Study the oxidation stability of local base oil using Azophenol derivatives

A.M.Ashmawy[3], M.I.Nessim[2], W.I.El-Dougdoug[1], M.H.Arief[1] and M.H.Zidane[1]
[1]Chemistry, Dept., Faculty of science, Benha University, Benha, Egypt
[2]Evaluation and Analysis Dept., Faculty of science, Egyptian Petroleum Research Institute, Egypt
[3]Chemistry, Dept., Faculty of science, Al- Azhar University, Egypt
E-mail:ashraf_ashmawy2002@azhar.edu.eg

Abstract:
2-(tert-butyl)-4-(((4-methoxyphenyl)-phenol (Ia) and 2-(tert-butyl)-4-(4-nitrophenyl)diazenyl(Ib) were produced as the local oil supply antioxidant and examined. The structures were clarified using standard analytical techniques (elemental analysis FT-IR, 1H-NMR and mass spectroscopy). Oxidation stability was investigated before and after adding various Ia and Ib concentrations through change in total acid number (TAN) and viscosity. The findings were discussed and the effectiveness classified as follows: Ia > Ib. Ia > Ib. A good agreement with the experimental findings was shown by the quantum chemical calculations (E-HOMO, E-LUMO and E-LUMO-E-HOMO).

Keywords: Local base oil, Oxidation stability, Total Acid Number (TAN), Viscosity, Quantum chemical calculations.

1.Introduction

Complex mixes of hydrocarbons and additives comprise of lubricating oil. It plays an important function in internal combustion engines and is utilised to reduce the friction of the moving components and to clean the various parts. The oil lubrication process is a highly complicated process in which the basic oil is degraded and additives are reduced simultaneously [1, 2].

Motor oils degradation may influence motor characteristics, such as development of combustion chamber deposits (CCDs)[3-9] and particle emissions[10]. Oxidation and heat damage engine oil[11, 12]. Motor oil oxidation may be investigated using several techniques [13, 14].

Without lubricant additives, the development of a modern engine would be impossible. Since then, in collaboration with the oil and automotive industries, the lubricants business has focused on promoting the longevity and performance of engine and drive systems using lubricants. Advances in vehicle design are the beginning of new performance demands which, in turn, drive the development of new lubricant and additive technologies[15, 16].

The inclusion of antioxidants was thus extremely necessary to preserve the oil by reducing oxidation degradation during industrial application[17]. Most of the compact Azo compounds exhibit antioxidant, anti-corrosive and anti-wear characteristics [15, 18, 19]. Two novel azo phenols have been produced and investigated for local basic oil as antioxidants.

1.Experimental

1.1 Raw material and Chemicals

The base oil sample was delivered from Co-operative Petroleum Co. with boiling range of 260-290°C.
Chemical products were bought from Sigma, Aldrich, and Merck Companies.
1.2Physicochemical characterisation of the base oil supplied:
The physical-chemical characteristics of base oil evaluated by ASTM.

1.3Synthesis

Azophenols have been produced in two stages [15]

Aniline derivatives (a-b) diazotization (0.05 mol) was dissolved in distilled water and (0.5) was hydrochloric acid. The liquid was cooled to 0oC in an ice bath, and a stirring drop wise sodium nitride solution (NaNO2) (0.05mol) was then added. The resultant mixture was swirled at 0o C for 30 min, maintaining the temperature between 0 to 5o C.

Coupling

2-tert is added to the sodium hydroxide solution (0,05 mol). Butyl phenol (0,05 mol) forms the phenoxide complex (I). The solution was then chilled to 0 – 5 °C and applied to the diazonium compounds (a – b). The reaction mixture was acidified into compounds after addition (Ia – b). The product was removed and recrystallized from ethanol production, respectively, 82 percent, 90 percent.

Prepared compounds (Ia and Ib) characterization:
In this phase, the following techniques were used to characterise all prepared azodys;

Primary analysis

Elemental microanalysis for isolated solid dyes C, H, N and S were conducted using CHNS-932 (LECO) Vario Elemental Analyzers in the Microanalytical Center of Cairo University.

