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RESEARCH ARTICLE

PREPARATION AND EVALUATION OF SOME AZO-PHENOL DERIVATIVES AS ANTIOXIDANTS FOR EGYPTIAN BASE STOCK (I)

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ABSTRACT

The oxidation stability of local base stock in the presence of two prepared Azo-compounds, namely 2-sec-butyl-4-((4-methoxyphenyl)-diazanyl) phenol (I) and 2-sec-butyl-4-((4-nitrophenyl)-diazanyl) phenol (II), was studied. The structures of the prepared compounds were carefully investigated via elemental analysis, I.R., ¹H-NMR spectroscopy, and electron ionization mass spectroscopy (EI-MS). The oxidation reaction was tested using the change in total acid number (TAN), viscosity, and infrared (IR) spectroscopy. The data showed that compound (I) is more efficient than compound (II). The quantum chemical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, energy gap ($E_{\text{HOMO}}-E_{\text{LUMO}}$), the dipole moment and charge densities were calculated. The theoretical calculations were in good agreement with experimental results.

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INTRODUCTION

A lubricant is a substance introduced between two moving surfaces to reduce friction, improve efficiency, and reduce wear. A lubricant may also serve the function of dissolving or transporting foreign particles, carrying away contaminants and debris, preventing corrosion or rust, sealing clearances, and dissipating heat (Dieter, 1984; Bhushan, 2002; Ludema, 1996). Base oils are the major components of lubricants, representing usually 85% or more of the formulation. The base oil is produced from petroleum crude oil by various processing steps (Haus et al., 2003). Mineral lubricating oils are used in present of air whereby oxidative chemical reactions can take place, so additives are necessary to enhance aspects of base oil performance and replace compounds which may have been lost in the refining of oil. Additives packages are usually around 10% w/w of the final lubricant. Many additives have been developed to meet special lubrication needs such as reducing the oxidation and thermal degradation of base oil. Also they reduce wear, minimize rust and corrosion, lessen the deposition of harmful deposits on lubricated parts and prevent destructive metal-to-metal contact (Allison, 1973; Allyson et al., 2001; Vamos, 1978). Oxidation is one of the most important reactions 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 (Korcek et al., 1986). Hence, antioxidant additives became highly required to decrease oil oxidation, with secondary effect of reducing corrosion of certain types of sensitive bearing materials (Haus et al., 2003). Antioxidants act in two different ways by radical scavengers, and by inhibition of peroxides (Allyson et al., 2001). 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. It is well known that organic compounds which act as inhibitors are rich in heteroatoms, such as sulphur, nitrogen, and oxygen (Hosseini et al., 2003; Subramanyam et al., 1993). These compounds and their derivatives are excellent oxidation inhibitors in a wide range of media and are selected essentially from empirical knowledge based on their macroscopic physicochemical properties. Azo compounds were used as antioxidants in lubricating oils (John et al., 1985; Edwin et al., 1946).

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity (Kraka and

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Cremer, 2000). The employed computational methodology (Karelson and Lobanov, 1996) and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study (Hinchliffe, 1994; Hinchliffe, 1999). The study of oxidation processes and their inhibition by organic Inhibitors is a very active field of research (Bouayed *et al.*, 1999). Many researchers report that the inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons (Quraishi and Sardar, 2002; Stupnišek-Lisac *et al.*, 1994). The inhibiting mechanism is generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface (Touhami *et al.*, 2000; Tang *et al.*, 2006). Recently, theoretical prediction of the efficiency of oxidation inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations (Hosseini *et al.*, 2003). In the present work, new two azo-phenol derivatives have been prepared and evaluated as antioxidant for base oil.

Experimental

Raw Materials

Base Stock Oil

Egyptian hydrofinished base stock oil (HBS) was obtained from Co-operative Petroleum Company.

Reagents

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

Preparation of additives (I and II) (Trzaska and Galewski 2009; Craig, R.'a Gerald *et al.*, 1975)

(i) Diazotization

A mixture of aniline derivatives (4-methoxyaniline, 4-nitroaniline) (0.05 mol) was dissolved in distilled water and (0.05 mol) of dilute hydrochloric acid. The mixture was cooled in ice bath to zero. Sodium nitrite (0.05 mol) was added drop wise while stirring. Maintaining the temperature from 0-5°C, the resulting mixture was stirred for 1h.

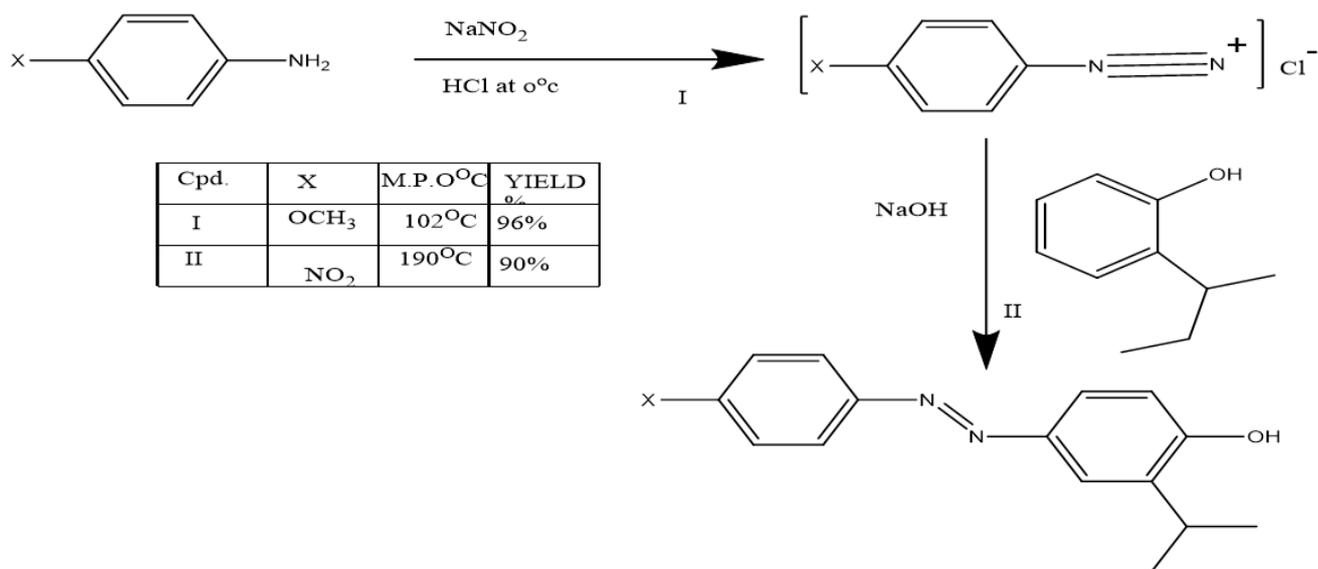
(ii) Coupling

A solution of phenol of (0.05 mol) phenol was dissolved in (0.05 mol) NaOH in 15 ml of water, was cooled to 0-5°C in an ice bath. This solution was then gradually added to the prepared diazonium solution. The mixture was stirred for further 20 min. The product was acidified by acetic acid. The product was filtered, washed with distilled water and recrystallized from acetic acid.

