



Studies on the Additive Performance of Azo Phenol Liquid Crystal as Antioxidant for Base stock

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ABSTRACT

Two novel azo phenols mesogenic group namely 2-sec-butyl-4-(p-tolyldiazenyl)phenyl 4-(dodecyloxy) benzoate I_{12a}, and 4-((4-bromophenyl)diazenyl)-2-sec-butylphenyl 4-(dodecyloxy) benzoate I_{12b} were synthesized. The prepared compounds were characterized using FT-IR, ¹H-NMR, Mass Spectroscopy and Elemental Analysis. Their mesophase was investigated by Differential Scanning Calorimetry (DSC). Their antioxidant efficiency for Egyptian lubricating base oil was tested via monitoring the oxidation reaction through the change in total acid number (TAN) and viscosity. The obtained results showed that, the efficiency of these compounds was ranked as follows I_{12b} > I_{12a}.

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Introduction

Degradation of engine oils may affect engine properties, for example through formation of combustion chamber deposits (CCDs)[1-6] and particulate emissions[7]. Engine oil is degraded due to oxidation and heat[4, 8, 9]. The oxidation of engine oil can be studied using several methods [3, 10, 11]. In these methods physical and chemical properties of oil during the oxidation process is studied, for example weightloss, sludge forming tendency and change in the viscosity and total acid number of oil versus formation/degradation of compounds in oil[10].

Oxidation of oils undergoes three oxidation stages and the stage in which the oxidation test is stopped is decisive for evaluation of oil ageing[12]. The first oxidation stage is the inhibition period. In this stage, properties of the oil are relatively stable and the oxidation extent is very small. Duration of the inhibition period is predominantly affected by temperature and by the concentration of antioxidants. This stage terminates after depletion of synthetic antioxidants and oxidation of oil starts to be more pronounced. The second oxidation stage is the breakdown stage, in which oxidation is not influenced by synthetic antioxidants. The most pronounced effect on oxidation rate can be seen in a composition of the oil and in concentration of natural oxidation inhibitors [13, 14]. Increased oxidation rate also deteriorates properties of the oil. The final oxidation stage is characterised by a slow oxidation rate due to a high oil viscosity. Oil contains a high concentration of oxidation products which can be partly polymerised and high oil viscosity then limits the access of air or oxygen into oil by a limited rate of diffusion [13, 14].

Liquid crystals are anisotropic viscoelastic materials; the combination of fluid-like flow with crystal like anisotropy makes their phases interesting as modifiers of interfacial behavior when applied as lubricants or additives to lubricants.

Liquid crystal materials can improve the lubricity of a lubricant, and while it is not yet fully understood how they work, there are some explanations that refer to their orientation and surface activities[15]. With respect to different flow directions, the anisotropy of the viscosity coefficients is a unique property of the liquid crystalline phase. The ability of liquid crystalline materials to form ordered boundary layers with good load-carrying capacity, while lowering the friction coefficients, wear rates, and contact temperatures of sliding surfaces, has been widely demonstrated[16].

Many researchers have been studying the tribological effect of liquid crystals on oils. A study on six types of cholesteric liquid crystals with four mineral oils found improvements in wear reduction over all of them[17]. Also, it gave a chemical explanation of the deformation of the monolayer and the advantage of cholesteryl chloride over the other liquid crystals, due to its chlorine content. Another research studied 14 additive materials from different families of liquid crystals[18]. They were tested with different oil bases by rubbing a steel-steel couple, and the results were positive for all of them over all tested temperatures (from 27°C to 50°C). In addition, they found that the change in viscosity had little effect on the results. In an attempt to achieve ultra-low friction, a mesogenic fluid mixture was used[19]. Comparing the tribological performance of ionic and neutral liquid crystal additives, all experiments showed that the ionic liquid crystals had less wear [20]. In a related effort, seven different ionic liquid crystals were tested[21]. The goal of our present work is to prepare new monomeric (LCs), azo phenol derivatives, and applying them as good antioxidants.

Experimental

1. Raw material

Samples of Hydro finished base oil (HBS) were delivered from Co-operative Petroleum Company, Cairo, Egypt. Other all reagents were purchased from Merck, Aldrich and Fluka chemical companies.