Fourier Infrarot Spectroscopy Transform (FT-IR)
The sample's absorption spectrum (FT-IR) was obtained using a 1650 spectrophotometer type APerkin-Elmer FT-IR; model "Vector 22."

Spectroscopy of HNMR

The chemicals produced were characterised by 1HNMR. Spectroscopy. Using1HNMR. Type a 300 MHz variable with TMS as internal standard (Germany 1999). (University of Cairo).

Spectroscopy of mass

The mass spectroscopy was performed using the SHIMADZU GC/MS-QP5050A direct intake unit (D1-50).

Regional centre for mycology; University of Al-Azhar.

Study of Oxidation Stability

In accordance with the ASTM standard D-943 test procedure, the thermal oxidation stability test was performed. The oil sample is reacted to the Fe and Cu catalysts at 120 °C at various times with oxygen (99.95% pure) (24, 48, 72, 96 h).

Total number of acids

In accordance with the ASTM D-664 potentiometric titration technique, a total acid number (TAN) was calculated for fresh and all oxidised oleic samples with or without addition of azo compounds at various concentrations (50, 100 and 200 ppm). The samples were warmed to 40oC and shaken for 10 minutes before to the test.

Viscosity

Viscosity at 40oC for fresh and all oxidised oil samples was performed in the glass capillary viscometer procedure with or without the addition of azo compounds at various concentrations (50 100 and 200 ppm) according to ASTM D- 445-IP 71.

Quantum chemical calculation

Hyperchem software version 8.03 for quantum chemical calculations from hypercubeInc[20].

3. Results and discussion
Evaluation of base stock

The physico-chemical properties of local base stock used in this study represent in table (1).

Table (1) discussed the physico chemical characteristics of the base stock sample under study. The viscosity at 40°C is 52.34 cSt. And the total acid noumber is 0.067 mg KOH / gram.

Characterization of the prepared azo phenols compounds (Ia-Ib):

The prepared compounds were characterized by elemental analysis, IR,
^{1}H-NMR spectrophotometer and electron ionization mass spectroscopy (EI-MS).

### 3.2.1. Elemental Analysis:

Elemental analysis was performed for the synthesized azophenols (Ia-Ib), and the obtained results are shown in Table (2).

The data obtained from Table show that the calculated values of the elements were in good compatibility with the found.

IR Spectroscopy:

IR spectroscopy for the synthesized azophenols (Ia-Ib) tabulated in table (3).

The data obtained in table (3), illustrate the functional groups of compound Ia - Ib.
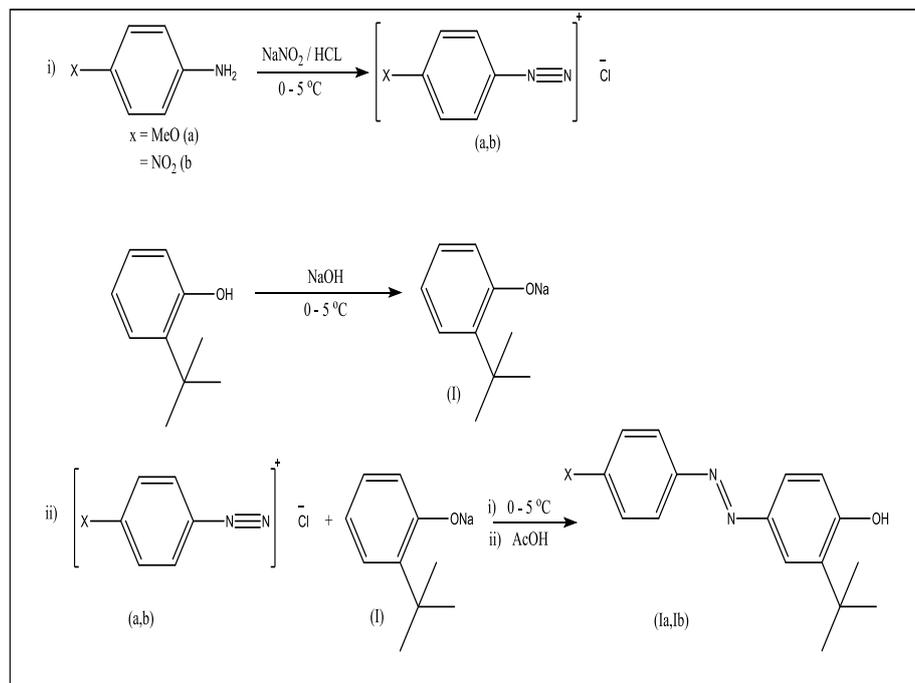
Scheme (1) Preparation of Ia and Ib.

