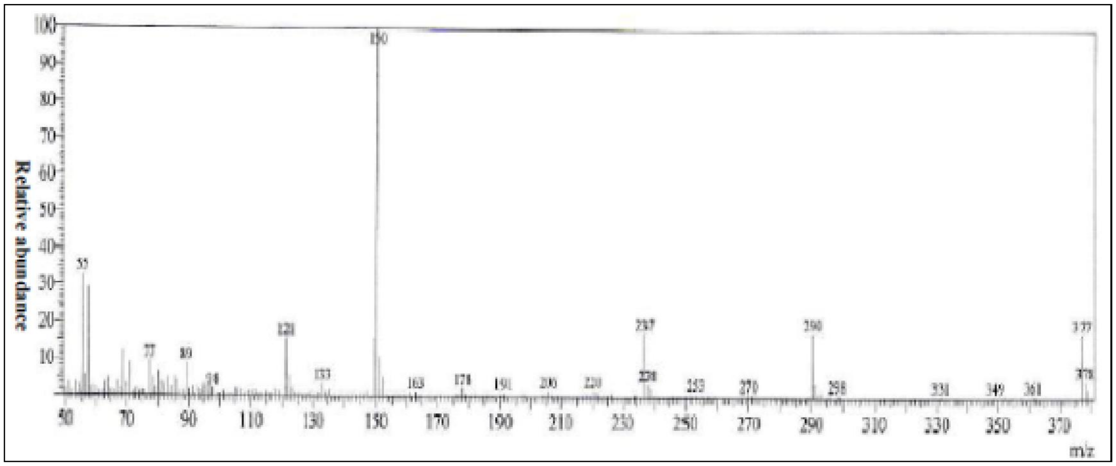
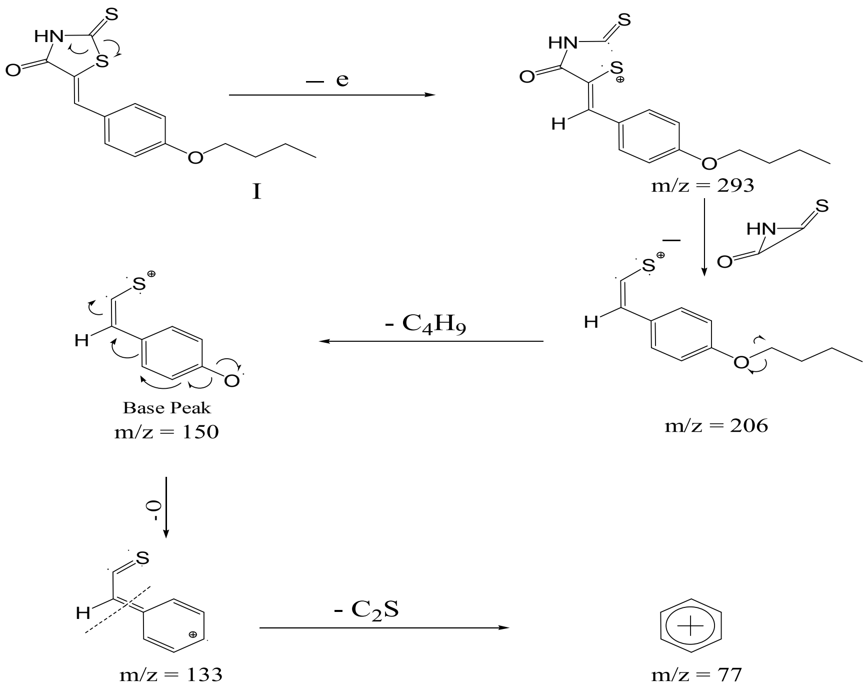


Figure 6: Mass spectra of the prepared compound (II)

