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Studies on Some Thiazolidinones as Antioxidants for Local Base Oil

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IN THIS work, 5 thiazolidinone derivatives of the type 5-benzylidene -2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (101), 5-(4-butoxybenzylidene)-2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (102), 5-(4-hexyloxybenzylidene)-2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (103), 5-(4-octyloxybenzylidene)-2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (104) and 5-(4-decyloxybenzylidene)-2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (105) are synthesized and characterized using conventional tools analyses. They are tested as antioxidants for local base stock and the efficiency of these compounds, as antioxidants, was monitored through studying the change in total acid number and viscosity, the results reveal that the efficiency order is ranked as follows 105 > 104 > 103 >102 > 101. The quantum chemical parameters such as the lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO) energy levels and the energy gap (E_{HOMO}-E_{LUMO}) were calculated. The experimental results were on the same line with the quantum chemical calculations.

Keywords: Base stock, Antioxidants, Oxidation stability, Total acid number, Viscosity and Thiazolidinones.

Introduction

Lubricating oils are always in contact with air, often at high temperatures [1]. Temperatures can range from ambient for transformers to over 300°C in the sump of a modern car engine. Under such conditions and in the presence of many metals, the mineral oil will undergo a series of oxidative chemical reactions leading to an increase in viscosity and acidity, which lead to the corrosion of metal parts and the formation of carbonaceous deposits [2], Therefore that reduces the efficiency of the system [3]. Usually, lubricating oils operate at higher severities of temperatures and pressure; therefore it is required to improve thermal and oxidative stability and excellent temperature-viscosity characteristics allowing the oil to meet the demanding requirements for use in industrial application [4]. Consequently, the addition of antioxidants became very required to protect the oil by decreasing the oxidative degradation during industrial application [5]. Most of the heterocyclic compounds which have compact structure possess antioxidant, anticorrosion and antiwear properties [6-8]. Heterocyclic compounds have been reported as antiwear and extreme pressure additives such as thiadiazoles and benzotriazoles [9-13]. Mohammed et al [14] studied the oxidation stability of local base stock in the presence of two antioxidants. Otherwise, Nessim et al studied the effect of some heterocyclic compounds and azo compounds as antioxidants for base oil [15-17]. Quantum chemical techniques 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 [18, 19]. This paper is an extended work of discussing the efficiency of newly prepared compounds as antioxidants for local base oil. Also, we studied the relationship between quantum chemical calculations and experimental efficiencies of the 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}) and the energy gap ΔE (E_{HOMO}-E_{LUMO}).

Experimental

Raw material and reagents

Hydro finished base oil sample was delivered from Co-operative Petroleum Company, Cairo, Egypt. All reagents purchased from Merck, Aldrich and Fluka chemical companies. They were of analytical grade and utilized without further purification.

Analysis

Melting points were determined via Gallenkamp melting point apparatus. The chemical structures of the synthesized compounds were well established via elemental analysis [using CHNS-932 (LECO) vario elemental analyzers], Infra-Red, [using a Perkin-Elmer FT-IR type 1430 spectro-photometer], ^{1}H-NMR [using ^{1}H-NMR (type varian mercury VX-300 NMR spectrometer) 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] in Micro analytical Center Laboratory, Cairo University, Giza , Egypt.

Preparation of antioxidants (101-105)

The preparation was carried out in three steps

a) Synthesis of alkoxybenzaldehydes

A solution of tetrabutylammonium bromide (0.3g,0.93 mmol), 4-hydroxybenzaldehyde (1.5g, 12.29 mmol) in dry tetrahydrofuran (20ml), powdered potassium hydroxide (0.5g, 8.9 mmol) and n-alkyl bromide (n-butyl bromide,n-hexyl bromide,n-octyl bromide and n-decyl bromide) (12.02mmol) was added and blended at room temperature for 6h. The blend was then filtered and washed with 10% cold sodium hydroxide (2 x 25ml) to remove any 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 [14, 15].

b) Synthesis of rhodanine derivatives (96-100)
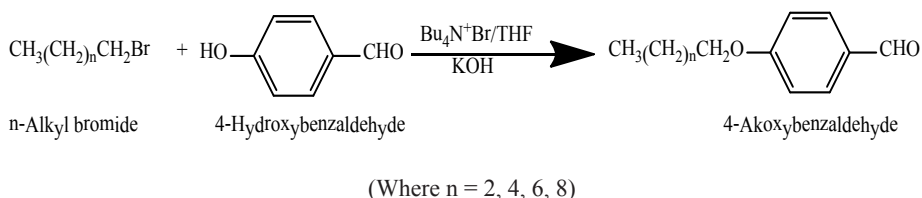*I) 5-(4-Alkoxybenzylidine)-2-thioxo-4-oxo-1,3-thiazolidine (96-99)*

4-n-alkoxybenzaldehyde (0.010 mole) is added to a solution of 2-thioxo-4-oxo-1,3-thiazolidine (1.33g,0.010 mole) in the presence of anhydrous sodium acetate (1.23g,0.015 mole) and glacial acetic acid (20 ml). The whole blend is refluxed for 2 or 3 hours, allowed to stand at room temperature and the precipitated product is separated off, washed several times with cold water and recrystallized from glacial acetic acid with ethanol (99.9%) [14, 15].

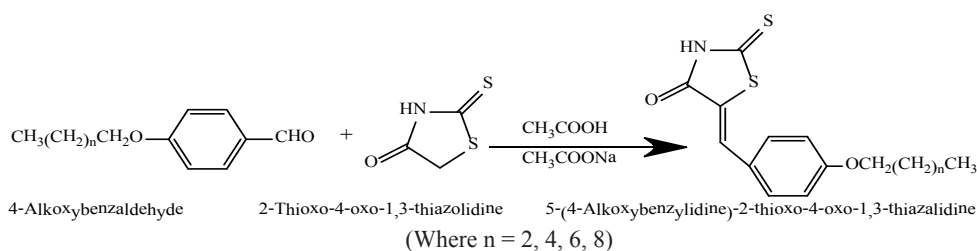*II)   5-benzylidene-2-thioxo-4-oxo-1,3-thiazolidine (100)*

5-benzylidene-2-thioxo-4-oxo-1,3-thiazolidine was obtained according to the reported method by Khazaei et al. [20].

c) Synthesis of antioxidants (101-105)

Piperidine (0.93g, 0.011 mole) is added to 2-thioxo-4-oxo-1,3-thiazolidine derivatives (96-100) in the presence of ethanol (50 ml)(0.010 mole) and the whole mixture is refluxed until the hydrogen sulphide gas ceased to evolve (~3 hours). The reaction mixture is cooled, filtered, dried and recrystallized from ethanol to give antioxidants as pale yellow crystals [21].