Table (1) the physicochemical properties of the Base Stock.

Test	RESULT	TEST METHOD
Density @ 15.5 ^{O}C, g / L	0.8817	ASTM D - 1298
Pour Point, ^{O}C	-6	ASTM D - 97
Viscosity @ 40 ^{O}C	52.34	ASTM D – 445
@ 100 ^{O}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, oc	220	ASTM D – 92
Aniline point	100.5	ASTM D – 611
Molecular Weight	468.9	-

Table (2) Elemental analysis of synthesized azophenols Ia-Ib.

Element Cpd.	m.p. ^{o}C	C% Calc.	Obs.	H% Calc.	Obs.	N% Calc.	Obs.
Ia	110	71.81	71.41	7.09	6.50	9.85	8.67
Ib	160	64.20	65.36	5.72	6.49	14.04	13.97

**Table (3)** Infra-Red spectra of Ia –Ib.

Cpd.	$\Box$ cm^{-1} OH	CH aliphatic	C=C	N=N	C-O-C	C-Br	NO2
Ia	3440	2958	1585	1504-1443	1265	-	-
Ib	3467	2958	1590	1520-1451	-		1269

Table (4) ^{1}H NMR for prepared compounds (Ia-Ib).

Cpd. H$^+$Type	a	b	C	d	e	f	g	h
Ia	9.61	7.91	7.89	7.66	7.02	6.80	3.89	1.48
Ib	10.6	8.39	8.01	7.87	7.76	7.02	1.41	-

Table (5) Mass spectroscopy for Ia and Ib.

