



Molecular Crystals and Liquid Crystals

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Preparation and evaluation of some novel liquid crystals as antioxidants

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ABSTRACT

Four liquid crystal compounds of the form 2-sec-butyl-4-[(4-X-phenyl) diazenyl) phenyl-4-(octadecyloxy] benzoate symbolized as 118_a , 118_b , 118_c , and 118_d were prepared in which the substituent (X) was taken CH₃O-, CH₃-, Br-, and -NO₂, respectively. Characterization of prepared compounds is done using FT-IR, ¹H-NMR, mass spectroscopy, and elemental analysis. Their mesophase was investigated by differential scanning calorimetry. Their antioxidant efficiency for Egyptian lubricating base oil was tested via monitoring the oxidation reaction through the change in total acid number. The obtained results showed that the efficiency of these compounds was ranked as follows $118_d > 118_c > 118_b > 118_a$.

KEYWORDS

Antioxidants and DSC; liquid crystals; lubricating oil; TAN

Introduction

The most important parameter that affect the lube oil degradation is its oxidation stability [1]. Oxidation products are the primary cause of metal corrosion, viscosity increasing, and sludge formation in lubrication systems [2]. An investigation of the chemical nature of these products was undertaken to provide a better understanding of primary oxidation and the subsequent behavior of these primary oxidation products [1, 2].

Oil deterioration results in a loss of lubrication, with the signals showed by the appearance of sludge. Efforts aimed to reduce sludge formation may extend the life span of the lubricant and prevent failure in service. The latter, however, cannot be achieved without the understanding of the processes of sludge formation and the nature of the oxidation products [3]. Although qualitative information is available, which reports the presence of acids, aldehydes, ketones, esters, and lactones in the oxidation of used crankcase lube oils, information on the extent of oxidation is scant [4–7].

Today, many efforts have been made papers, Conference recommendations, or books and inventions in an attempt to use monomeric liquid crystals (LCs) whether as lubricants or as additives for lubricating oils. The improvement of the efficiency of lubricants is of important technological and economic relation as it is estimated that 50% of the energy consumption is wasted as friction [8, 9].

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LCs are soft materials that spontaneously form several types of ordered structures and thermally change their physicochemical properties [10]. Since the time of their discovery, LCs have been very extensively investigated. The exploration of LCs included molecules with different shapes (rod-like, disc-like). Also there are different possibilities of substitution and combination of linking units in designing of new molecular structures [11].

The ordered LCs have received much attention, as potential lubricants, due to the longrange orientation of their molecules [9, 12–17]. Most LCs studied until present are thermotropic phases constituted by polar neutral organic molecules [18]. The goal of our present work is to prepare new monomeric (LCs), azo phenol derivatives, and applying them as good antioxidants.

Experimental

Raw material

Samples of hydro-finished base oil were delivered from Co-operative Petroleum Company, Cairo, Egypt. All other reagents were purchased from Merck, Aldrich, and Fluka chemical companies.

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 1:





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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 [19].
- Step two: Preparation of 4-(4-substituted phenyl azo) phenol:
- Two azo phenols were prepared as reported previously [20].
- 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, dicyclohexylcarbodiimide and 4-(dimethylamino) pyridine 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 [21].

Characterization of the prepared compounds

The chemical structure of the prepared compounds was 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," Nuclear Magnetic Resonances (NMR), using ¹H-NMR (type Varian 300 MHz) with the TMS as internal standard zero compound, 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 1–2 mg.

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°C with a pure oxygen with flow rate (0.1 L/hr) up to 96 hr. The prepared compounds were added with different percents. The change in total acid number (TAN) of oil samples were examined (after 24, 48, 72, and 96 hr) according to ASTM test methods D-664.

Results and discussion

The physicochemical properties of local base stock used in this study represented in Table 1.

Characterization of compounds 118_{a-d}

The prepared compounds were characterized by elemental analysis, FT-IR, ¹H-NMR, mass spectroscopy. Their mesophase behavior was investigated by differential scanning calorimetry (DSC). The chemical structure of compounds I18_{a-d} was elucidated using the following.

Elemental analysis

Elemental analysis was performed for the synthesized azophenols $I18_{a-d}$, and the obtained results are shown in Table 2. The data obtained from Table 2 show that the calculated values of the elements were in good compatibility with that measured.

Test	Result	Test method
Density @ 15.5°C, g/L	0. 817	ASTM D-1298
Pour point, °C	Zero	ASTM D-97
Viscosity at 40–100°C	52.34	ASTM D-445
	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	la	ASTM D-130
Flash point, °C	220	ASTM D-92
Aniline point, °C	100.5	ASTM D-611
Molecular weight	468.9	—

Table 1. The physicochemical properties of the base stock.

Table 2. Elemental analysis of newly prepared compounds, 118_{a-d} .