The main scheme of preparation is shown as follows

Oxidation stability study

The oxidation test was carried out according to ASTM D-943 standard method. The operating temperature was changed to 120°C instead of 90°C. The oxidation cell in the static mode contained 200 ml. base stocks, and activated copper and iron wires Catalysts. The base stock sample was subjected to oxidation with pure oxygen (99.95%) at a flow rate of 0.1 liter/hour for maximum 96 hours. The characterized azo-phenol derivatives compounds (I-II) were added in different concentrations (200, 400 and 600 ppm). The oil sample after, 24, 48, 72 and 96 hours of oxidation time were analyzed for viscosity, total acid number and infra-red spectroscopy.



(Scheme I)

Total Acid Number (TAN) and viscosity

Total acid number and viscosity were carried out according to ASTM standard test methods (D-664 and D- 445), respectively).

FT-IR Spectroscopy

Infra-red spectra of the oxidized samples at different periods were recorded on FT-IR Spectrophotometer, Model 960M000g, ATI Mattson Infinity Series, USA. The spectra of the studied samples were measured in the range of 4000 – 400 cm^{-1} with a suitable scan resolution 4 cm^{-1} and scan rate 32 $\text{cm}^{-1}/\text{min}$. Elemental analyses were carried out in the Micro analytical center, the center publication for research, Cairo, Egypt. By Elementary Viro El Microanalysis. ^1H NMR spectra recorded on a Varian 300 MHz (Germany 1999) using TMS as internal standard (Cairo University). Mass spectroscopy using direct inlet unit (D1-50) of SHIMADZU GC/MS-QP5050A. At the regional center for mycology; AL-Azhar university.

RESULTS AND DISCUSSION

The physicochemical properties of the base stock are carried out according to ASTM standard test methods. The results are tabulated in Table (1)

Table 1. Show the physicochemical properties of the Base Stock

Test	RESULT	TEST METHOD
Density @ 15.5 °C, g / L	0.8817	ASTM D - 1298
Pour Point, °C	-6	ASTM D - 97
Viscosity @ 40 °C	52.34	ASTM D - 445
@ 100 °C	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	I a	ASTM D - 130
Flash point, °C	220	ASTM D - 92
Aniline point	100.5	ASTM D - 611
Molecular Weight	468.9	

Confirmation of the structures for I and II

The structure of I and II is elucidated via the following tools of analysis:

Elementary analysis of I and II

Table 2. Calculated and observed data of compounds I and II

Element Cpd.	C%		H%		N%	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
I	71.81	71.54	7.09	6.84	9.85	9.61
II	64.95	63.96	6.41	5.01	13.37	13.69

Table 3. Infra-Red spectra of I and II

Cpd.	Stretching of, (ν , cm^{-1})						
	OH	CH _{aromatic}	CH _{aliphatic}	C=C	N=N	C-O-C	NO ₂
I	3550-3415	2962	2868	1584	1453	1251	-
II	3416 broad	2961	2874	1593	1455	-	134

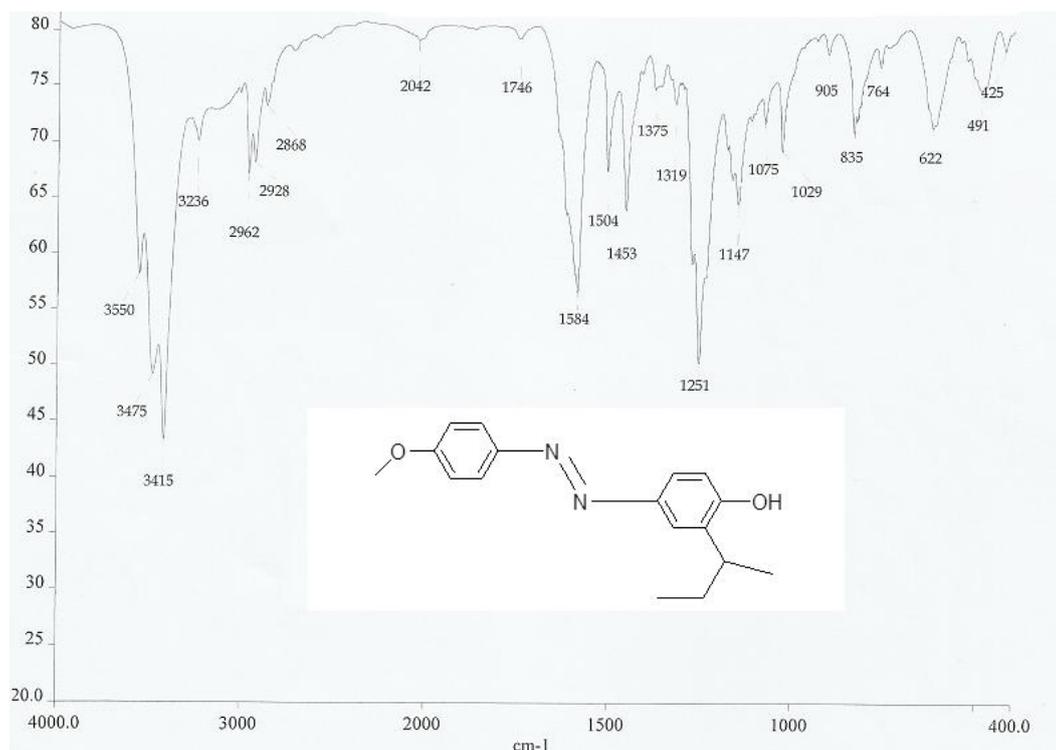


Fig. 1. Infrared spectrum of the prepared compound (I)

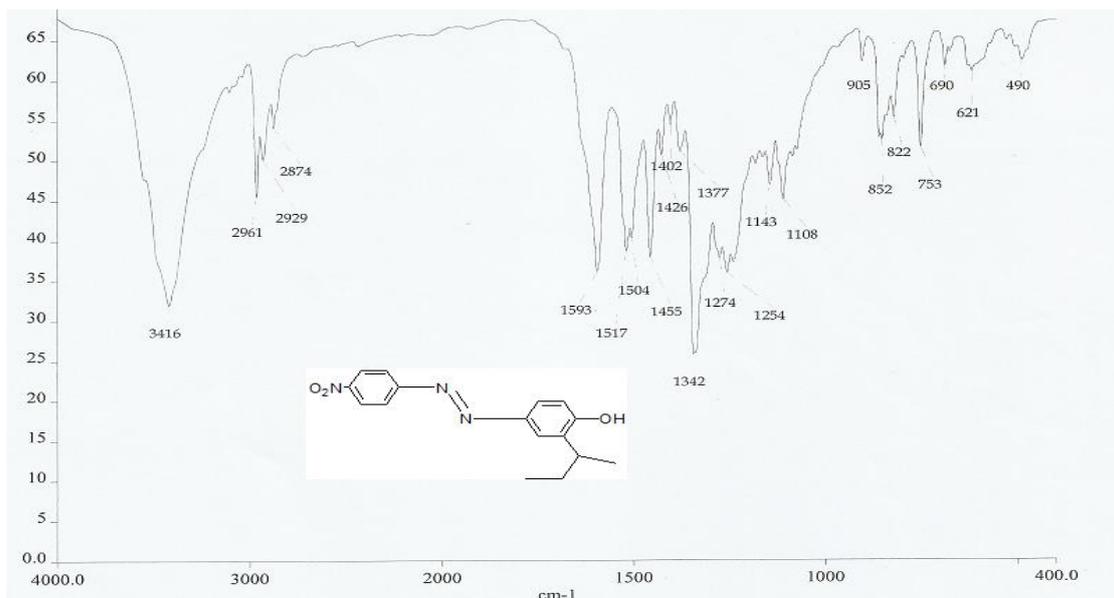


Fig. 2. Infrared spectrum of the prepared compound (II)