Cpd.	Molecular formal	m/z obs.	m/z cal.
Ia	$C_{17}H_{20}N_2O_2$	284	284
Ib	$C_{10}H_{17}N_3O_3$	299	299
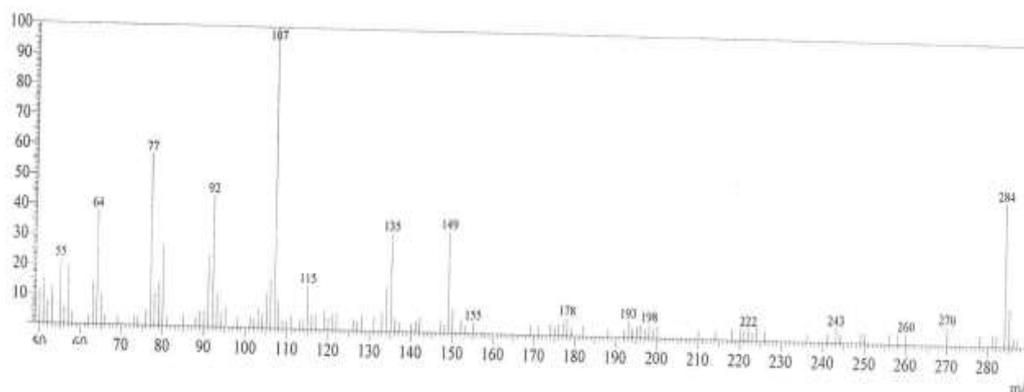
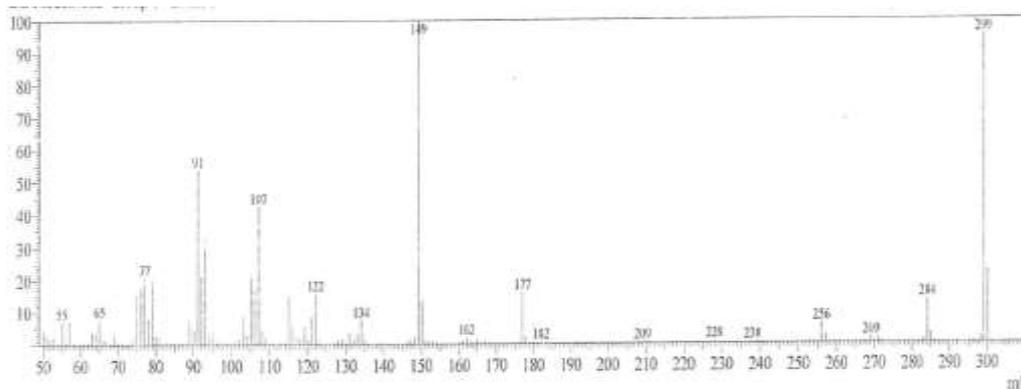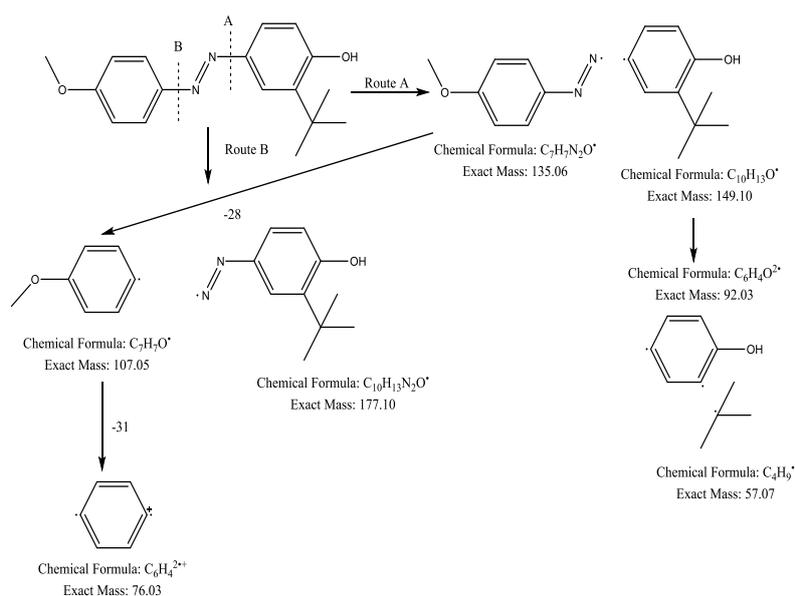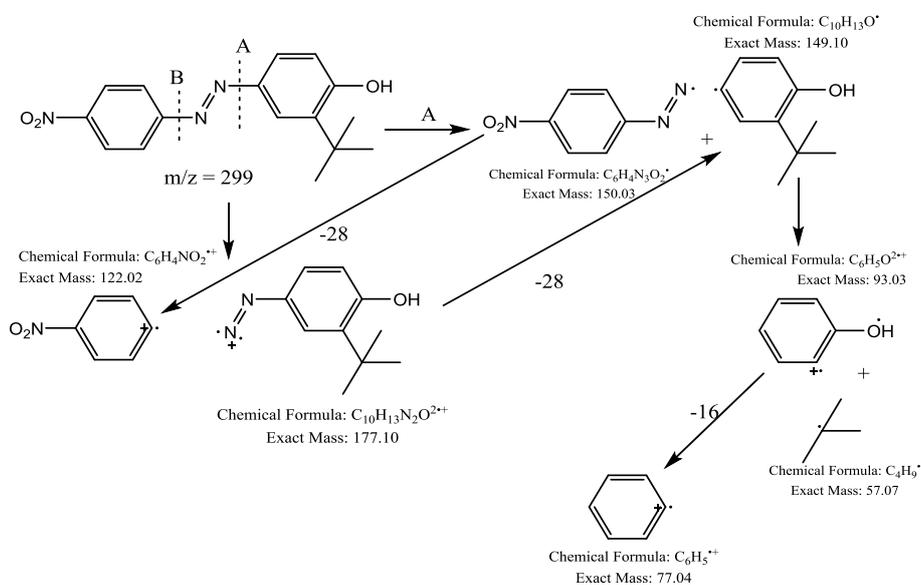**Fig. (1)** Mass spectroscopy of the prepared compound (Ia).