	Analysis calculation (found)								
	C	%	Н	%	В	r%	N%		
Cpd.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	
l18 _a	76.79	76.54	9.21	8.92	—	—	4.26	4.81	
118 _b	78.7	76.95	9.44	9.05	_	_	4.37	5.03	
118	69.77	69.39	8.14	8.01	11.32	10.88	3.97	4.12	
118 _d	73.29	73.96	8.55	9.12	—	—	6.25	6.35	

Infrared spectra of compounds $I18_{a-d}$

Infrared absorption bands for compounds 118_{a-d} 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-C18). Moreover, it can be noted that the ester C=O absorption bands are not greatly affected by the nature of the substituents (MeO-, Me-, Br-, or NO₂-). 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 MeO-, Me-, Br-, or NO₂-. Thus, in the electron withdrawing (NO₂-) substituted derivative I18_d, conjugative interaction takes place between NO₂- and the lone pair of the ester oxygen, via the phenylazo moiety (Fig. 6).

¹H-NMR spectroscopy

Chemical shift of the prepared compounds are given in Tables 4–7.

	Stretching of vibrations (\boldsymbol{v}) in cm ⁻¹									
Compound	CH aromatic	CH aliphatic	N=N	C=0	C-O-C	Br	NO ₂			
118,	2916	2849	1436	1732	1241	_	_			
l18 _b	2917	2849	1467	1734	1252		_			
118	2917	2849	1467	1735	1252	658	_			
118 _d	2918	2849	1517	1724	1254	_	1344			

Table 3. Infrared spectra of I18_{a-d}.

Table 4. Chemical shifts of compound I18_a.



Table 5. Chemical shifts of compound I18_b.



Mass spectroscopy

Molecular ion peak of the prepared compounds are given in Table 10 and Figures 1–4. From the previous table and figures we noted that the molecular ion peaks were in accordance with the calculated molecular weight for all the prepared compounds.

Differential scanning calorimetry

In order to investigate the effect of terminal substituents (*X*) on the mesophase behavior of compounds $I18_{a-d}$ the number of carbon atoms in the alkoxy substituent kept constant (C₁₈H₃₇O-). The substituent *X* varied between CH₃O-, CH₃-, Br-, and NO₂-. Table 8 compares the transition temperatures of the four compounds (I18_{a-d}).

From tables we observed proton (a) for I8a-I18d possess high chemical shift because of its attachment to the carbonyl ether group (withdrawing group). The effect of the azo group on the protons (b) gave a high chemical shift. The presence of the bromide and nitro group in compounds I18a-I18d gave very high chemical shift (8.463ppm and 8.383ppm) respectively



Table 6. Chemical shifts of compound 118_c .

Table 7. Chemical shifts of compound I18_d.



Where (s) singlet, (d) doublet, (t) triplet, (m) multiplet and σ chemical shift.



Figure 1. Mass spectra of the prepared compound (I18_a).



Figure 2. Mass spectra of the prepared compound (I18_b).



Figure 3. Mass spectra of the prepared compound (118_c) .

because of the high attractive power. Furthermore, the ester group in compounds I18c-I18d effect the value of protons (b) [8.129 and 8.129] respectively. In case of all four compounds I18a-I18d the aromatic protons (g) have the lowest (δ) values due to the presence of the ether oxygen. Despite, the aliphatic protons (i, j, k, k-, l, m, n and o) have different (δ) values according to their position to the ether bond. The j protons Ina have higher (δ) value 3.305 ppm, than I18a (δ) 3.209ppm, due to ether oxygen in the methoxy group.



Figure 4. Mass spectra of the prepared compound (118_d).

Table 8. Comparison of the transition temperatures of the compounds (118_{a-d}) .

Compound	T _{s-s}	T _m	T _{A-N}	T _c
118	9.43	49.55	_	62.16
l18 _b	16.96	38.88		51.50
l18	18.25	41.39	50.23	56.00
118 _d	—	46.86	_	78.42



Figure 5. Dependence of T_c on the polarizability anisotropy $\Delta \alpha \times$ of the Car-x bonds for series 118_{a-d} .



Figure 6. Conjugative interaction within the nitro-substituted homologue I18_d.



Figure 7. Conjugative interaction within the methoxy substituted homologue I18_a.

It is well recognized that the stability of the mesophase would be augmented by an increase in the polarity of the mesogenic part of the molecule (Fig. 5). Thus in the nitro analogue, the polarity of the mesogenic portion as a whole, Fig. 6, should be increased, which stabilized the mesophase. This heuristics is in accordance with the observed results, Table 8, that the nitro analogue has the highest clearing (T_c) temperature. On the contrary, the molecules of the methoxy and methyl analogues (Fig. 7) are expected to possess lower dipolar character that would lead to derivatives with lower T_c values.

Evaluation of the synthesized compounds as antioxidants using change total acid number

The TAN defined the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in 1 g of oil. It is important to valuate the amount of additive reduction, acidic contamination, and oxidation of lubricant degradation. It is an important quality measurement of crude oil and used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. The TAN value indicates to the crude oil refinery 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 TAN is an 196 👄 A. M. ASHMAWY ET AL.

analytical test to determine the deterioration of lubricants. The more acidic a lubricant is, the more degradation occurs. As a fluid degrades, the levels of corrosive acids increase, along with the danger of component failure.