Table 4. Chemical Shifts of compound (I, II)

I					II							
Type of proton	a	b	C	d	e	F	g	h	i	j	K	
Chemical Shift ppm	I 10.03	7.81	7.65	7.57	7.09	6.95	3.85	3.33	3.05	1.61	0.83	
	II 10.5	8.38	7.97	7.72	7.02	6.61	3.06	1.9	1.61	0.79	-	
Spin multiplicity	I s	s	d	d	d	d	s	m	m	d	t	
	II s	d	d	s	d	d	m	m	d	t	-	

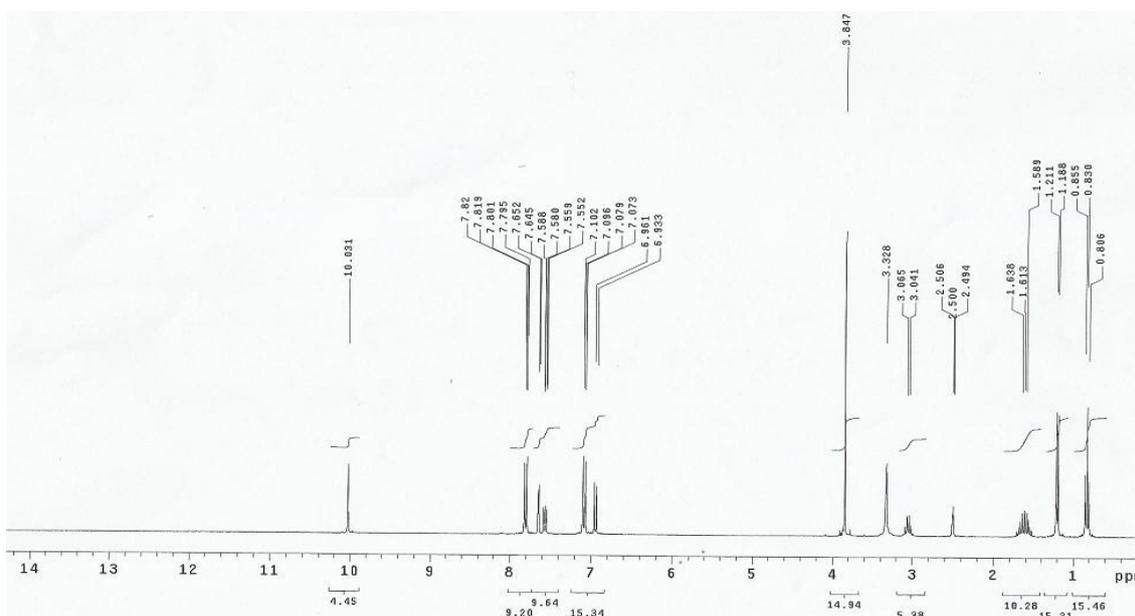


Fig. 3. ¹H NMR of the prepared compound (I)

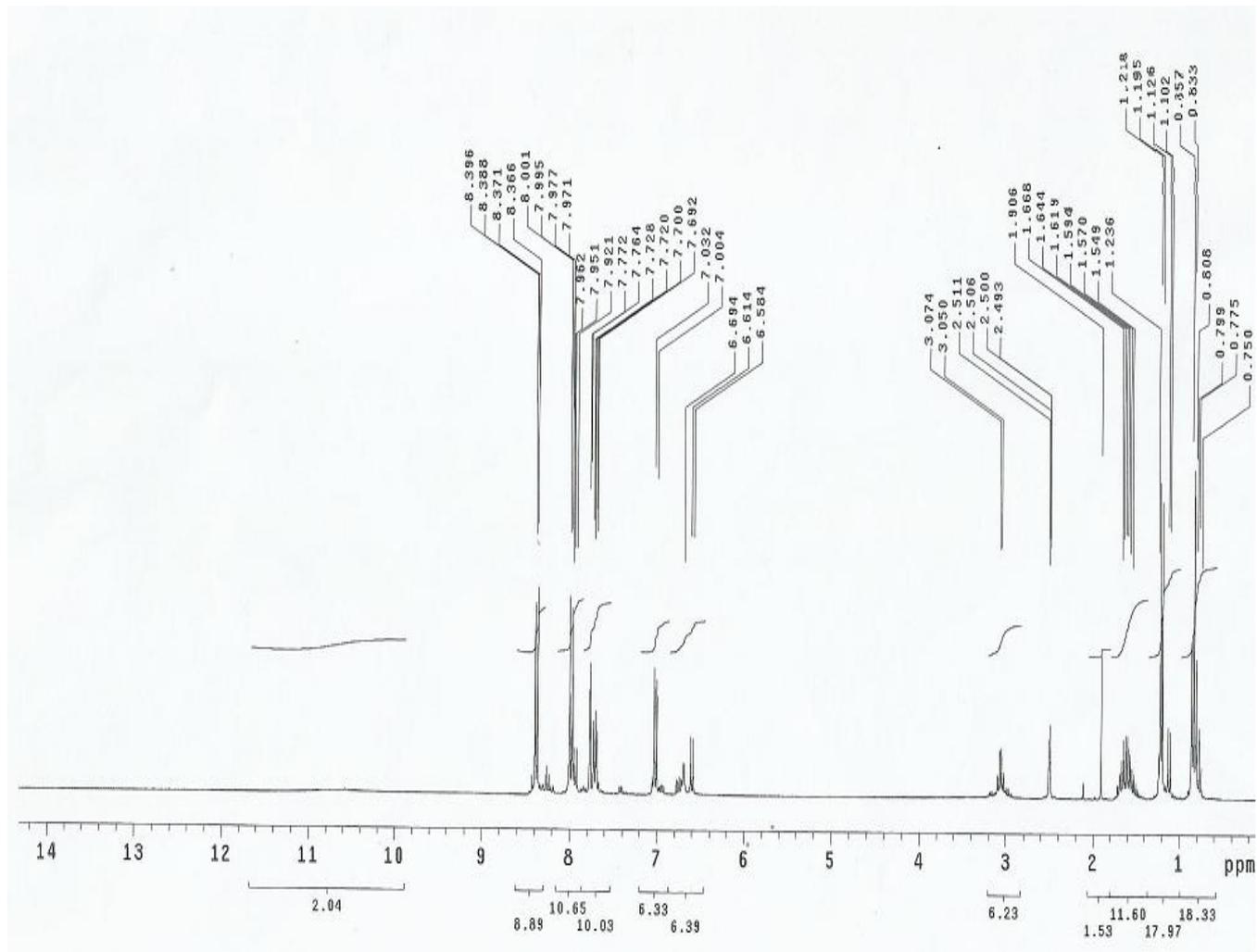
Fig. 4. ^1H NMR of the prepared compound (II)

Table 5. Mass spectra for (I)

ROULE A		ROULE B	
m/z	Molecular Formula	m/z	Molecular formula
284	$\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2]^+$	284	$\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2]^+$
227	$\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_2]^+$	253	$[\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}]^+$
107	$\text{C}_7\text{H}_7\text{N}_2\text{O}]^+$	177	$[\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}]^+$
77	$\text{C}_6\text{H}_5]^+$	149	$[\text{C}_{10}\text{H}_{13}\text{O}]^+$
		93	$[\text{C}_6\text{H}_5\text{O}]^+$

Table 6. Mass spectroscopy for (II)