Fig. (2) Mass spectroscopy of the prepared compound (Ib).

Scheme (2) Routes of fragmentation (Ia).

Scheme (3) Routes of fragmentation (Ib).

3.2.3 ^{1}HNMR

The following are shown in Table 4: Due to the attachment of the -OH to the aromatic ring, which makes the hydroxyl proton more blind, the large chemicals shift (Ś) of the hydroxyl proton (a) (9.61-10.6 ppm) (because of the high electronegativity of the aromatic ring through conjugation). The aromatic protons (b, c, d, e and f) have distinct values of chemical shift (т), since they are unsymmetrical. The aliphatic protons (g and h) vary in their location to the aromatic ring. 3.

2.4 Spectroscopic mass

The connection between the fragmentation behaviour and structure of azophenol molecules is significant since it is necessary for the interpretation of mass spectrums of unknown azophenols. The determination of molecular weight is the fundamental information that comes from the analysis of mass spectra. Tables (5), figures (1, 2) and scheme indicate the molecular ion peak of the produced compounds (2,3).

From the preceding table and images we noticed that the molecular ion peaks for all produced compounds were according to the estimated molecular weight.

3.3. Assessment of produced chemicals as base oil antioxidant add-ons:

The investigation of the oxidation stability of a base oil shows that it is capable of oxidation of the oil under heat stress with stand and in the presence of a copper catalyst. The production of carbonyl group Figure 4 is prevented by the additives, i.e. by adding azophenols to the oil as part of heat oxidation, the overall acid level is always reduced. Total acid values are listed in Tables (6) and shown visually in Figure 5.

Table 6 and Figure 5 show that Ia and Ib additives are present. Total acid values are provided for 24, 48, 72 and 96 hours following thermal oxidation of the base oil. First of all, by raising the additive dosage from 50 parts per million to 200 parts per million, the overall acid numbers drop. Second, the total acid figures have always shown a bad result; with base oil either all times intervals.

It is possible to observe that the findings are varied by 24 hours studying the impact of additive concentrations employed on the total number of acids after thermal oxidation. The excellent efficient results were obtained at all doses for component Ia. When we utilised 200 parts per million (TAN 0.022 mg of COH/g sample) concentration after 24 hours.
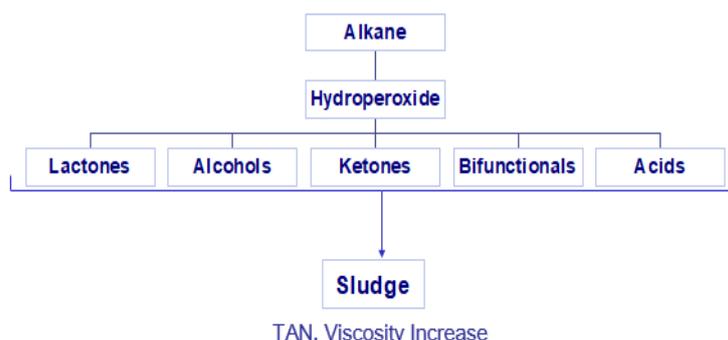

Fig. (4) oxidation of hydrocarbon.

Table (7) Variation of TAN with Oxidation Time and Concentration Ia-Ib.

Time	Total Acid Numbers, mg KOH / g Sample x 10^2						
	Base oil	Base oil+ Ia			Base oil+ Ib		
	-	50ppm	100ppm	200ppm	50ppm	100ppm	200ppm
24	0.58	.0545	0.0540	0.0222	0.1822	0.167	0.129
48	1.19	0.093	0.0652	0.058	0.290	0.181	0.148
72	1.96	0.135	0.111	0.096	0.392	0.276	0.249
96	2.77	0.150	0.141	0.101	0.472	0.375	0.324

Table (8) Variation of viscosity with Oxidation Time and Concentration Ia-Ib.