The TAN value itself cannot be used to predict the corrosive nature of an oil, as the test only measures the amount of acid in a sample, not the specific quantities of different acidic compounds in the sample. Two samples might have the same TAN value, but one has high levels of corrosive acids while the other much lower levels of the same corrosive acids. An increase in viscosity and the formation of gums and resins are two other negative effects which can be attributed to an increased TAN value. A rise in TAN is indicative of oil oxidation due to time and/or operating temperature. Trend as well as absolute values should be used to monitor TAN levels.

The synthesized antioxidants were added to the base stock. The blends obtained were subjected to severe oxidation conditions at 120°C. Samples were taken at specific time intervals (24, 48, 72, and 96 hr) of oxidation. Usually the TAN of the oil increases by increasing the oxidation time. The increment of TAN values is due to the oxidation processes which produce peroxides. These peroxides undergo further reaction to form a variety of oxygenated compounds such as alcohols, aldehydes, and ketones. The TAN is affected by the formation of carboxylic acids after prolonged oxidation and increases with increasing carbonyl formation which deteriorates the lubrication ability of the oil [22, 23].

1. Initiation:

 $RH+I \rightarrow R + IH$

- 2. Propagation: $R \cdot + O_2 \rightarrow ROO$ $ROO \cdot + RH \rightarrow ROOH + R$
- 3. Termination: $R \cdot + R \cdot \rightarrow R \cdot R$ $ROO \cdot + ROO \rightarrow$ Stable products

From Table 9, Figs. 8–10, we can see that generally the TAN of the oxidized base stock increases by increasing the duration time. First of all, after 24 hr, the TAN decreases by

			Base Stock + Additive $\times 10^2$										
T :	Da	Ba	nse oil + '	18 _a	Ba	ise oil + '	18 _b	Ba	nse oil +	18 _c	Ba	ise oil +	18 _d
(hours)	stock	100	250	500	100	250	500	100	250	500	100	250	500
24	37	35	33	32	30	27	33	28	25	20	17	14	13
48	79	51	46	42	41	38	35	32	30	27	25	24	20
72	162	70	54	50	42	40	37	36	34	32	31	29	27
96	201	72	60	52	48	45	41	40	38	36	41	35	32

Table 9. Variation of total acid number, TAN, with and without additives.

^a The TAN of the base stock at room temperature is 0.067 mg KOH/mg sample.

Table 10. Mass spectroscopy for I18_{a-d}

Compound	Molecular formula	m/z obs.	m/z cal.
118 _a 118 _b 118 _c	$\begin{array}{c} C_{42}H_{60}N_{2}O_{4} \\ C_{42}H_{60}N_{2}O_{3} \\ C_{41}H_{57}BrN_{2}O_{3} \end{array}$	656.34 640.94 705.81	656.94 640.09 705
l18 _d	C ₄₁ H ₅₇ N ₃ O ₅	671.91	671.91



Figure 8. Variation of total acid number (TAN) of base oil without and with 100 ppm I18_{a-d} additives.



Figure 9. Variation of total acid number (TAN) of base oil without and with 250 ppm I18_{a-d} additives.



Figure 10. Variation of total acid number (TAN) of base oil without and with 500 ppm I18_{a-d} additives.

increasing the concentration of the additive added from each of the four compounds used. The base oil + 118_d showed the best results.

Increasing the oxidation period to 48, 72, and 96 hr, the TAN also decreases by increasing the concentration dose of any additive used. Again the base oil + 118_d gave the best results.

Looking in Table 9, we can see that the base oil $+118_a$ shows TAN at 100 ppm after 24 hr, base oil $+118_b$ shows the same at 500 ppm after 48 hr while the base oil $+118_d$ shows the same after 96 hr. Using 500 ppm from 18a after 24 hr, 100 ppm from 18c after 48 hr or 500 ppm after 72 hr and 500 ppm from 18d after 96 hr, one can notice that TAN of 0.032 mg KOH/g sample were obtained from each. Although the 118_c gave the best condition, TAN of 0.20 mg KOH/g

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sample, by using 500 ppm after 24 hr, but this compound showed less efficiency compared with 118_d at 48, 72, and 96 hr.

The results obtained after 24 hr from 18a using 100 ppm, after 48 hr from 18b using 500 ppm and from 18d after 96 hr using 250 ppm are the same (TAN 0.35 mg KOH/g sample). But, although it is more economical to use low concentration from the additive added, it is more efficient to use high concentration to run more operating time. So the 18d is more efficient because it gave the same results after long operating period.

Conclusions

The results obtained in this work indicate the following:

- 1. Four prepared compounds had properties of LCs.
- 2. In our study, LCs give more efficiency as antioxidant.
- 3. The prepared antioxidants proved to be successful in enhancing the oxidation stability of the base stock.
- 4. The above (total acid number) data reveal that the most effective concentration is 500 ppm.
- 5. From the previous data we noted that the inhibition efficiency of the two prepared antioxidants is ranked as follows: $I18_d > I18_c > I18_b > I18_a$.

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