(Where n = 2, 4, 6, 8)

Scheme1. Synthesis of 4-n-Alkoxybenzaldehyde.

(Where n = 2, 4, 6, 8)

Scheme 2. Synthesis of 5-(4-Alkoxybenzylidine)-2-thioxo-4-oxo-1,3-thiazolidine 96-99.
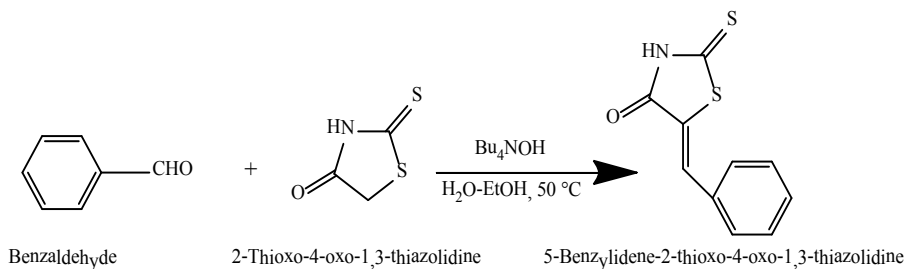
Scheme 3. Synthesis of 5-benzylidene-2-thioxo-4-oxo-1,3-thiazolidine 100.

TABLE 1. Melting point and Yield % of the synthesized rhodanine derivatives (96-100).

Compound	M.p. (°C)	Yield (%)	Ref.
5-(4-butoxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine (96)	174 -176	80	[14]
5-(4-hexyloxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine (97)	160 -164	75	[15]
5-(4-octyloxybenzylidene)-2-thioxo-4-oxo-1,3-thiazolidine (98)	130 -133	78	[15]
5-(4-decyloxy-benzylidene) -2-thioxo-4-oxo-1,3-thiazolidine (99)	120 -124	85	[14]
5-benzylidene-2-thioxo-4-oxo-1,3-thiazolidine (100)	201-204	83	[20]
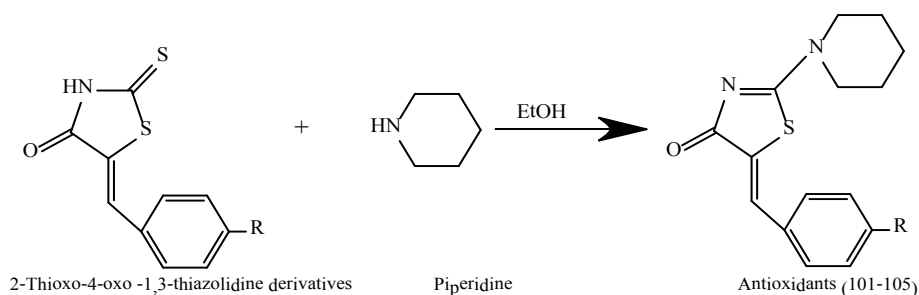
(Where R= -H, -OC$_4$H$_9$, -OC$_6$H$_{13}$, -OC$_8$H$_{17}$ and –OC$_{10}$H$_{21}$).

Scheme 4. Synthesis of Antioxidants (101-105).

TABLE 2. Melting point and Yield % of the synthesized antioxidants.

Compound	M.p. (°C)	Yield (%)	Ref.
101	212-214	80	[22]
102	118-121	78	----
103	260-263	81	----
104	200-203	77	----
105	150-152	83	----

Oxidation stability study

The oxidation test was carried out according to ASTM D-943 standard test method [23]. The oxidation cell within the static mode contained 200 ml base stock, and copper and iron wires as catalysts. The base stock sample was exposed to oxidation at 120°C with pure oxygen (99.95%) at a flow rate of 0.1 liters/hour for maximum 96 hours. The characterized compounds (101-105) were added with different concentrations (100, 200 and 300 ppm). The oil samples were studied (after 24, 48, 72 and 96 hours respectively) through the change of viscosity and total acid number (TAN). The last two parameters were done for the oxidized samples according to ASTM standard test methods D-664 and D- 445, respectively [24,25].

Quantum chemical calculations

Quantum mechanical program chem bio draw ultra 12 [26], was used for the molecular modeling. The calculations were based on Ab initio (HF/3-21G).

Results and Discussion

Physicochemical properties of the Base Oil

The physicochemical properties of the delivered base oil were carried out according to ASTM standard test methods. The results were tabulated in Table 3.

Elucidation of structures (101-105)

The chemical structure of compounds (101-105) was elucidated using the following tools of analysis:

TABLE 3. Physicochemical properties of the base oil.

Test	Result	Standard Test Method
Density @ 15.5 °C, g / cm³	0.8998	ASTM D - 1298
Pour Point, °C	0	ASTM D - 97
Viscosity @ 40 °C	172.9998	ASTM D − 445
@ 100 °C	15.83	
Viscosity Index (VI)	93.31	ASTM D − 2270
Total Acid Number (TAN)	0.00216	ASTM D − 664
Color	4	ASTM D − 1500
Ash Content, wt %	0.008	ASTM D − 482
Carbon residue	0.325	ASTM D − 524
Copper Corrosion	1a	ASTM D − 130
Flash Point, °C	232	ASTM D − 92
Aniline Point	106	ASTM D − 611
Wax Content, wt %	2.72	UOP-46

Elemental analysis

TABLE 4. Elemental analysis of (101-105) structures*.

Compound	Element							
	C%		H%		N%		S%	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
101	66.15	65.76	5.92	6.02	10.29	10.48	11.77	11.87
102	66.25	66.06	7.02	6.97	8.13	8.03	9.31	9.65
103	67.71	67.66	7.58	7.48	7.52	7.45	8.61	8.83
104	68.96	68.86	8.05	8.09	6.99	6.81	8.00	8.25
105	70.05	70.39	8.47	8.77	6.53	6.17	7.48	7.20

*The observed results were in great similarity with the calculated values.

Infrared spectroscopy

TABLE 5. IR spectra (ν , cm^{-1}) of compounds (101-105).