ROULE A		ROULE B	
m/z	Molecular Formula	m/z	Molecular formula
299	$\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_3]^+$	299	$\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_3]^+$
242	$\text{C}_{12}\text{H}_8\text{N}_3\text{O}_3]^+$	253	$\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}]^+$
150	$\text{C}_6\text{H}_4\text{N}_3\text{O}_2]^+$	149	$\text{C}_{10}\text{H}_{13}\text{O}]^+$
122	$\text{C}_6\text{H}_4\text{NO}_2]^+$	120	$\text{C}_8\text{H}_8\text{O}]^+$
76	$\text{C}_6\text{H}_4]^+$	92	$\text{C}_6\text{H}_4\text{O}]^+$
		75	$\text{C}_6\text{H}_3]^+$

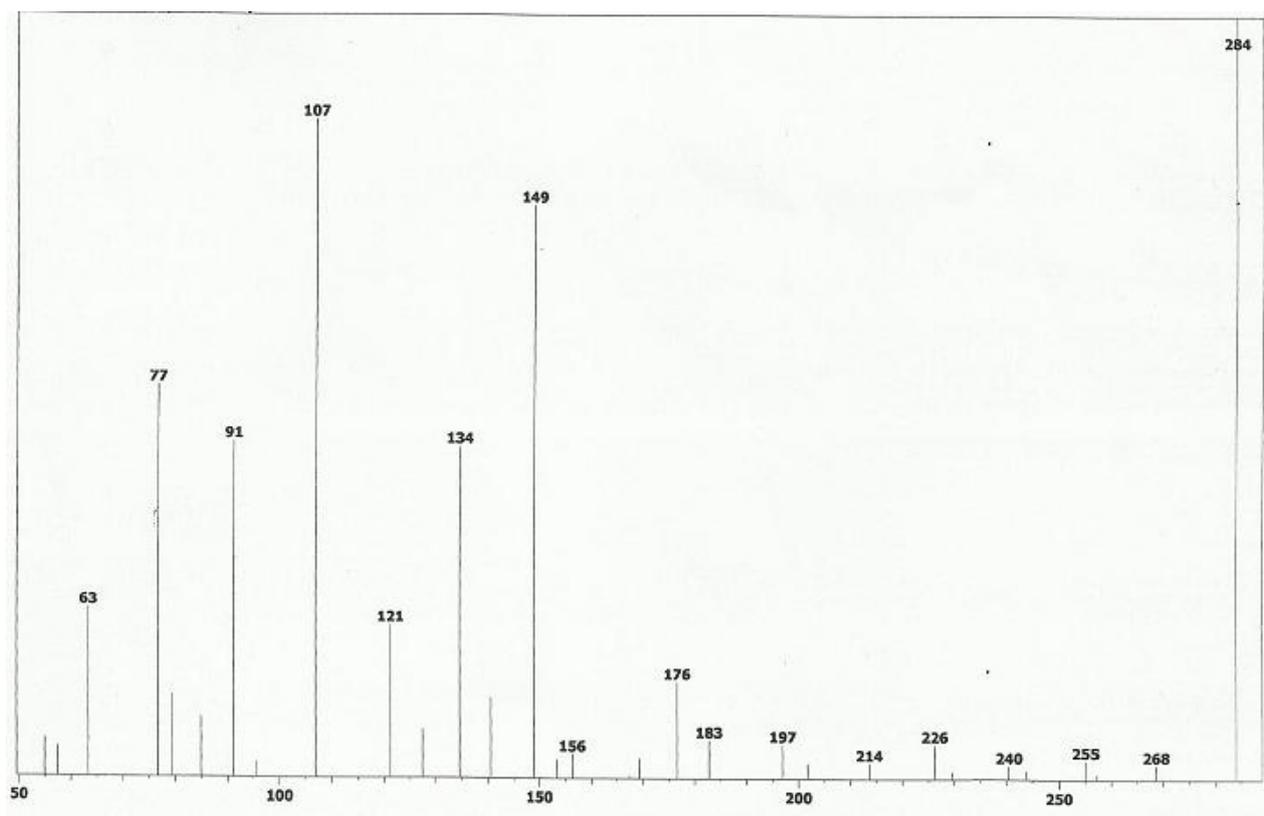


Fig. 5. Mass spectra of the prepared compound (I)

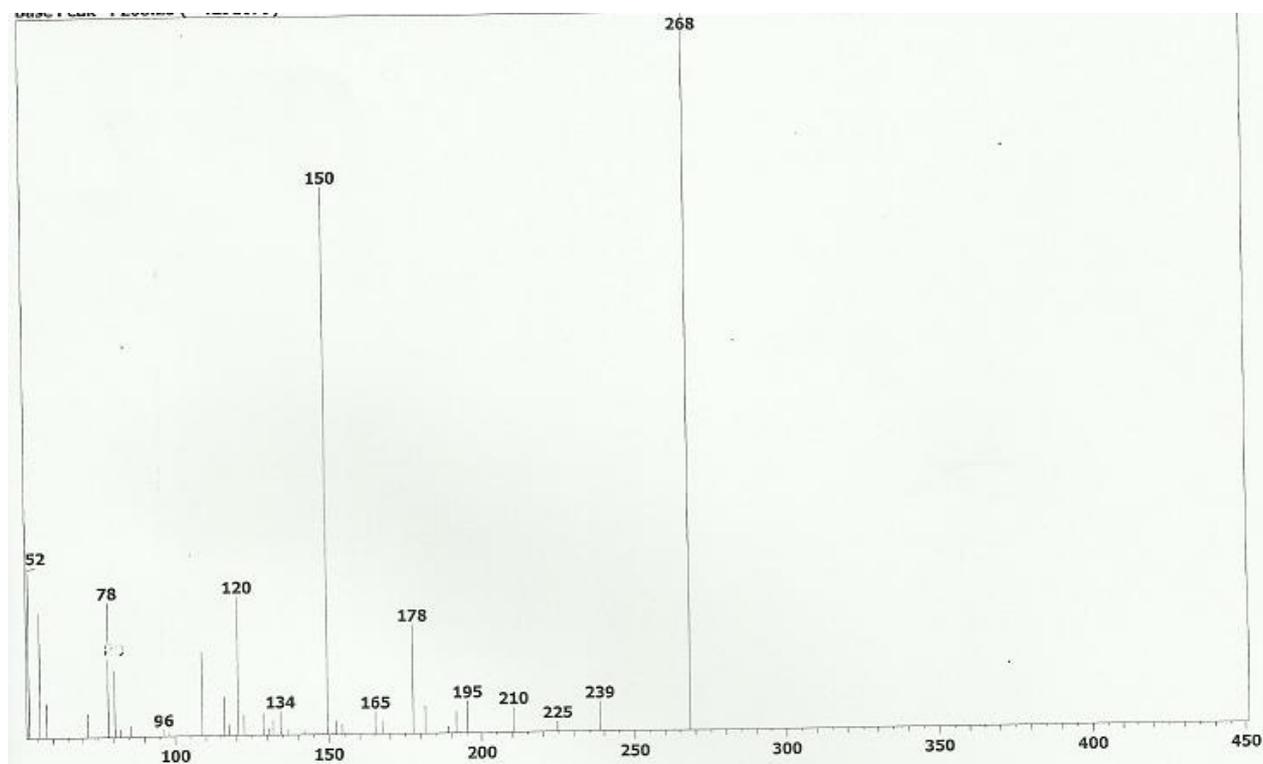
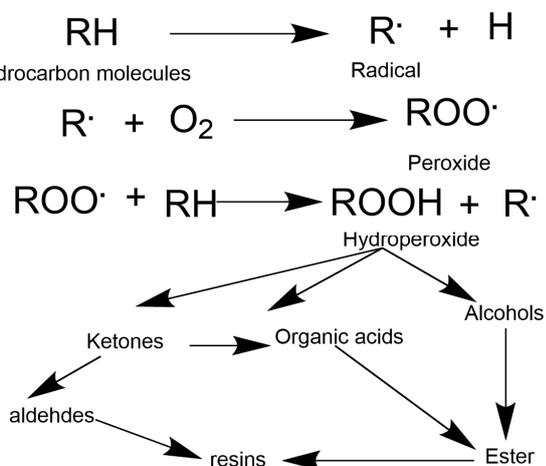