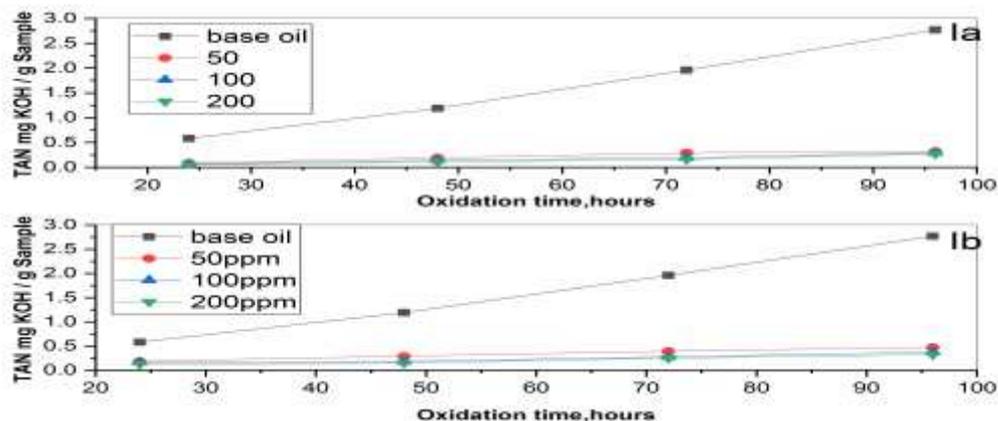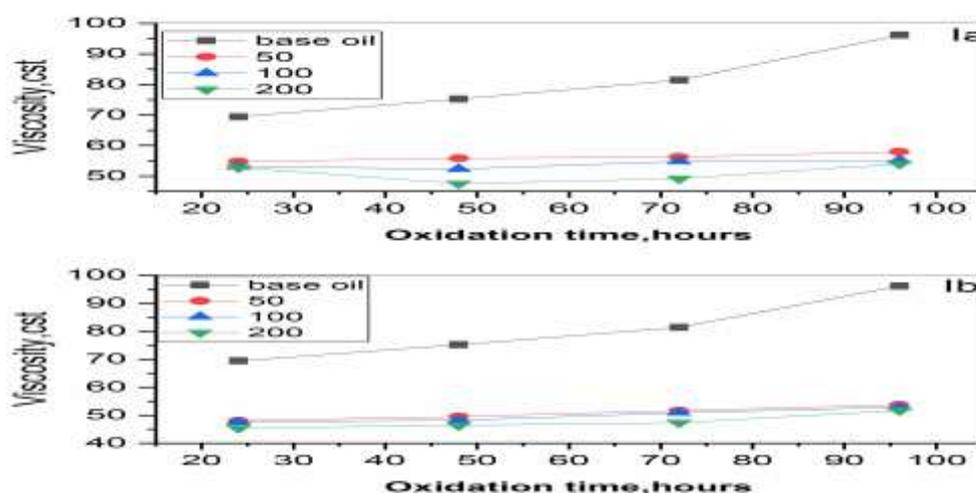| Time	Kinematic Viscosity @ 40°C, Cst.						
	Base oil	Ia			Ib		
		50ppm	100ppm	200ppm	50ppm	100ppm	200ppm
24	69.4	54.81	53.12	52.82	48.01	47.61	45.42
48	75.2	55.81	52.31	47.51	49.51	48.21	46.36
72	81.4	56.23	54.82	49.20	51.64	50.93	47.35
96	96.2	57.97	55.10	54.01	53.71	52.82	51.72

Fig. (5) TAN for prepared compound Ia and Ib.

Fig. (6) Viscosity for prepared compound Ia and Ib.

3.3.2. Change in viscosity:

Date of the cinematic viscosity of the basic oil with and without additions is shown in Table (7) and Figure (6).