Compound	Stretching of (ν , cm^{-1})							
	-N-	CH aliphatic	C=C aromatic	C=N imine	C-O-C	C=C aliphatic	C=O*	Aromatic zone (bending vibration)
101	1250	2952-2914	1509	1650	-	1583	1686	825
102	1249	2922-2850	1509	1657	1256	1588	1687	826
103	1255	2921-2878	1515	1652	1254	1610	1689	824
104	1255	2918-2855	1512	1667	1253	1602	1692	828
105	1256	2922-2875	1507	1665	1258	1605	1688	823

* The infrared spectra of the prepared compounds showed (ν C = O) at some lower wave numbers as compared with the respective saturated analogues which are consistent with the existence of an α-β unsaturated carbonyl group system.
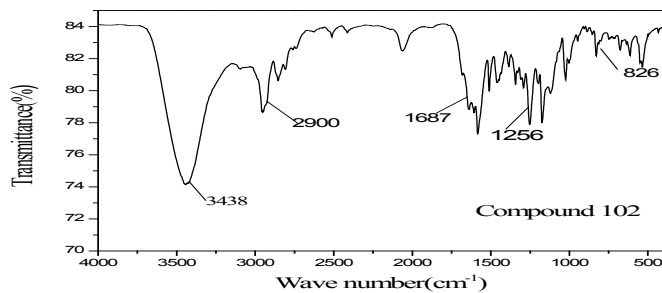
Fig. 1. Infrared spectrum of the prepared compound (102).

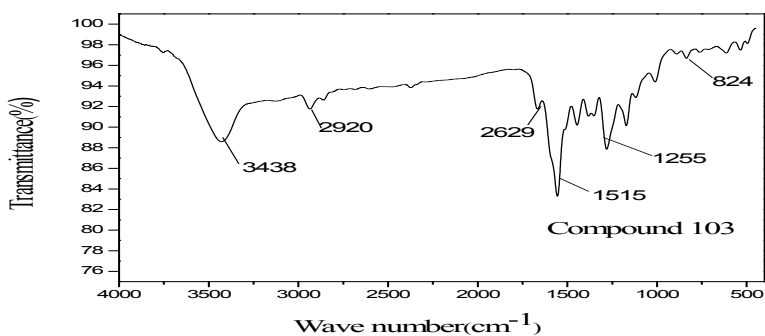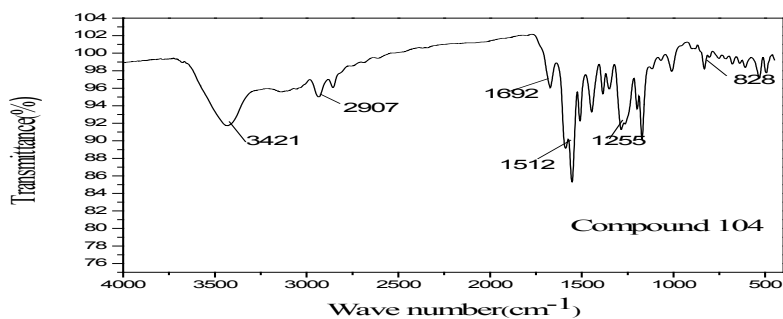**Fig. 2. Infrared spectrum of the prepared compound (103).**

Fig. 3. Infrared spectrum of the prepared compound (104).

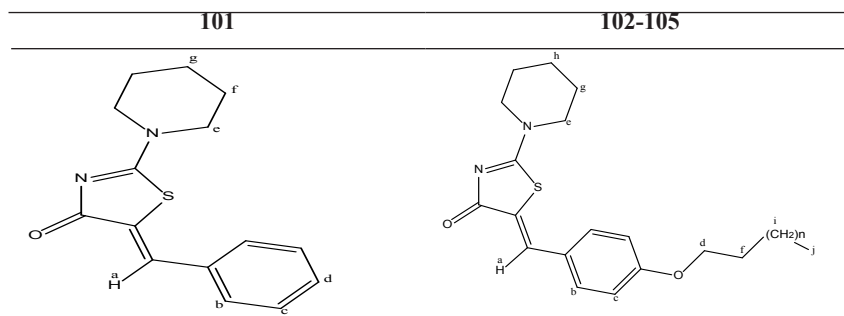*¹H-NMR spectroscopy*

TABLE 6. Chemical structures of compounds 101-105.

101	102-105

TABLE 7. ^{1}H-NMR chemical shifts (δ ppm) of compounds 101-105.

Type of H$^+$ Compound		a	b	C	d	e	f	g	h	i	j
101	Chemical shift	7.839	7.542	7.454	7.414	3.832	2.124	1.345	-	-	-
	spin multiplicity	(s)	(d)	(d)	(t)	(t)	(m)	(m)	-	-	-
102	Chemical shift	7.755	7.493	6.977	4.004	3.571	1.830	1.798	1.777	1.337	0.983
	spin multiplicity	(s)	(d)	(d)	(t)	(t)	(m)	(m)	(m)	(m)	(t)
103	Chemical shift	7.530	7.464	6.884	3.899	3.595	2.506	1.985	1.665	1.289	0.896
	spin multiplicity	(s)	(d)	(d)	(t)	(t)	(m)	(m)	(m)	(m)	(t)
104	Chemical shift	7.611	7.531	6.914	4.039	3.886	3.314	2.512	1.721	1.276	0.861
	spin multiplicity	(s)	(d)	(d)	(t)	(t)	(m)	(m)	(m)	(m)	(t)
105	Chemical shift	7.604	7.550	6.882	4.023	3.912	3.310	2.501	1.715	1.268	0.852
	spin multiplicity	(s)	(d)	(d)	(t)	(t)	(m)	(m)	(m)	(m)	(t)

Table 7 illustrated the following :
- In the case of compound 101, the data revealed that all protons are consistent with their expected values.
- Protons of type I, (102-105) having approximate δ values, (1.337-1.268 ppm, respectively).
- The highly shielded triplet (j) protons appeared at 0.983 – 0.852 ppm for compounds 102-105, respectively.
- The olefinic deshielded protons (a), with singlet splitting, having the δ values of 7.839 – 7.604 ppm for the four compounds 102-105, respectively.

- Aromatic protons (b and c) appeared at the expected δ values, where (b) protons are more deshielded than (c) protons.
- In the case of methylene protons (d), (attached directly to the withdrawing oxygen atom for 102-105), they have the values of 4.004, 3.899, 4.039 and 4.023 ppm, respectively.
- Piperidine protons (e, g and h) possessed the values consistent with the theoretical values.