Fig. 6. Mass spectra of the prepared compound (II)

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

Total Acid Number (TAN)

The prepared additives were added to local base stocks. The blend obtained were subjected to severe oxidation condition 120 °C. sample were taken at intervals of 24 hours and up 96 hours of oxidation. Usually the total acid number of the oil increases by increasing the oxidation time. The increment of TAN value is due to oxidation processes which produce peroxides. These peroxides undergo further reaction to form alcohols, aldehydes and ketones. The total acid number 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 (Hassan 1998; Hassan *et al.*, 2000; Aucelio *et al.*, 2007; Suzuki *et al.*, 2009).



Scheme VI: Schematic Representation of Oxidation of Mineral oil.

From Table (7) the total acid number increases from 0.067 mg KOH/g to 2.01 mg KOH/g when thermally oxidized for 96 hours.

Table 7. Total Acid Numbers and Viscosities of the Base Stock at different Times without Additives

Total acid numbers, mg KOH/g Sample				Viscosity, cst at 40 °C			
24 hrs	48 hrs	72 hrs	96 hrs	24 hrs	48 hrs	72 hrs	96hrs
0.94	1.02	1.20	2.01	59.38	64.33	68.49	77.70

Effect of substituted alkyl additives

In presence of additives I, and II the results of the total acid numbers are given after thermal oxidation of the base oil for 24,48,72,96 hours, Table (8-11). First of all, the total acid numbers decrease by increasing the additive dose from 200 ppm to 600 ppm. Among the two azo phenols I, and II, the efficiency order of these compounds towards decreasing TAN is ranked as follows I > II.

Effect of additives concentration

The data shown in Figures (7-9) represent the relation between the total acid number and the oxidation time using the additive concentrations of 200, 400 and 600 ppm. Figures (1) showed the relation between the additives concentrations (I and II) and

the total acid numbers with the oxidation periods (24, 48, 72 and 96 hrs). Figure (1) (with 200 ppm of I and II) showed that the fresh base stock oil and the compound II additive gave poor results of total acid numbers than compound I. Figure (2) showed that, with the concentration of 400 ppm, the order of increasing inhibition efficiency is ranked as follows: I > II > Fresh. In case of Figure (3), with additive concentration of 600 ppm, it is clear that there is a marked increase in the total acid number on using the additives and the order of increasing efficiency was as follows: I > II > Fresh sample.

Table 8. TAN after 24 hours

Conc.	Total Acid Numbers, mg KOH / g Sample x 10 ⁻²	
	Compound I	Compound II
200 ppm	57	77
400 ppm	37	50
600ppm	32	40

Table 9. TAN after 48 hours

Conc.	Total Acid Numbers, mg KOH / g Sample x 10 ⁻²	
	Compound I	Compound II
200 ppm	61	85
400 ppm	41	59
600ppm	37	46

Table 10. TAN after 72 hours

Conc.	Total Acid Numbers, mg KOH / g Sample x 10 ⁻²	
	Compound I	Compound II
200 ppm	64	88
400 ppm	56	67
600ppm	45	49

Table 11. TAN after 96 Hours

Conc.	Total Acid Numbers, mg KOH / g Sample x 10 ⁻²	
	Compound I	Compound II
200 ppm	78	108
400 ppm	63	92
600ppm	48	90

Viscosity

Viscosity is one of the most important properties for the characterization of lubricants. It is a measure of internal friction in a fluid. In general, the viscosity of base oil increases with the operating time of oxidation. The increase in viscosity is due to the polymerization in the molecular structure. During oxidation, the oil degrades from peroxides to carboxylic acids, thus forming a long chain molecular structure.

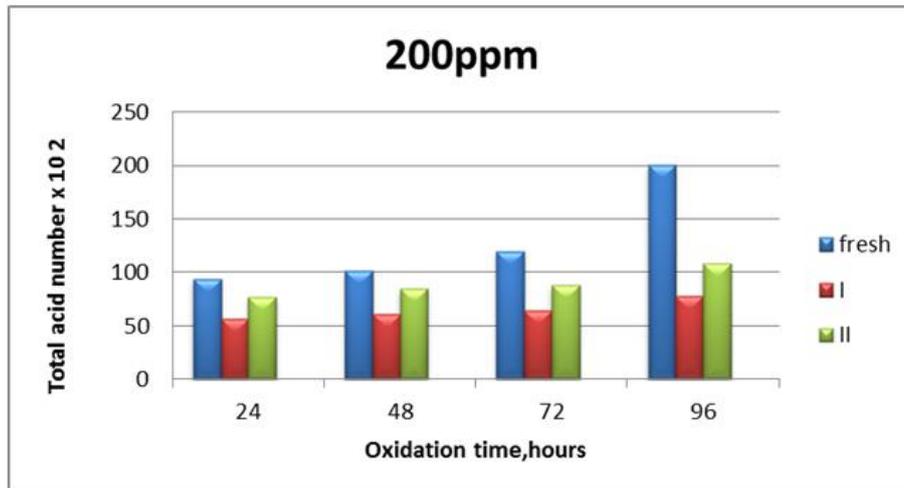


Figure 7. Variation of Total Acid Number (TAN) of base oil without and with 200 ppm of compound I and II

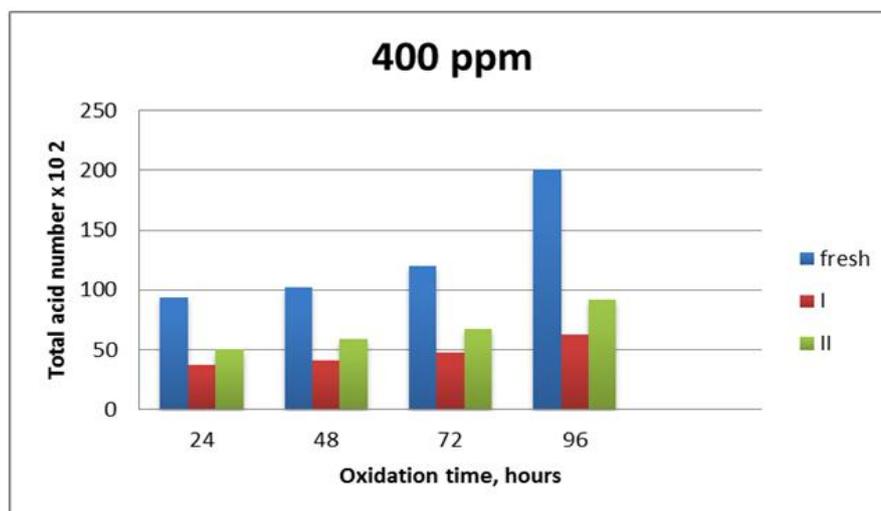


Figure.8. Variation of Total Acid Number (TAN) of base oil without and with 400 of compound I and II