The findings in table 7 showed that viscosity rates varied from 54.81 to 57.97 Cst (100 ppm) and 52.82 to 54.01 Cst following thermal oxidation of the base oil up to 96 hours in the presence of antioxidants Ia. The effectiveness of these antioxidants is rated as follows from prior findings at a concentration of 200 ppm: Ia > Ib. Ia > Ib. The presence of additive antioxidants retards base oxidation either with oxygen reactions or with primary oxidation products, such as organic radicals. This stops the radical reaction of the chain. Therefore, antioxidants preserve the lubricant sacrificially and are depleted gradually throughout this process. Once antioxidants are exhausted, the oxidation of the base oil is permitted to interact at high temperatures with the liquid. The oxidation of basic stocks leads to bigger oligomeric molecules, and smaller oxidation products for other fractions. [22]

3.4. Quantum chemical calculation

For possible relations with the inhibitor efficiency of the azo moleculae, the calculation of certain quantium chemical parameters such as the energy in the molecular orbital, EHOMO (high occupied molecular orbital energy) and ELUMO (lowest occupied molecular orbital energy) were determined in Figure 7 and Table4. HOMO energy is frequently linked with the capacity to donate electron to a molecule. Less negative HOMO energies as well as better adsorption connections and possibly higher inhibitory effectiveness are typically read as [23], as shown in Table 4, where the energy gap in the compound Ia is the lowest. The theoretical calculations are also consistent with the experimental findings.

Table (8) Calculated chemical parameters for the synthesized compounds Ia-Ib.

Cpd	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
Ia	-3.999	-1.376	2.623
Ib	-6.303	-2.197	4.106
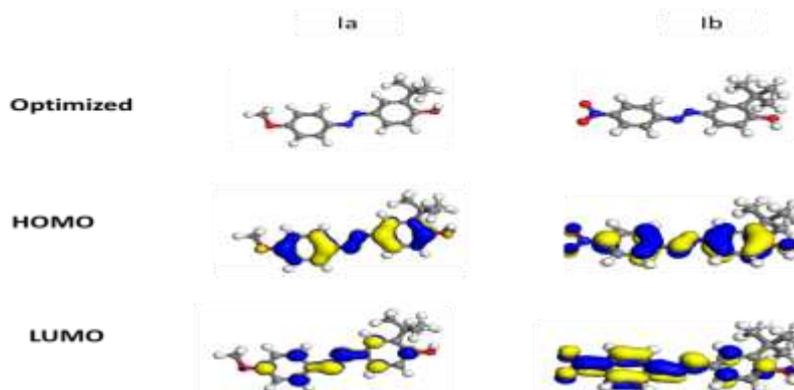
Fig. (7) Optimized structures, and iso surface plots of HOMO, LUMO level of compound Ia-Ib.

4. Conclusion

We may infer from the findings gained in this study by indicating:

- All Azo phenol compounds shown to be antioxidant successful
- § Increasing the concentration, both TAN and viscosity always decrease.
- We observed the most effective chemical Ia because of the donor group's presence.
- The results show that for all chemicals the highest effective concentration is 200 ppm.

Reference

[1] L. Guan, X. Feng, G. Xiong, and J. Xie, "Application of dielectric spectroscopy for engine lubricating oil degradation monitoring," *Sensors and Actuators A: Physical.vol.*168,pp.22-29, 2011.

[2] A. Borin, and R. J. Poppi, "Application of mid infrared spectroscopy and iPLS for the quantification of contaminants in lubricating oil," *Vibrational Spectroscopy.vol.*37,pp.27-32, 2005.

[3] L. B. Ebert, *Chemistry of engine combustion deposits*: Springer.vol.22,pp122-155,1985.

[4] J. Wang, and M. Sublette, *High Temperature Liquid Lubricant Development Part I: Engine Tests* SAE Technical Paper.vol.12,pp.48-71,1993.

[5] J. S. Kim, B. S. Min, D. S. Lee, D. Y. Oh, and J. K. Choi, *The characteristics of carbon deposit formation in piston top ring groove of gasoline and diesel engine,* SAE Technical Paper.vol.44,pp.199-148,7191.