Mass spectroscopy

From mass spectroscopy data, the molecular ion peaks of the prepared compounds were in good matching with the calculated molecular weight.
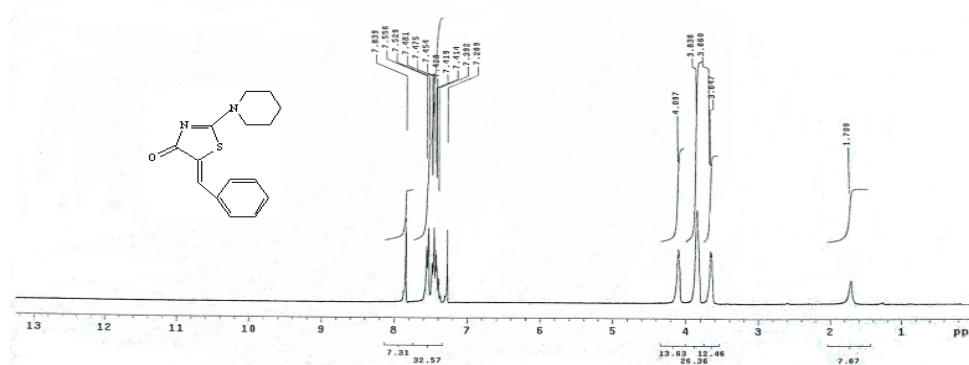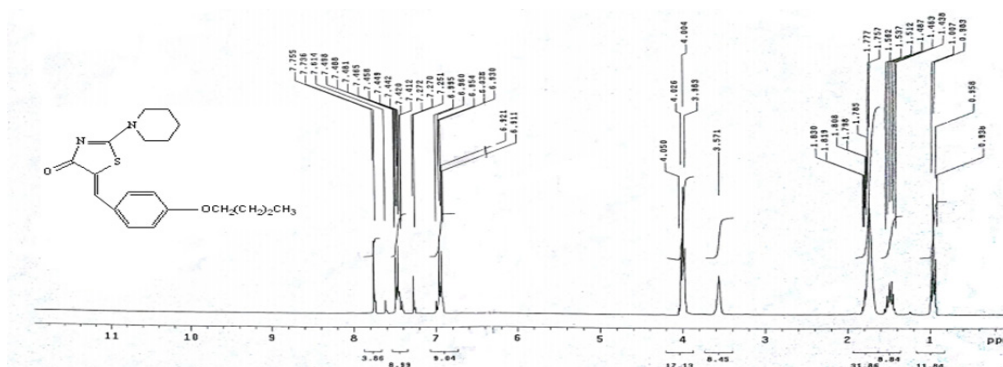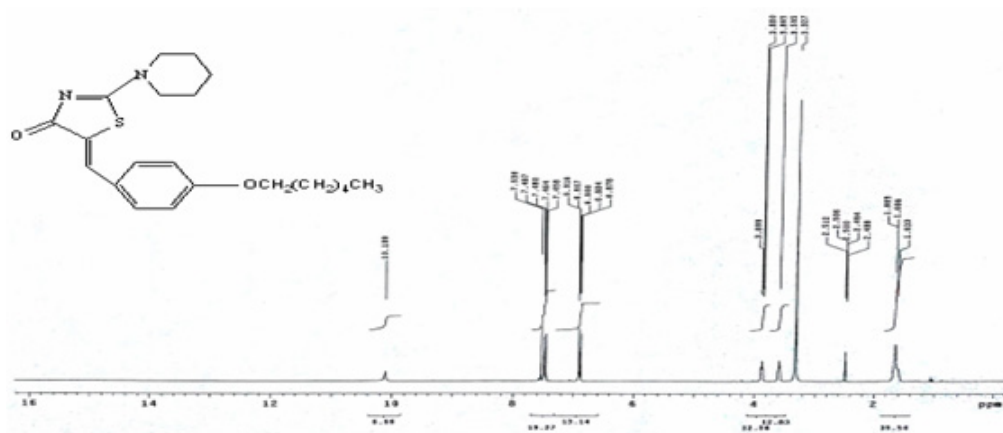

Fig. 4. ^{1}H-NMR of the prepared compound (101).

Fig. 5. ¹H-NMR of the prepared compound (102).

Fig. 6. ¹H-NMR of the prepared compound (103).

Where (s) = singlet, (d) = doublet, (t) = triplet and (m) = multiplet.

TABLE 8. Mass spectroscopy of compounds 101-105.

Compound	Molecular formula	m/z
101	$C_{15}H_{16}N_2OS$	272
102	$C_{19}H_{24}N_2O_2S$	344
103	$C_{21}H_{28}N_2O_2S$	372
104	$C_{23}H_{32}N_2O_2S$	400
105	$C_{25}H_{36}N_2O_2S$	428

Fig. 7. Mass spectra of the prepared compound (102).

Fig. 8. Mass spectra of the prepared compound (103).

Fig. 9. Mass spectra of the prepared compound (104).

Oxidation of base stock without any additives (blank sample)

Usually, the total acid number (TAN) of the oil increases by increments the oxidation time. The increasing of TAN values is due to the oxidation processes which produce peroxides. These peroxides undergo further reaction to form a lot of oxygenated compounds such as alcohols, ketones and aldehydes. The TAN is affected by the formation of carboxylic acids after oxidation and increases with increasing carbonyl formation which deteriorates the lubrication ability of the oil.

The oxidation of the base oil without additives is tabulated in Table 9. The TAN values increase from 0.00216 mg KOH/g sample with the oxidation time intervals (from 24 to 96 hours) to 2.7799 mg KOH/g sample when thermally oxidized.

Scheme 5. Oxidation of base oil.

TABLE 9. Total acid numbers (TANs) and viscosities of the base oil at different times without additives.