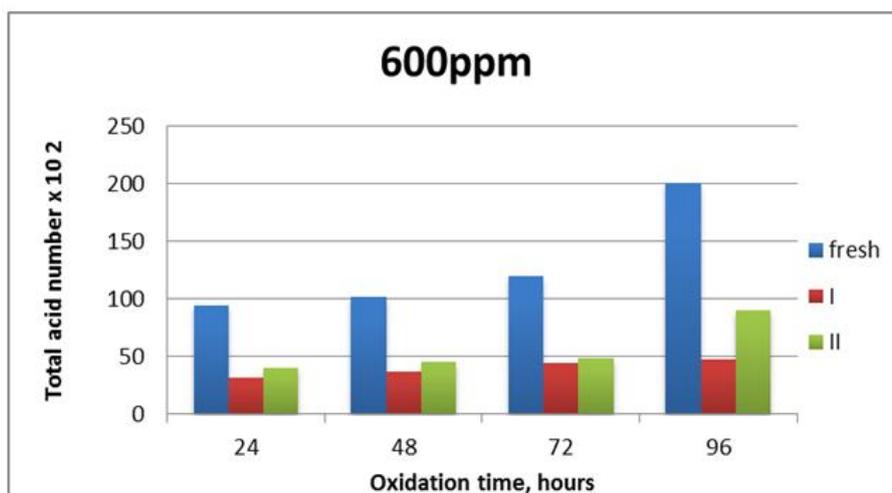


Figure 9. Variation of Total Acid Number (TAN) of base oil without and with 600 ppm of compound I and II

This structure can polymerize to form big molecules with significantly high viscosity indicating that 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 Tables (12-15) and graphically represented in Figures (10-12).

Table 12. Viscosity after 24 hours

Conc.	Viscosity x 10 ²	
	Compound I	Compound II
200 ppm	5527	5730
400 ppm	5390	5588
600ppm	5301	5339

Table 13. Viscosity after 48 hours

Conc.	Viscosity x 10	
	Compound I	Compound II
200 ppm	5611	5801
400 ppm	5423	5590
600ppm	5390	5520

Table 14. Viscosity after 72 Hours

Conc.	Viscosity x 10 ²	
	Compound I	Compound II
200 ppm	5680	5891
400 ppm	5434	5745
600ppm	5429	5549

Table 15. Viscosity after 96 Hours

Conc.	Viscosity x 10 ²	
	Compound I	Compound II
200 ppm	5752	6450
400 ppm	5690	6010
600ppm	5520	5950

Infrared Studies

Infrared spectroscopy (IR) is a powerful tool for investigating oil sample degradation. In general, an oil sample will form different oxygen-containing compounds at different oxidative stages.

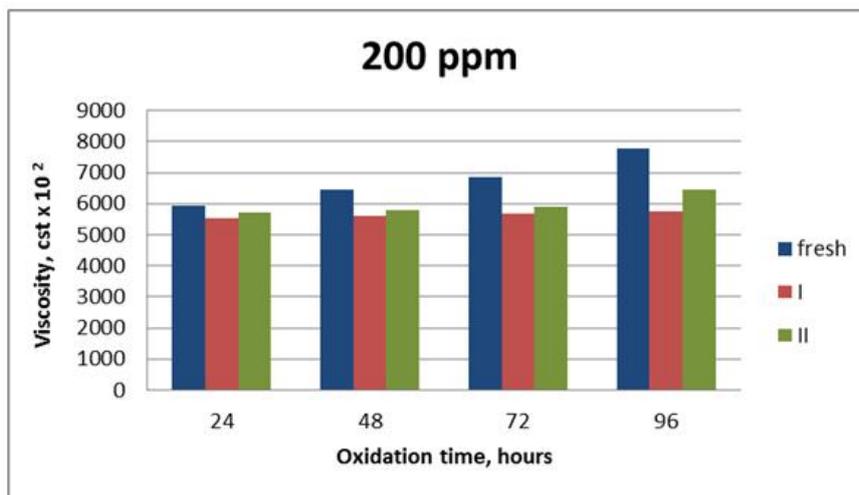


Figure 10. Variation of Viscosity of base stock without and with 200 ppm of compound I and II

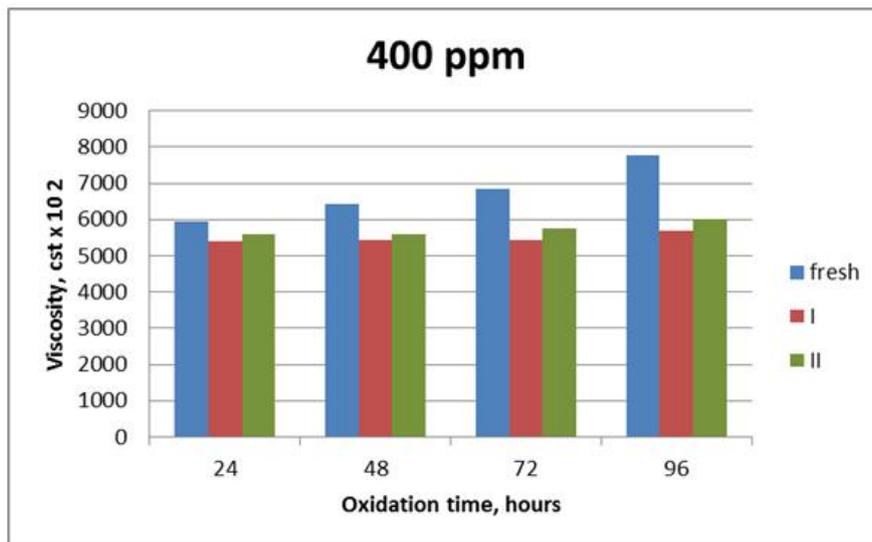


Figure 11. Variation of Viscosity of base stock without and with 400 ppm of compound I and II

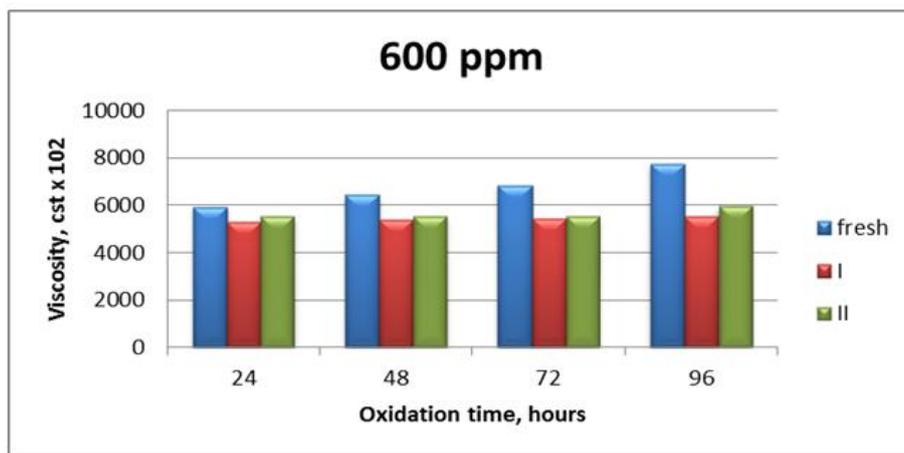


Figure 12. Variation of Viscosity of base stock without and with 600 ppm of compound I and II

IR was therefore used to monitor the changes in oxygen-containing functional groups in response to high temperature, in order to determine the thermal oxidative mechanism for the lube base oil sample (Ozen and Mauer, 2002). The degree of degradation upon exposure to oxidation was monitored by changes in the structure (FTIR). Oxidative degradation led to generation of carbonyl groups in oxidation products. Carbonyl peak Index (CPI) was used to characterize the degree of oxidation of the studied oil. These have been calculated by the baseline method (Prieri *et al.*, 2008). Tables (16-19) show the values of the carbonyl peak index of the studied oil samples.