[6] H. Sandquist, I. Denbratt, F. Owrang, and J. Olsson, "Influence of fuel parameters on deposit formation and emissions in a direct injection stratified charge SI engine," *SAE Transactions.*vol.14,pp.1537-1548,2001.

[7] A. M. Ashmawy, E. Elnaggar, D. I. Osman, and M. I. Nessim, "Studies on the additive performance of azo phenol liquid crystal as antioxidant for base stocks," *Elixir Appl. Chem .vol.*100,pp.43637-43641,2016.

[8] F. Owrang, H. Mattsson, A. Nordlund, J. Olsson, and J. Pedersen, "Characterization of combustion chamber deposits from a gasoline direct injection SI engine," *SAE transactions.*vol.15,pp.752-761,2003.

[9] J. Basta, A. El-Bassoussi, A. Salem, M. Nessim, M. Ahmed, and S. Attia, "Preparation and evaluation of some benzimidazole derivatives as antioxidants for local base oil," *Egyptian Journal of Petroleum.*vol.26,pp.933-941,2017.

[10] G. Tondelli, M. Carriero, and A. Pedicillo, "Combustion chamber deposits: Fuel and lubricant effects on exhaust hydrocarbon emissions measured by fast FID analyzer," *SAE transactions.*vol.17,pp.2053-2061,2000.

[11] T. Fischer, S. Bhattacharya, R. Salher, J. Lauer, and Y. Ahn, "Lubrication by a smectic liquid crystal," *Tribology transactions.*vol.31,pp.442-448,1988.

[12] R. M. Mortier, S. T. Orszulik, and M. F. Fox, *Chemistry and technology of lubricants*: Springer.vol.22,pp.188-200,2010.

[13] K. Egorova, B. Zuseva, V. Filimontseva, and A. Zeitseva, "Investigation of oxidation stability of certain mineral oils by means of infrared spectroscopy," *Chemistry and Technology of Fuels and Oils.*vol.12,pp.790-793,1976.

[14] F. Noel, "Thermal analysis of lubricating oils," *Thermochimica Acta.*vol.4,pp.377-392,1972.

[15] A. M. Ashmawy, S. K. Attia, M. I. Nessim, E. s. M. Elnaggar, and A. A. El-Bassoussi,

"Study on some azo liquid crystals as antioxidants for local base oil," *Molecular Crystals and Liquid Crystals*.vol.668,pp.78-90,2018.

[16] Z. Pawlak, *Tribochemistry of lubricating oils*: Elsevier.vol.22,pp.147-150,2003.

[17] A. Bhattacharya, T. Singh, V. Verma, and K. Nakayama, "The role of certain substituted 2-amino-benzothiazolylbenzoylthiocarbamides as additives in extreme pressure lubrication of steel bearing balls," *Wear*.vol.136,pp.345-357,1990.

[18] D. Basil, and R. W. Weiss, "Functional fluid containing azo benzene derivatives as antioxidants," Google Patents.vol.55,pp.700-744,1968.

[19] T. F. DeRosa, R. W. Von Allmen, B. J. Kaufman, and R. J. Jennejahn, "VI improver, dispersant, and antioxidant additive and lubricating oil composition," Google Patents.vol.33,pp.166-180,1992.

[20] K. Khaled, and M. Al-Qahtani, "The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: chemical, electrochemical and theoretical studies," *Materials Chemistry and Physics*.vol.113,pp.150-158,2009.

[21] N. Wu, Z. Zong, Y. Fei, J. Ma, and F. Guo, "Thermal Degradation of Aviation Synthetic Lubricating Base Oil," *Petroleum Chemistry*.vol.58,pp.250-257,2018.

[22] R. Ma, W. Li, Q. Zhao, D. Zheng, and X. Wang, "In Situ Synthesized Phosphate-based Ionic Liquids as High-Performance Lubricant Additives," *Tribology Letters*.vol.67,pp.60,2019.

[23] M. Nessim, A. Bassoussi, D. Osman, H. Khalil, and A. Ashmawy, "Preparation and evaluation of some azo-phenol derivatives as antioxidants for Egyptian base stock," *International Journal of Current Research*.vol.6,pp.9203-9216,2014.