2.2. Preparation of azo phenol derivatives:

The preparation of 2-Sec-butyl-4-[(4-x-phenyl) diazenyl] phenyl-4-(octadecyloxy) benzoate took place through three steps according to scheme one:

Step one: Preparation of 4-(octadecyloxy) benzoic acid:

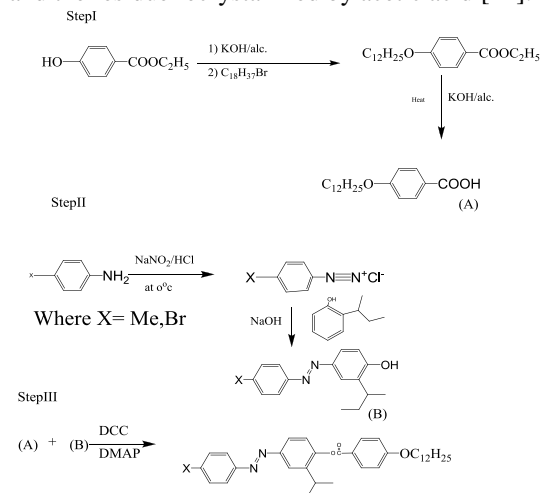
4-(octadecyloxy) benzoic acid was prepared from ethyl 4-hydroxybenzoate and the appropriate 1-bromooctadecane; the ester was then saponified to the corresponding acids using alcoholic potassium hydroxide, by the method described previously [22].

Step two: Preparation of 4-(4-Substituted phenyl azo) phenol:

Two azo phenols were prepared as reported previously [23].

Step three: 4-(octadecyloxy) benzoic acid with 4-(4-Substituted phenyl azo) phenol:

One molar equivalent of both the 4-(4-substituted phenyl azo) phenol and 4-(octadecyloxy) benzoic acid were dissolved in methylene dichloride. To the resulted solution, Dicyclohexyl carbodiimide (DCC) and 4-(Dimethylamino) pyridine (DMAP) were added as a catalyst, and the solution was left to stand overnight with stirring at room temperature. The solution was filtered off and the solute was distilled off and the residue recrystallized by acetic acid [24].



Scheme 1. Preparation of additives (I_{12a}-I_{12b}).

2.3. Characterization of the prepared compounds

The chemical structure of the prepared compounds were well established by Elemental analyses using CHNS-932 (LECO) Vario Elemental Analyzers, IR; using A Perkin-Elmer FT-IR type 1650 spectro-photometer"; Model "Vector 22", Mass spectroscopy was one using direct inlet unit (D1-50) of SHIMADZU GC/MS-QP5050A, and calorimetric investigation was made using a polymer laboratories differential scanning calorimeter, PL-DSC, England, with nitrogen as a pure gas. Typical heating and cooling rates were 20 K/min., and sample masses were 1-2mg.

2.4. Evaluation of the prepared compound as antioxidant

Evaluation of the prepared compounds as antioxidants was carried out according to ASTM D-943 method. Where the cell contained 200 ml base stock in the static mode, and copper and iron wires were used as catalysts. The base oil samples were subjected to oxidation at 120 oC with pure oxygen with flow rate (0.1 liter/hour) up to 96 hours.

The prepared compounds were added with different percents. The change in total acid number (TAN) and viscosity of oil samples were examined (after 24, 48, 72 and 96 hours) according to ASTM test methods (D-664 and D-445), respectively).

Results and Discussion

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

Table 1. The physicochemical properties of the Base Stock.

Test	Result	ASTM
Density @ 15.5 °C, g / L	0.8817	ASTM D - 1298
Pour Point, °C	Zero	ASTM D - 97
Viscosity cSt at 40°C	52.34	ASTM D - 445
at 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 °C	100.5	ASTM D - 611
Molecular Weight	468.9	-

1. Characterization of compounds I_{18a-d}

3-1- Characterization of compounds I_{12a} and I_{12b}

The chemical structure of compounds I_{12a} and I_{12b} were elucidated using the following:

3-1-1-Elemental analysis

Elemental analysis was performed for the synthesized azophenols derivatives I_{12a} and I_{12b} and the Obtained results are shown in Table (2).

Cpd.	Analysis calculation(found)							
	C%		H%		Br%		N%	
I12a	77.66	78.42	8.69	9.06	-	-	5.03	4.3
I12b	67.62	67.99	7.30	7.42	12.85	13.36	4.51	4.3

The data obtained from table (2) shows that the calculated values of the elements were in good compatibility with that measured.