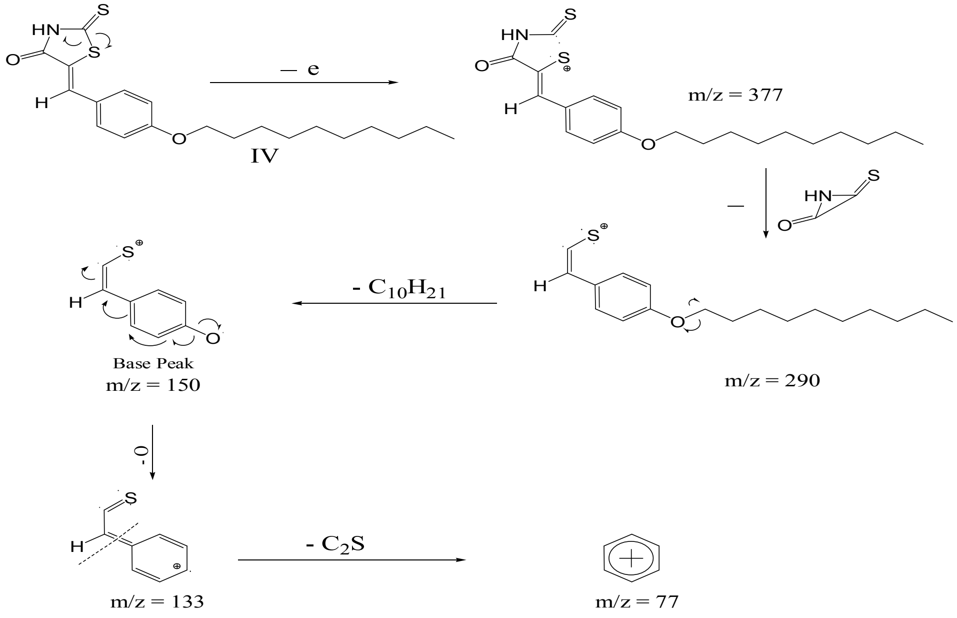
The schematic fragmentation of compounds I and II are illustrated as follows:

- **Route of fragmentation of compound (I)**:



Scheme 3: Schematic fragmentation of compound (I)

- **Route of fragmentation of compound (II):**



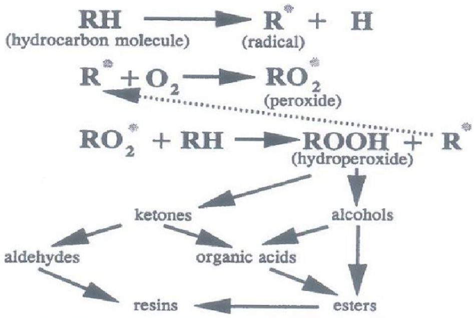
Scheme 4: Schematic fragmentation of compound (II)

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 ^{o}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.

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.



Scheme 5: Schematic representation of oxidation of mineral oil

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

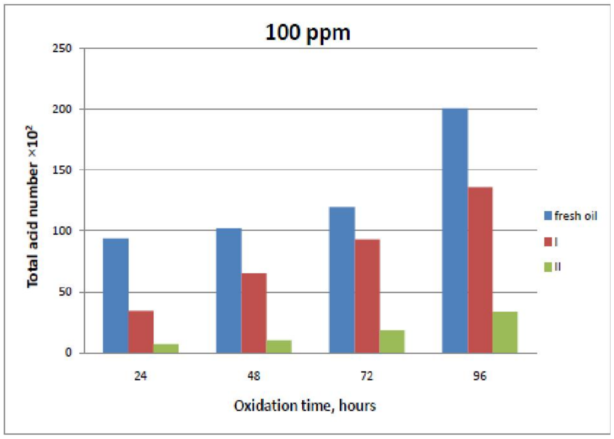
Oxidation time interval (hrs)									
Total acid numbers, mg KOH /g Sample ×10^2					**Viscosity, cst at 40 °C×10^2**				
Zero	24 hrs	48 hrs	72 hrs	96 hrs	zero	24 hrs	48 hrs	72 hrs	96 hrs
6.7	94	102	120	201	5234	5938	6433	6849	7770

Effect of substituted alkyl additives

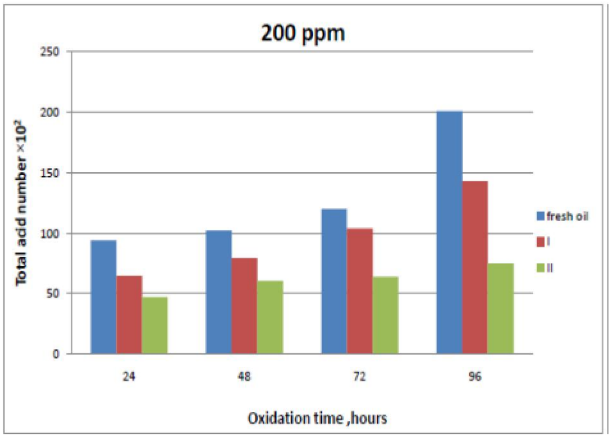
Results of the TAN in presence of the antioxidants **I** and **II**, having short and long alkyl chain lengths, respectively, after thermal oxidation of the base oil up to 96 hours, are given in Table 9. First of all, the TANs increase by increasing the additive dose from 100 to 300 part per million. Among the two rhodanine derivatives compounds I, and II, the efficiency order of these compounds towards decreasing TAN is ranked as follows: II> I.