Oxidation time interval (hrs)									
Total acid numbers, mg KOH /g Sample $\times 10^2$					Viscosity, cst at 40 °C$\times$10				
0 hrs	24 hrs	48 hrs	72 hrs	96 hrs	0 hrs	24 hrs	48 hrs	72 hrs	96 hrs
0.216	58.79	119.7	196.0	277.99	1729.98	1818	1842	1870.1	1904.2
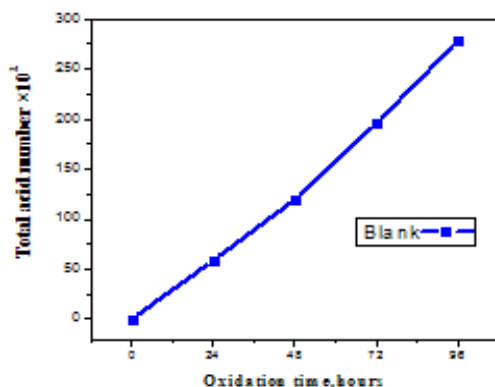
Fig. 10. Variation of TAN of the base oil without additives.
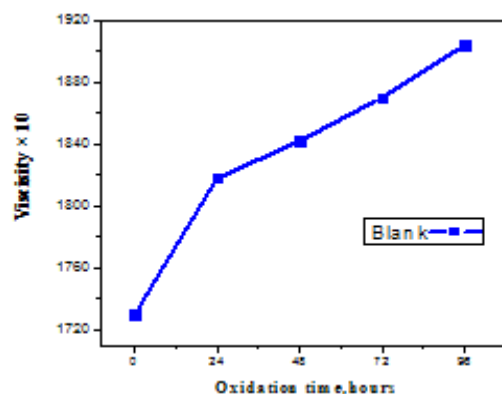

Fig. 11. Variation of the viscosity of the base oil without additives.

Evaluation of the prepared compounds as antioxidants for base stock

a) Total acid number (TAN)

The prepared antioxidants were added to the delivered base oil. The blends obtained were exposed to severe oxidation conditions at 120 °C. Samples were taken at specific time intervals (24, 48, 72 and 96 hours) of oxidation.

• *Effect of substituted alkyl additives*

Results of the TAN in existence of the antioxidants 101,102,103,104 and 105, having short and long alkyl chain lengths, respectively, after thermal oxidation of the base oil up to 96 hours, are given in Table 10. First of all, the TANs decrease by increasing the additive dose from 100 to 300 part per million. Among the five thiazolidinone derivative compounds; 101,102,103,104 and 105, the efficiency order of these compounds towards decreasing TAN is ranked as follows:

105 > 104 >103 >102 > 101.

• *Effect of additives concentration*

The data, shown in Fig.12 (a, b and c) represent the relation between the TAN and the oxidation periods (24, 48, 72 and 96 hr) when the additive concentrations correspond to 100, 200 and 300 ppm for compounds 101,102,103,104 and 105 were used, respectively. Figure 12a shows that with the additive concentration corresponds to

100 ppm, the fresh base stock and the compounds (101,102,103 and 104) gave poor results of the TAN comparing to TAN of compound 105. Figure 12b discloses that, with the concentration of 200 ppm, the order of increasing inhibition efficiency is ranked as follows: 105 >104> 103> 102> 101 > fresh. It is evident from Fig. 12c that, with 300 ppm. additives concentration, there is a noticeable increase in the TAN on using all the additives and the order of increasing efficiency was as follows: 105 >104> 103> 102> 101 > fresh sample.
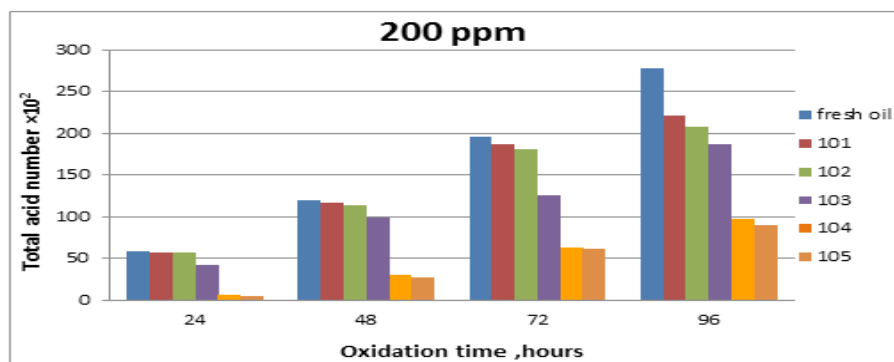
b) Viscosity

Viscosity is one of the most significant 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 increments with the operating time of oxidation. The increases in viscosity are due to the polymerization in the molecular structure. That is, during the oxidation, the oil breaks down from peroxides to carboxylic acids, which polymerize to a long chain molecular structure. The latter greatly enhances the viscosity and showing that the heavy lubricant deterioration exists. The viscosity is always reduced by the addition of additives to the oil as a result of thermal oxidation. The data of the viscosities are tabulated in Table 11 and graphically represented in Fig. 13a-c.

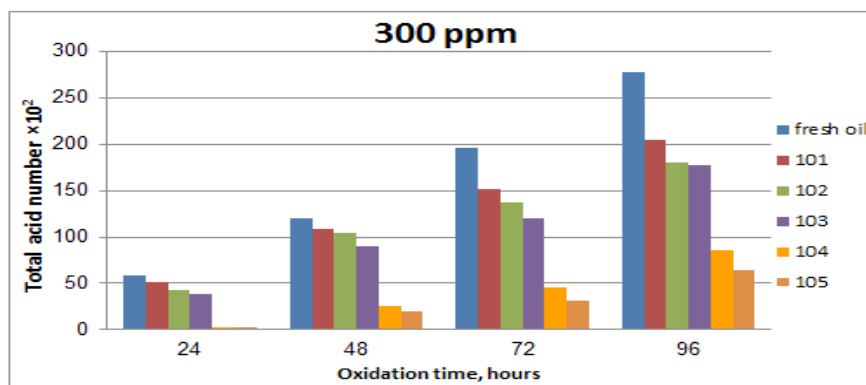**TABLE 10. TAN variation with oxidation time at different additive concentrations.**