3-1-2- Infrared spectra of compounds I_{12a}, I_{12b}:

Table 3. Infra-Red spectra of I_{18a,b}.

	V C=O	V C-O	Br
I12a	1729.79	1249.85	-
I12b	1732.58	1244.60	654

Infrared absorption bands for compounds I_{12a} and I_{12b} are given in table (3). From Table 3, small shifts were observed in the carbonyl absorption bands with the effect of the alkoxy-chain length (O-C₁₂). Moreover, it can be noted that, the ester C=O absorption bands are not greatly affected by the nature of the substituents (Me-, Br-). This can be attributed to their weak effect on the polarization of the ester C=O group through the phenylazo group. Nonetheless, the ester oxygen absorption bands are affected by the electronic nature of Me -, Br-. Thus, in the electron withdrawing (Br-) substituted derivative I_{12b},

3-1-3- Mass spectroscopy

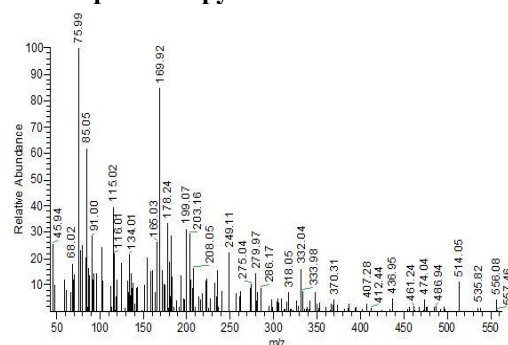


Fig. 1 Mass spectra of the prepared compound (I_{12a}).

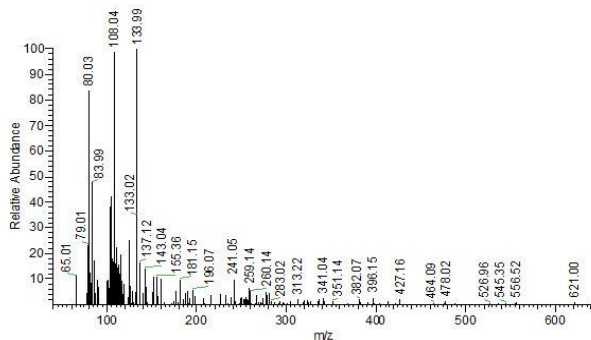


Fig. 2. Mass spectra of the prepared compound (I_{12b}).

From the previous figures (3, 4), we noted that the molecular ion peaks were in accordance with the calculated molecular weight for I_{12a} and I_{12b}.

3-1-4- Differential Scanning Calorimetry (DSC)

In order to investigate the effect of substituents on the phase behavior of the investigated compounds, the DSC analyses for compounds I_{12a} and I_{12b} were carried out. The transition temperatures observed are summarized in table (4) **Table 4. Transition temperatures (in °C) and enthalpy of transitions (in KJ/Mole) for compounds I_{12a,b} as determined by DSC.**

Cpd.	Heating				Cooling	
	T _m	ΔH	T _c	ΔH	T _m	ΔH
I _{12a}	68.78	71.06	132	43.33	77.21	7.50
I _{12b}	65.19	48.69	-	-	31.19	19.98

Where T_m= solid- smectic. T_c= smectic -isotropic transition. In order to investigate the effect of terminal substituents (X) on the mesophase behavior of compounds I_{12a} and I_{12b} the number of carbon atoms in the alkoxy substituent kept constant (C₁₂H₂₅O-). The substituent x varied between CH₃- and Br-.

3.2. Evaluation of the synthesized compounds as antioxidants

a) Using change in TAN

The total acid number (TAN) is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil. It is used to estimate the amount of additive depletion, acidic contamination and oxidation of lubricant degradation. To the crude oil refinery, The TAN value indicates the potential of corrosion problems. Testing for TAN is essential to maintain and protect equipment, preventing damage in advance. TAN testing is a measure of both the weak organic acids and strong inorganic acids present within oil. The potential of corrosion problems. Testing for TAN is essential to maintain and protect equipment, preventing damage in advance. TAN testing is a measure of both the weak organic acids and strong inorganic acids present within oil.

Table 5. Variation of total acid number, TAN with oxidation time and concentration.