Effect of additives concentration

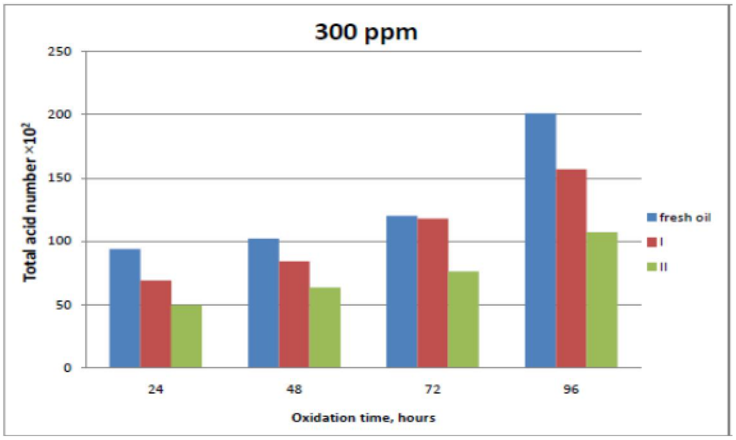
The data depicted in Figures 7a,7b and 7c represented the relation between the TAN and the oxidation periods (24, 48, 72 and 96hrs) when the additive concentrations corresponds to 100, 200 and 300 ppm for compounds **I** and **II** were used, respectively. Figure 7a shows that with the additive concentration corresponds to 100 ppm, the fresh base stock and the compound I additive gave poor results of the TAN than compound II. 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. Additives concentration, there is a marked increase in the TAN on using all the additives and the order of increasing efficiency was as follows: II > I > Fresh sample.