| Compound	Concentration (ppm)	Total acid number, mg KOH / g Sample ×10²			
		Oxidation time (hours)			
		24	48	72	96
Blank	-----------	58.79	119.7	196.0	277.99
101	100	57.34	117.8	189.6	260.1
	200	56.9	115.9	187.2	221
	300	52	109	152.1	204
102	100	57.13	116.3	185	257.3
	200	56.75	114.3	180	207
	300	43	105	137	180
103	100	47	105	139	198
	200	42	98	126	187
	300	38	90	120	177
104	100	7.21	36.71	67	158
	200	6.44	30	63.29	96.66
	300	3.39	25.1	45.33	86.3
105	100	6.8	30	65	94
	200	4.8	27	61	90
	300	2.7	20	31	64.03
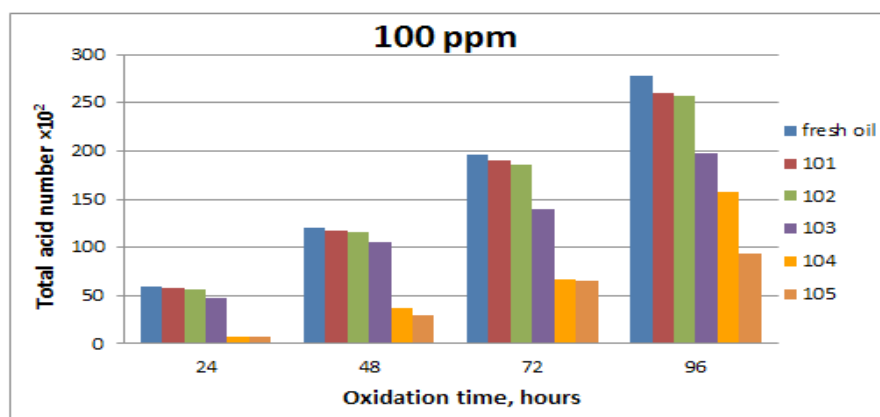
(a)

(b)

(c)

Fig. 12. Variation of TAN of the base oil without and with 101,102,103,104 and 105 additives of concentration: (a) 100 ppm, (b) 200 ppm, and 300 ppm.

**TABLE 11. Viscosity variation with oxidation time and different additive concentrations.**

Compound	Concentration (ppm)	Viscosity, cst at 40 ºC ×10			
		Oxidation time (hours)			
		24	48	72	96
Blank	-----------	1818	1842	1870.1	1904.2
101	100	1814.8	184	1869	1903
	200	1811	1838	1867	1899
	300	1806	1836.1	1861.4	1873.1
102	100	1811	1839.8	1868	1902
	200	1807.5	1836.9	1862	1897.9
	300	1799.3	1834.7	1859.1	1866.3
103	100	1801.3	1826.3	1859	1875.5
	200	1798.6	1818	1842.7	1861.3
	300	1787.3	1810.7	1841.1	1856.6
104	100	1768.9	1782.5	1821.3	1852.6
	200	1752.1	1779.6	1824.5	1839.3
	300	1748.1	1771.3	1800.9	1821.7
105	100	1751.1	1778.8	1823.7	1839.3
	200	1747.1	1764.3	1821.3	1836.5
	300	1739.7	1760.2	1799.5	1808.1
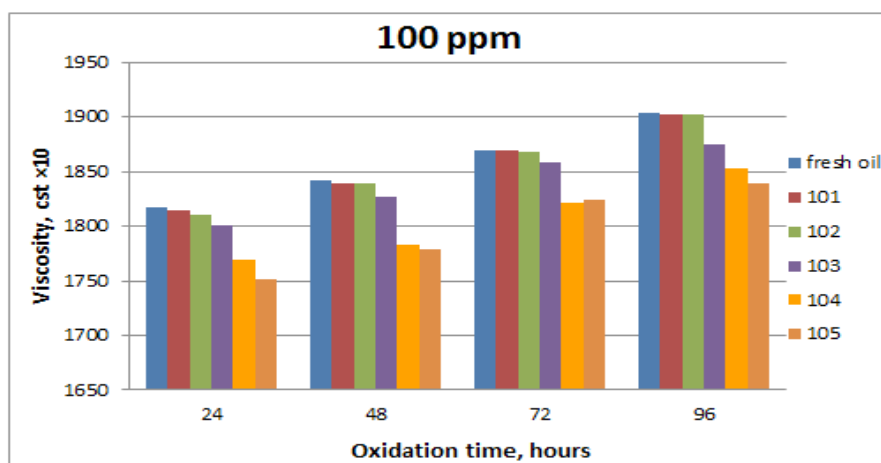
(a)
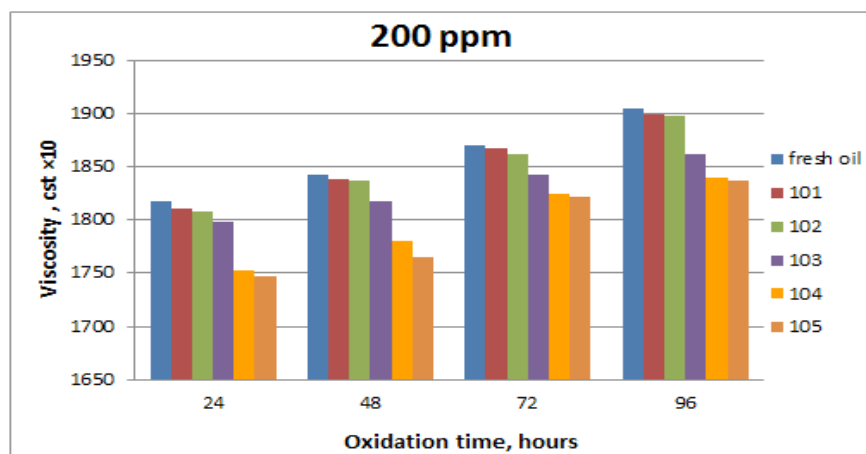
(b)
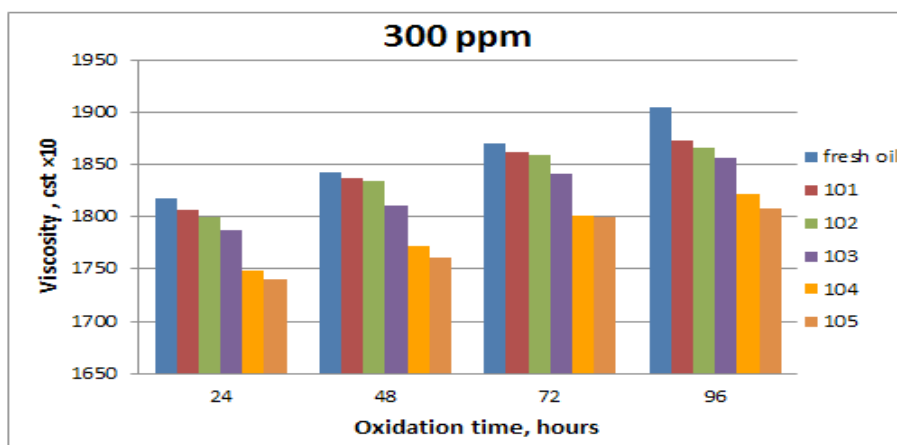
(c)

Fig. 13. Variation of the viscosity of the base oil without and with 101,102,103,104 and 105 additives of concentration: (a) 100 ppm, (b) 200 ppm, and 300 ppm.