Time (Hrs)	Base Stock *	Total Acid Numbers, mg KOH / g Sample x 10 ²					
		Base oil + 12a			Base oil + 12b		
24	37	25	27	22	8	6.3	6.2
48	79	55	47	40	48	45	39
72	162	71	63	50	68	57	45
96	201	100	99	96	99	98	67

*The TAN of the Base Stock at room Temperature is 0.067 mg KOH / mg Sample.

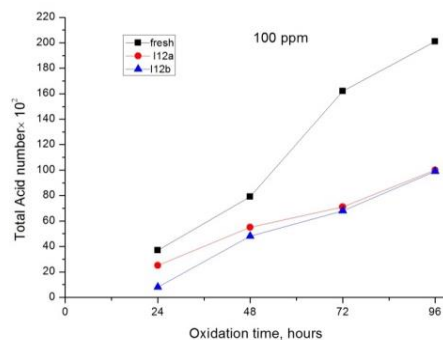


Fig 3. Variation of Total Acid Number (TAN) of base oil without and with 100 ppm I_{12a}, I_{12b} additives.

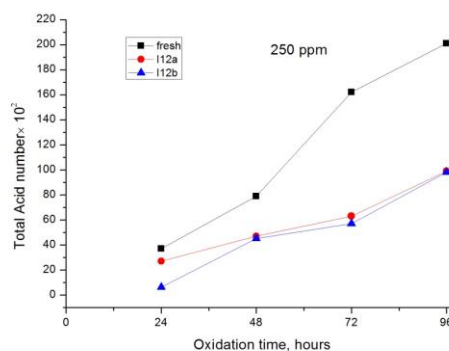


Fig 4. Variation of Total Acid Number (TAN) of base oil without and with 250 ppm I_{12a}, I_{12b} additives.

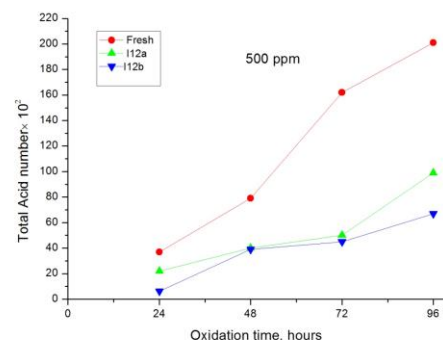


Fig 5. Variation of Total Acid Number (TAN) of base oil without and with 500 ppm I_{12a}, I_{12b} additives.

Looking in Table 3.2 and Figures 3 through 5, we can conclude the following:

Generally, the total acid number decreased by the addition of the synthesized compounds. This is clear from data of the oxidized base stock without additives and the data obtained after the addition of the two compounds. The data obtained after the addition of both additives [(I_{12a}) and (I_{12b})] showed the decrease of the total acid number by increasing the dose of the compounds. The data obtained showed that the compound (I_{12b}) is more effective than the compound (I_{12a}). With the (I_{12a}) the TAN decreased by the addition of 100 ppm, after 24 hours from 0.37 mg KOH / g sample to 0.25 mg KOH / g sample and from 0.79 mg KOH / g sample to 0.69 mg KOH / g sample after 48 hours. After 72 hours and 96 hours the decrease showed 0.55 mg KOH / g sample and 0.71 mg KOH / g sample respectively. On the other hand, by adding the same dose 100 ppm the (I_{12b}) showed 0.08, 0.48, 0.68 and 0.99 mg KOH / g sample after 24, 48, 72 and 96 hours respectively.

Addition of 250 ppm and 500 ppm decreased the TAN from 0.37 to 0.27 and 0.22 mg KOH /gm sample in case of (I12a) after 24 hours. While addition of same concentrations of (I12b) showed decrease in TAN after the same period to 0.063 mg KOH /gm sample and 0.062 mg KOH /gm sample. As we see from the table, the (I12b) is more effective as antioxidant. It causes depression in the TAN in comparison with that caused by the addition of (I12a). From the Table one can notice that 500 ppm of both compounds showed the best results.

b) Using change in Viscosity:

As carboxylic acid byproducts of oxidation dimerize (or associate), the median density of the molecules increases. This results in increased viscosity. Viscosity can be measured using kinematic or absolute methods.

Table 6. Variation of viscosity with Oxidation Time and Concentration.