Table 16. Base oil without and with different additives concentration after 24 hours

Conc.	Carbonyl peak index		
	Fresh oil	Compound I	Compound II
200 ppm		0.40	0.55
400 ppm	0.66	0.26	0.37
600ppm		0.23	0.33

Table 17. Base oil without and with different additives concentration after 48 hours

Conc.	Carbonyl peak index		
	Fresh oil	Compound I	Compound II
200 ppm		0.43	0.61
400 ppm	0.75	0.29	0.44
600ppm		0.23	0.33

Table 18. Base oil without and with different additives concentration after 72 hours

Conc.	Carbonyl peak index		
	Fresh oil	Compound I	Compound II
200 ppm		0.45	0.65
400 ppm	0.88	0.34	0.50
600ppm		0.32	0.36

Table 19. Base oil without and with different additives concentration after 96 hours

Conc.	Carbonyl peak index		
	Fresh oil	Compound I	Compound II
200 ppm		0.58	0.78
400 ppm	1.42	0.45	0.68
600ppm		0.35	0.62

Plotting the area of the carbonyl peak index appearing in the FT-IR spectra as a function of the oxidation time has already been demonstrated to provide an insight into the oxidation kinetics of hydrocarbons and into the effect of lubricant additives on the oxidation of base stocks (Pavia *et al.*, 1997). Fig. (13, 14 and 15) shows the changes of CPI as a function of oxidation time. It was observed that once oxidation of the base oil carbonyl formation accelerated and the carbonyl index values of the oils are shown to increase with the oxidation time. As the additive concentration was increased, carbonyl absorption decreased, indicating oxidation inhibition by the additive.

Correlation of the antioxidant character of the additives with their structures

Using the Ab initio (HF/3-21G) and semiempirical (MNDO) methods of calculations by Chem Bio Draw Ultra 12 software, the Huckel and Mulliken charges, the dipole moments, E_{HOMO} (the highest occupied molecular orbital) and E_{LUMO} (the lowest unoccupied molecular orbital) values were calculated. The charges representative atoms and other relevant quantum parameters were listed in Table 20. The optimized structure of the molecules and the electric/orbital density distributions of HOMO and LUMO illustrated in Fig. (16-19). Mulliken population analysis is mostly used for the calculation of the charge distribution in a molecule (Murrell *et al.*, 1985). These numerical quantities are easy to obtain and they provide at least a qualitative understanding of the structure and reactivity of molecules (Gruber, 1989). The dipole moment is another indicator of the electronic distribution in a molecule. It is one of the properties used to discuss and to rationalize the structure (Kikuchi, 1987). No significant relationship has been found between the dipole moment values and inhibition efficiencies. Besides, there is a lack of agreement in the literatures on the correlation between the dipole moment and inhibition efficiency (Gao and Liang, 2007; Khalil, 2003). Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species.

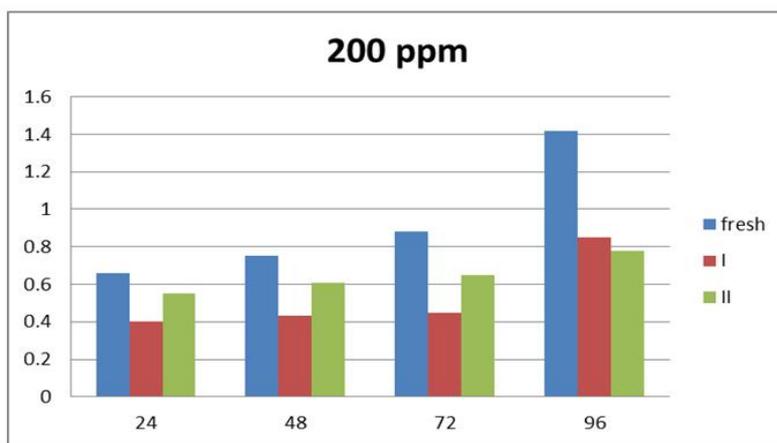


Figure 13. Variation of carbonyl peak index base stock without and with 200 ppm of I and II

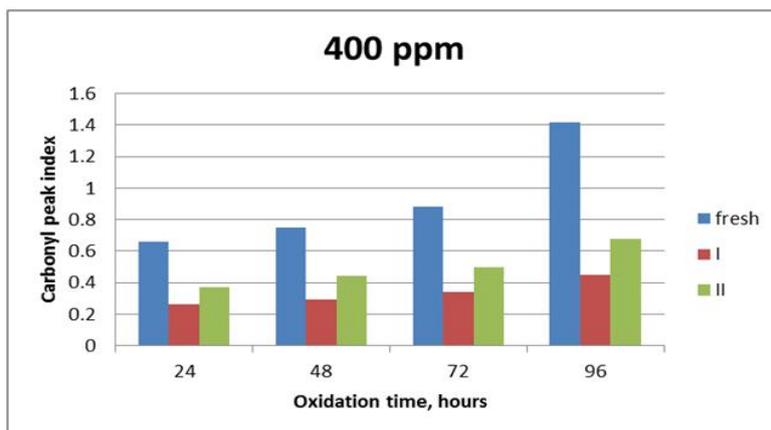


Figure 14. Variation of carbonyl peak index base stock without and with 400 of I and II

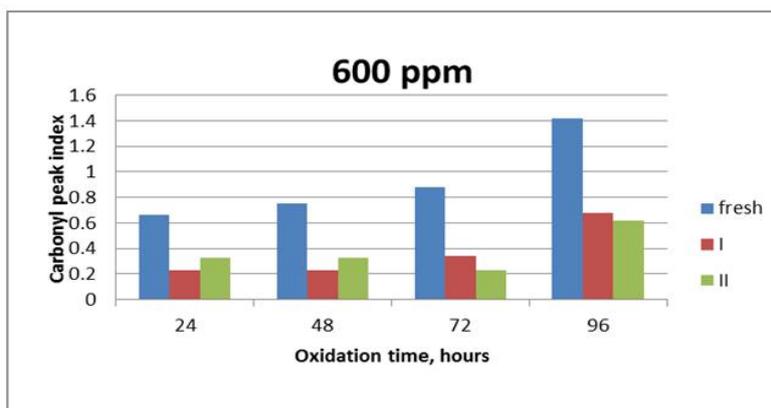
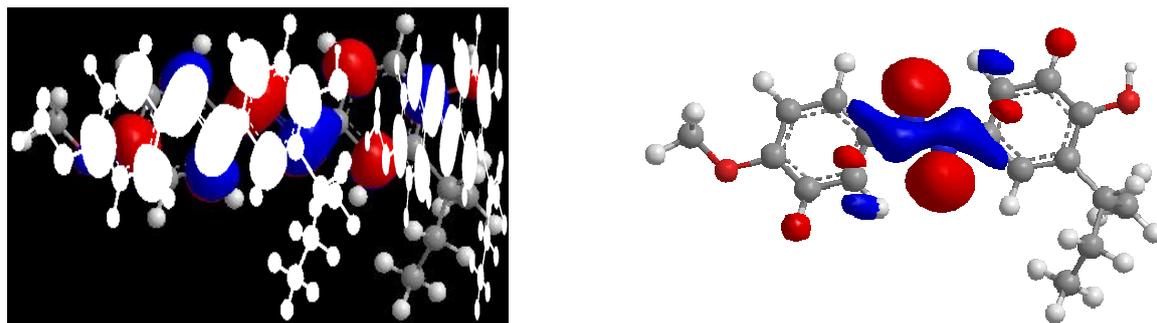