Quantum chemical calculations

Geometric structures of 5-benzylidene -2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (101), 5-(4-butoxybenzylidene)-2-(1-piperidinyl)-4-oxo-1,3-thiazolidine(102),5-(4-hexyloxybenzylidene)-2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (103), 5-(4-octyloxybenzylidene) -2-(1-piperidinyl) -4-oxo- 1,3-thiazolidine (104) and 5-(4-decyloxybenzylidene)-2-(1-piperidinyl)-4-oxo-1,3-thiazolidine (105) are given in Fig. 14 (a-e) , respectively. The optimized molecular structures of the studied molecules, using Ab initio (HF/3-21G), are shown in Fig. 15 a & b , 16 a & b, 17 a & b,18 a & b and 19 a & b , respectively. The calculated quantum chemical indices of E_{HOMO}, E_{LUMO} and the ΔE (E_{HOMO} - E_{LUMO}) energy gap data are given in Table 12.

It was reported that the lower values of the energy gap (ΔE) mean good inhibition efficiencies because the energy required to remove an electron from the last occupied molecular orbital is low, which facilitate the oxidation inhibition process [27]. Therefore from the data given in Table 12, compound (105) was the best antioxidant for the local base oil which is consistent with the experimental results.

TABLE 12. Quantum Chemical Parameters.

Quantum Parameters	101	102	103	104	105
E_{LUMO} (eV)	- 4.641	- 4.298	-3.028	-3.055	-3.045
E_{HOMO} (eV)	-9.634	-8.882	-6.246	-6.246	-6.242
ΔE (eV) $E_{LUMO} - E_{HOMO}$	4.993	4.584	3.218	3.201	3.197

Structure (101)

(a)

Structure (102)

(b)

Structure (103)

(c)

Structure (104)

(d)

Structure (105)

(e)
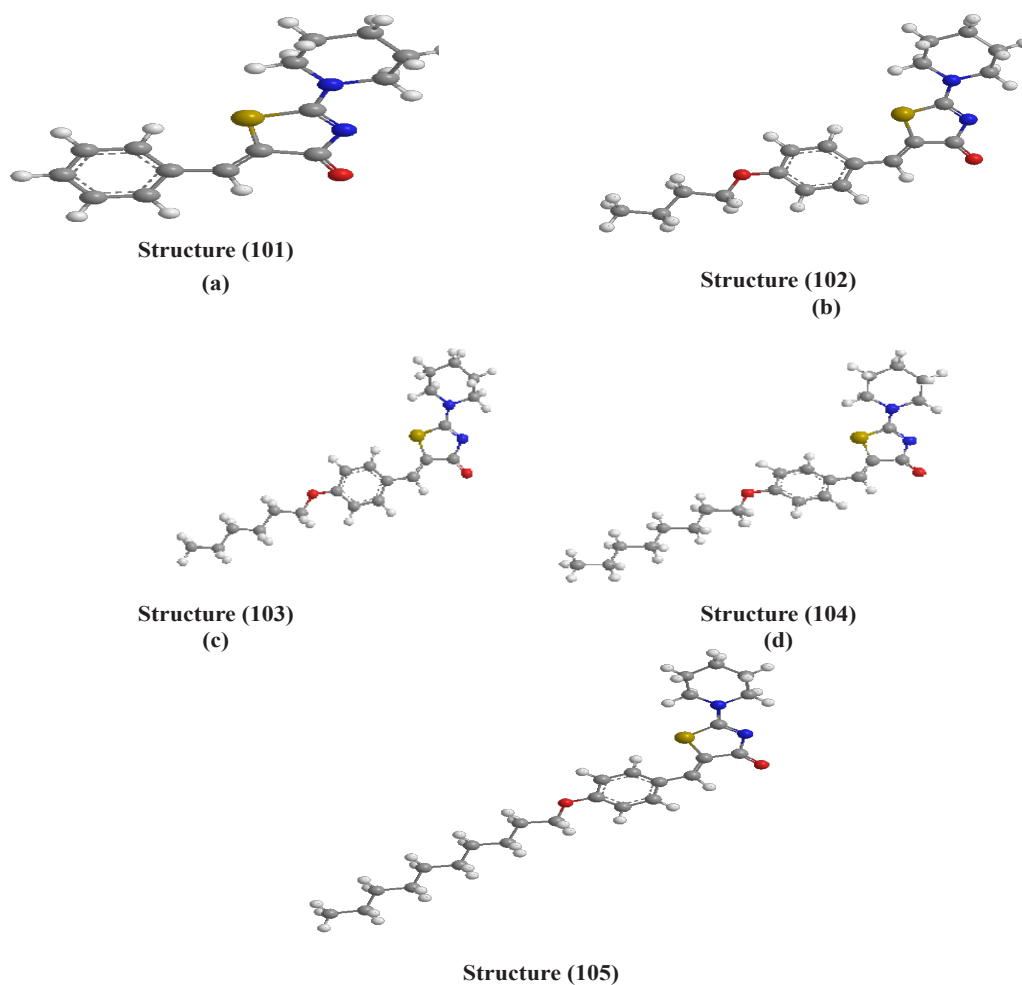
Fig. 14. Optimized structures of (101- 105).
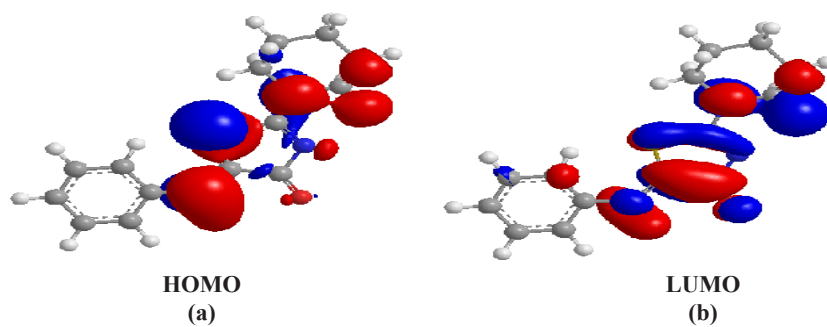
HOMO

(a)

LUMO

(b)

Fig. 15. The frontier molecule orbital density distributions of (101).