Time (Hrs)	Base Stock *	Kinematic Viscosity @40 ⁰ C, Cst.					
		Base oil + I2a			Base oil + I2b		
24	69.4	100	250	500	100	250	500
48	75.2	68.45	67.90	65.50	68.20	64.40	61.20
72	81.4	68.70	68.50	67.30	68.65	64.30	63.20
96	96.2	69.09	68.60	67.60	68.80	66.60	65.51

*The Kinematic Viscosity @40⁰ C of the base stock without any additive is 52.34 Cst

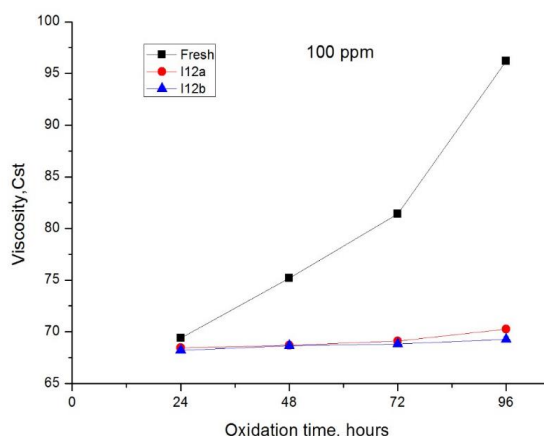


Fig. 6. Variation of Viscosity of Compounds without and with 100 ppm I12a,12b additives.

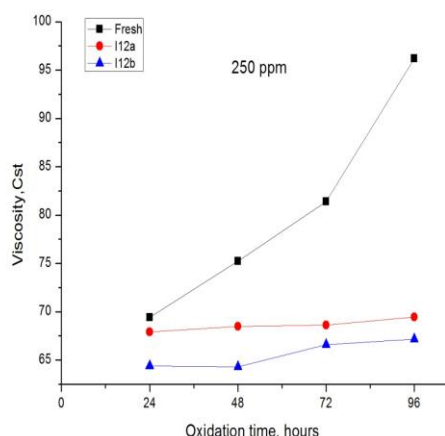


Fig 7. Variation of Viscosity of Compounds without and with 250 ppm I12a,12b additives.

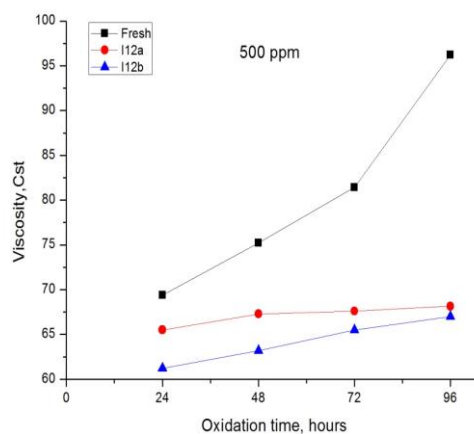


Fig 8. Variation of Viscosity of Compounds without and with 500 ppm I12a,12b additives.

From the data in Table (6), and Figures 6 through 8 one can note that:

The viscosity of the oxidized base stock always increases by increasing the oxidation period. Adding the synthesized compounds to the base stock caused appreciable increase in the viscosities of the base stock. For example, by increasing the oxidation period from 24 hours to 96 hours, the viscosity changes from 0.69 Cst and 0.962 Cst without additive to 0.685 Cst and 0.70 by adding 100 ppm of I-12 a respectively. At the same time, addition of the same concentration from I12 b, the viscosity changes to 0.68 Cst and 0.69 respectively. By increasing the concentration of the added compounds from 100 ppm to 500 ppm, the viscosity decreases from 0.69 to 0.66 after 24 hours at 100 ppm and from 0.68 cSt to 0.61cSt at 500 ppm after 96 hours. The table also revealed that the compound I-12 b is more effective than I-12 a.

Conclusion:

From the data obtained from this study we can concluded that:

1. The base stock showed bad results when oxidized without additive, that is it gave sharp increase in both total acid numbers and viscosities.
2. The addition of the two additives showed decrease in the total acid number and viscosities as compared to the base stock without additives.
3. Generally the compound I12b is more effective – gave good results – than the compound I 12a.
4. The concentration 500 ppm is the most effective concentration among the concentrations we are used.

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