(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 300 ppm

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

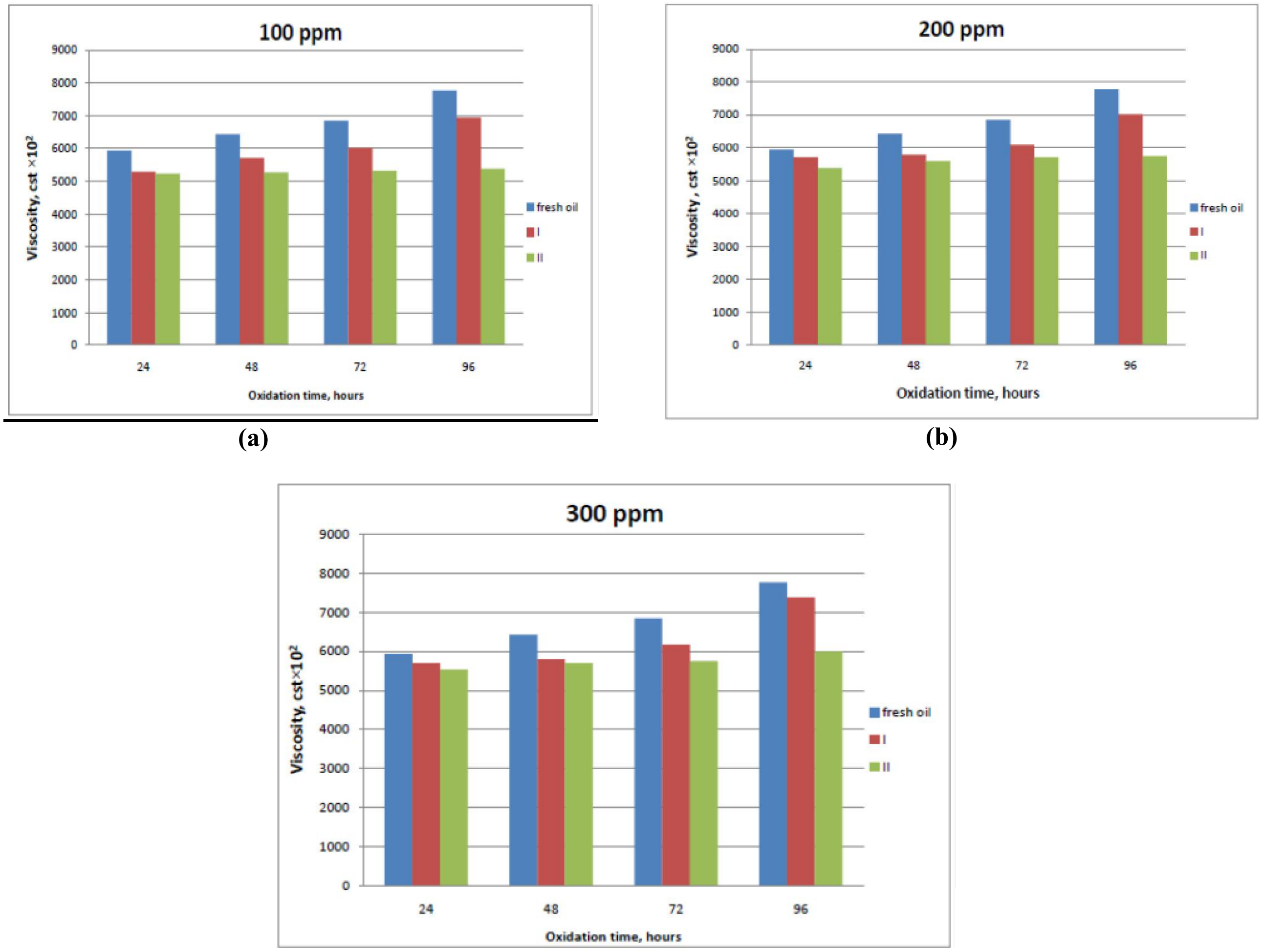
Compound	**Total acid number, mg KOH / g Sample $\times 10^2$**				
	Concentration (ppm)	**Oxidation time (hr)**			
		24	**48**	**72**	**96**
I	**100**	34.4	65.3	93.2	136.4
	200	64.8	79.2	104	143
	300	69	83.9	118	156.9
II	**100**	7.4	10.5	18.3	33.5
	200	47.1	60.6	64	75
	300	49.7	63.5	76.1	107

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 oil as a result of thermal oxidation. 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 $\times 10^2$**				
	Concentration (ppm)	**Oxidation time (hr)**			
		24	**48**	**72**	**96**
I	**100**	5290	5712	6013	6948
	200	5701	5782	6081	7021
	300	5735	5800	6170	7382
II	**100**	5236	5270	5320	5380
	200	5382	5591	5701	5739
	300	5532	5703	5750	5992



(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

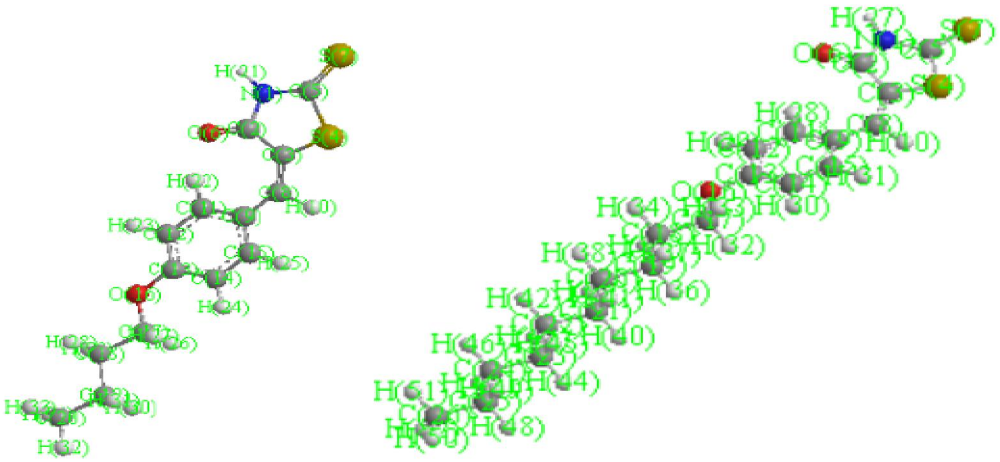
3.3.3 Quantum chemical calculations:

Geometric structures of 5-(4-butoxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine (I) and 5-(4-decyloxy-benzyl-idene)-2-thioxo-4-oxo-1,3-thiazolidine (II) are given in Figures 9a&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 10a&b and 11a&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 [22]. 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 [23]. 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 [24]. 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 [25],which facilitate oxidation inhibition process.