Figure 15. Variation of carbonyl peak index base stock without and with 600 ppm of I and II

Table 20. Quantum chemical parameters of I and II

Quantum parameters	HF(3-21G)		MNDO	
	I	II	I	II
E_{HOMO} (eV)	-4.122	-6.295	-4.122	-6.297
E_{LUMO} (eV)	-2.203	-2.195	-2.204	-2.193
ΔE (eV)	1.919	4.100	1.918	4.104
Huckel charge (eV)	$N_9 = 0.428$ $N_{10} = 0.425$	$N_7 = 1.109$ $N_8 = 0.619$ $N_9 = 0.558$	$N_9 = 0.428$ $N_{10} = 0.425$	$N_7 = 1.01$ $N_8 = 0.693$ $N_9 = 0.553$
Mulliken charge (eV)	$N_9 = -0.51$ $N_{10} = -0.51$	$N_7 = 0.27$ $N_8 = -0.39$ $N_9 = -0.36$	$N_9 = -0.113$ $N_{10} = -0.120$	$N_7 = 0.429$ $N_8 = -0.164$ $N_9 = -0.045$
μ (Debye)	2.9	7.64	2.27	6.79



HOMO

LUMO

Figure 16. The frontier molecule orbital density distributions of (I)

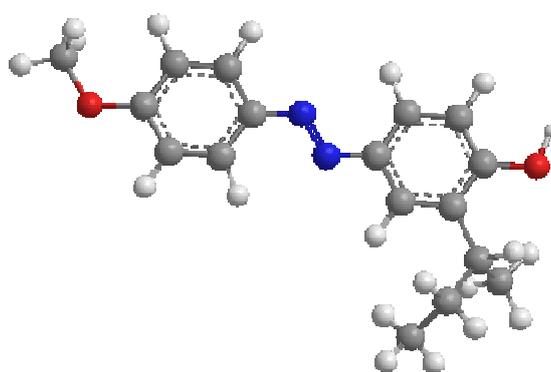
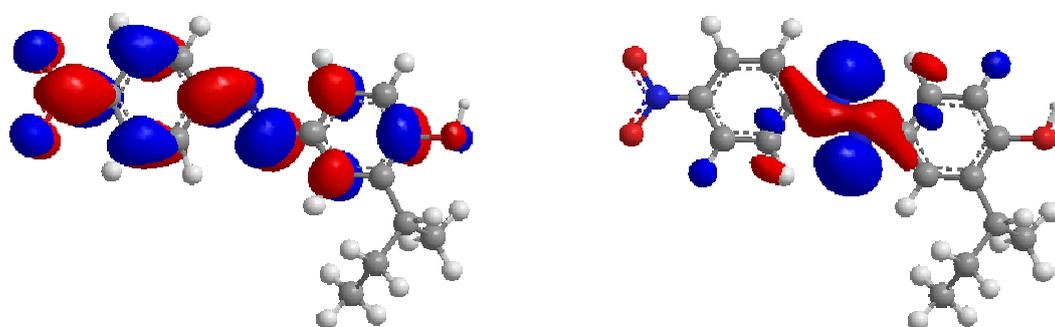


Figure 17. Optimized structure of (I)



HOMO

LUMO

Figure 18. The frontier molecule orbital density distributions of (II)

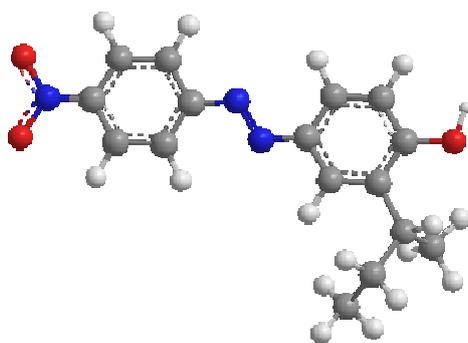


Figure 19. Optimized structure of (II)

The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants (Zcan and Dehri Prog, 2004).

- The results show also, by using the quantum chemical calculations (Ab initio {HF/3-21G} and the semiempirical gas phase MNDO, the compounds with low energy gap (ΔE) have good inhibition efficiencies which are in good agreement with the experimental results.

	B	5	17	27	6	10	11
24	0.58	0.275	0.31	0.288	0.2588	0.2538	0.293
48	-	0.3058	0.2482	0.2628	0.2268	0.2537	0.2649
72	2.1	1.82	0.398	0.565	1.42	1.202	1.27
96							
ΔE	-	6.150	6.281	5.767	6.120	6.266	5.985
H/F	-	44.1049	32.0942	3.7991	45.996	33.988	4.071
M-Ch	-	0.056	-	-	0.0577	-	-
Br							
Cl	-	-	-0.0114	-	-	-0.01	-
					0.0027	0.0029	0.0023
					0.0006	0.0003	0.0005
Na	-	-0.3157	-0.3155	-0.3279	-0.3086	-0.3089	-0.3391
				-0.3167			-0.3036
Ni	-	-0.0139	-0.0163	-0.0262	-0.0129	-0.0154	-0.0174
O	-	-0.3127	-0.3148	-0.3160	-0.3098	-0.3113	-0.3193
				-0.3570			-0.3579
H-Ch	-	-0.0979	-	-	0.0900	-	-
Br							
Cl	-	-	0.0929	-	0.1026	0.0933	-
					0.0787	0.1013	0.1013
						0.0787	0.0786
Na	-	-0.1446	0.4698	0.3181	0.4479	0.4465	0.3038
				0.4497			0.4484
Ni	-	-0.1446	-0.1496	-0.1468	-0.1453	-0.1511	-0.1480
O	-	-0.7594	-0.7467	-0.7582	-0.7629	-0.7665	-0.7715
				-0.7968			-0.8113
T-E	-	-83595	-84068	-94787	-93014	-93486	-104208

From Tables 19 and 20 it was found that the E_{HOMO} and the E_{LUMO} changed rulelessly, while the energy gap $E_{\text{LUMO}} - E_{\text{HOMO}}$; (the difference in energy between the E_{HOMO} and E_{LUMO}) decreased with increasing the inhibition efficiency. The energy gap (ΔE) is an important stability index (Lewis *et al.*, 1994). A large $E_{\text{HOMO}} - E_{\text{LUMO}}$ gap implies high stability for the molecule in chemical reactions (Zhou and Parr 1990), which means less inhibition efficiency. The values of (ΔE) indicate remarkably that the smaller energy gap results in a high oxidation inhibition efficiency, reflecting the stronger interaction between the inhibitors and metal surface. The interactions are probably physical adsorption (Lukovits *et al.*, 1997; Zcan and Dehri Prog, 2004).

Conclusion

The results obtained in this work, indicate the following:

- Increasing the oxidation time, always increase both of the total acid number, the viscosity and intensity of carbonyl group. The prepared antioxidant additives proved to be successful in controlling the oxidation stability of the base stock. We noticed for compound (I), with donating group, has more efficiency than compound (II).
- The data reveals that the most effective concentration is (600 ppm).

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