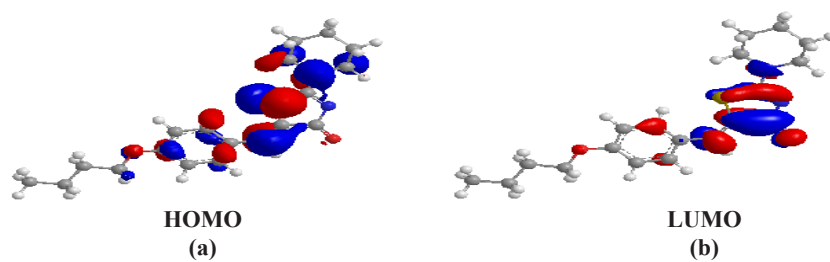**Fig. 16. The frontier molecule orbital density distributions of (102).**

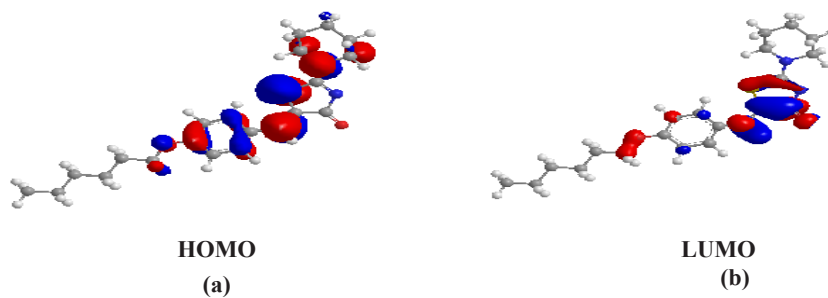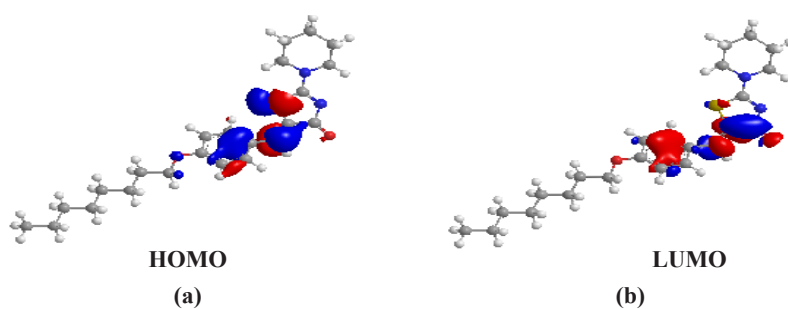**Fig. 17. The frontier molecule orbital density distributions of (103).**

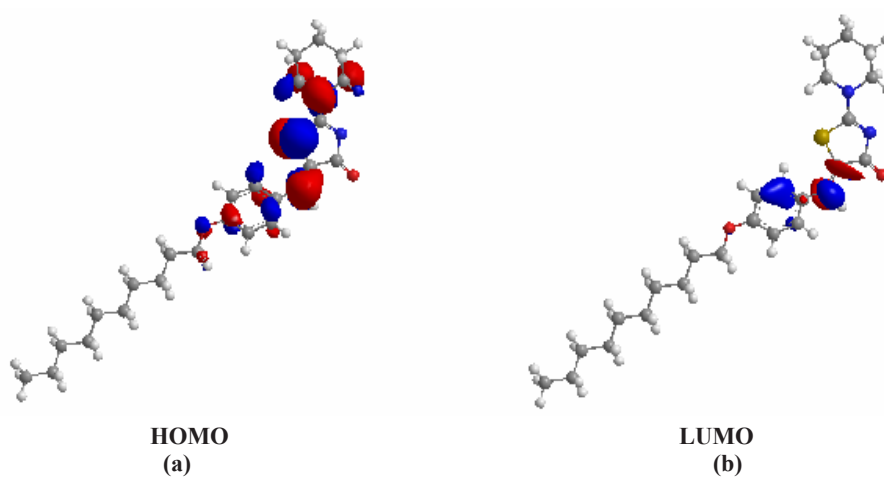**Fig. 18. The frontier molecule orbital density distributions of (104).**

Fig. 19. The frontier molecule orbital density distributions of (105).

Conclusion

The results obtained in this paper, show the following :

- Increasing the oxidation time, always increase both of the viscosity and the total acid number of the base stock.
- The prepared antioxidants (101,102,103,104 and 105) proved to be successful in controlling the oxidation stability of the base oil.
- We noticed for compound (105), with the long hydrophobic part, has the most efficiency.
- The data reveals that the most effective concentration is (300 ppm).
- Quantum chemical calculations were found to give good reasonable correlation with the results obtained by viscosity and total acid number (TAN).

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دراسه علي بعض الثيازوليدينونات كمثبطات اكسده للزيوت الاساسيه المحليه

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في هذا العمل تم تحضير خمس مشتقات الثيازوليدينونات من نوع ٥-بنزيلدين-٢- (١-بيبريدينيل)-٤- اوكسو-١، ٣-ثيازوليدين (١٠١) ، ٥-(٤- بيتوكسي بنزيلدين)-٢-(١-بيبريدينيل)-٤- اوكسو-١، ٣-ثيازوليدين (١٠٢) ، ٥-(٤- هكسيلوكسي بنزيلدين)-٢-(١-بيبريدينيل)-٤- اوكسو-١، ٣-ثيازوليدين (١٠٣) ، ٥-(٤- اوكتيلوكسي بنزيلدين)-٢-(١-بيبريدينيل)-٤- اوكسو-١، ٣-ثيازوليدين (١٠٤) ، ٥-(٤- دسيلوكسي بنزيلدين)-٢-(١-بيبريدينيل)-٤- اوكسو-١، ٣-ثيازوليدين (١٠٥) وقد تم التأكد من تركيبهم البنائي من خلال الادوات التقليديه للتحليل وتم اختبارهم كمثبطات اكسده للزيوت الاساسيه المحليه من خلال دراسه التغير في عدد الحمض الكلي واللزوجه وقد اظهرت النتائج ان ترتيب كفائه هذه المركبات المختبرة على النحو التالي ١٠٥<١٠٤<١٠٣<١٠٢<١٠١ . تم حساب طاقه كلا من المدار الجزيئي المشغول الاعلي (هومو) و المدار الجزيئي الغير مشغول الادنى (لومو) وفجوة الطاقه (فرق الطاقه بين المدارين هومو ولومو) للمركبات الخمس المحضره. واظهرت الحسابات الكيميائيه الكميه للمركبات المحضرة تطابقاً جيداً مع النتائج التجريبيه.