Table 11: Quantum Chemical Parameters

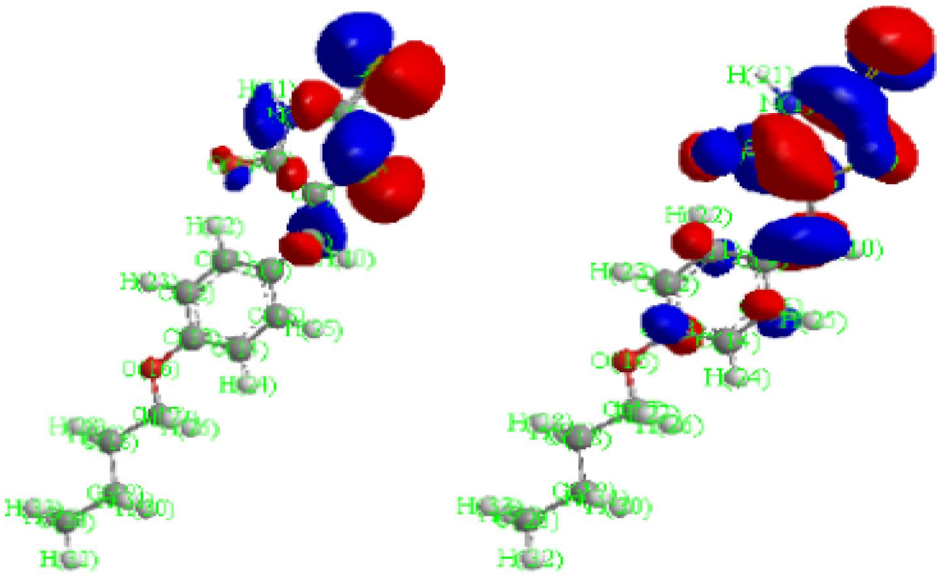
Compound	Quantum Parameters				
	Dipole Moment (Debye)	Dipole/Dipole (Kcal/mole)	E_{LUMO} eV	E_{HOMO} eV	ΔE eV $E_{LUMO} - E_{HOMO}$
Ab Initio HF/3-21G					
I	18.96	2.8985	-3.843	-7.980	4.137
II	5.981	2.8964	- 4.343	-7.798	3.455
Semiempirical AM1					
I	18.45	2.896	-3.844	-7.980	4.136
II	5.899	2.8961	- 4.341	-7.795	3.454



Structure (I) **Structure (II)**

(a) **(b)**

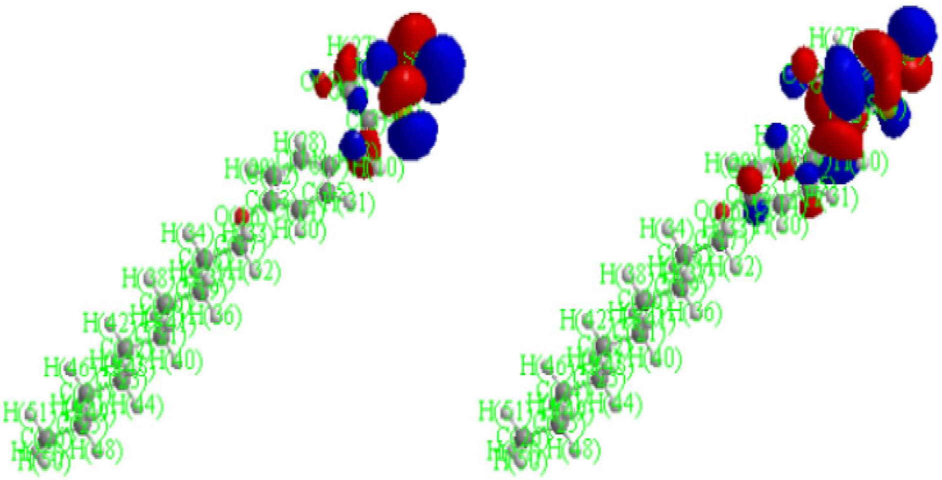
Figure 9: Optimized structures of (I) and (II)



HOMO **LUMO**

(a) **(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.

4. 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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