Antioxidant Additives for Lubricating Oils. Synthesis and Evaluation of some Polyfunctionalized Phenols Linked to Heterocycles

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Abstract

The polyfunctionalized Phenols Linked to heterocyclic derivatives, 6-Amino-3-ethyl-4-(4-hydroxy-3-methoxyphenyl)-1-phenyl-4H-pyrano[3,2-d]pyrazole-5-carbonitrile **(3),** Methyl-6-amino-5-cyano-2-ethyl-4-(4-hydroxy-3-methylphenyl)-4H-pyran-3-carboxylate **(4),** 5-Amino-7-(4-hydroxy-3-methoxyphenyl)-2-methyyl-4,7,7a-trihydropyrazolo[1,5-a]pyrimidine-6-carbonitrile **(5)** and 3-Amino-1-(4-hydroxy-3-methoxyphenyl)-4H-benzo[f]chromene-2-carbonitrile **(6)** were synthesized. The antioxidants activities of different dosages of these compounds **3-6**, using the turbine base oil with viscosity grade ISO 46, were evaluated. Oxidation test (RBOT) according to IP 229 was applied and the optimum dosage of the promising compound was determined. The formulated blend containing 1.6 % wt. of compound **3** gave higher oxidation stability than a blend containing 0.8 % wt. of international commercial antioxidant additive (**IA**).

Keywords: Phenols; Pyranopyrazole; Antioxidants; Turbine oil.

Introduction

Mineral lubricating oils are usually used in presence of air whereby oxidative chemical reactions can take place. The rate of these oxidative processes varies greatly with the nature of oils, the extent of processing in refining, the temperature, and the presence of a metallic catalyst.[1,2] Such oxidations have a drawback on the oil, thus leading to failures in lubrication that accompanied by damage of machines. Large degree of damage is due to the formation of viscous, solid bodies, or jelly-like emulsions which interfere with the regular distribution of the lubricant. Consequently, antioxidant additives became highly required to decrease oil oxidation, with a secondary effect of reducing corrosion of certain types of sensitive bearing materials.[3] Antioxidants can generally be considered as free radical inhibitors of peroxide decomposers, and may vary in chemical structures. Three types of additives have been proved to be successful in controlling the degradation of lubricating oils; radical

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scavengers, and hydroperoxide decomposers, as well as synergistic mixtures of both of them. Thus, various classes of compounds have been used as antioxidant- additives, such as phenols,[4-10] amines[11-13] and heterocyclic compounds[14-17] as well as synergistic mixtures of them and other additives.[18-23] In the present work, new polyfunctionalized phenols linked to oxygen and nitrogen heterocycles have been synthesized and evaluated as antioxidants for lubricating oils.

Experimental

All melting points are uncorrected. The IR spectra were recorded to detect the functional group in potassium bromide on Nicolit (FT-IR), model 320. The ^{1}HNMR measurements were carried out in DMSO which used as a solvent for the analyzed compounds on a Varian, 600 MHz spectrophotometer; chemical shifts are expressed on δ scale. Microanalyses were performed on Heraeus analyzer. The chemicals which were used in the synthesis of the target compounds were reagent grade and used without further purification.

Synthesis of Some Polyfunctionalized Phenols Linked to Heterocycles.

Synthesis of the Starting Compounds

The 4-(hydroxyl-3-methoxybenzylidine) molononitrile **1** was prepared by heating a mixture of 4-hydroxy-3-methoxy benzaldehyde (15.2 g, 0.1 mole), molononitrile (6.6 g, 0.1 mole) and drops of pipridine in ethanol (50 ml) under reflux for 30 minutes. Then the mixture was left for overnight, and the product was recrystallized from ethanol to give compound **1**. Compound 3-ethyl-1-phenyl-2-pyrazolin-5-one **2** was synthesized as described in literature. [24]

Syntheses of Polyfunctionalized Phenols Linked to Heterocycles, 3-6

A solution of 4-(hydroxyl-3-methoxybenzylidine)molononitrile **1** (20 g, 0.1 mole) and 0 3-ethyl-1-phenyl-2-pyrazolin-5-one **2**, or ethyl propionylacetate or 3-amino-5-methyl pyrazole or ß-naphthol (0.1 mole) in ethanol (50 ml) and two drops of pipridine was heated under reflux for 2 hours, cooled and poured onto water. The products were recrystallized from ethanol to give the corresponding compounds 6-amino-3-ethyl-4-(4-hydroxy-3-methoxyphenyl)-1-phenyl-4H-pyrano[3,2-d]pyrazole-5-carbonitrile **3**, Methyl-6-amino-5-cyano-2-ethyl-4-(4-hydroxy-3-methylphenyl)-4H-pyran-3-carboxylate **4**, and 5-amino-7-(4-hydroxy-3-methoxyphenyl)-2-methyyl-4,7,7a-trihydropyrazolo[1,5-a] pyrimidine-6-carbonitrile **5** whereas 3-amino-1-(4-hydroxy-3-methoxyphenyl)-4H-benzo[f]chromene-2-carbonitrile **6** was recrystallized from benzene.

Formulation of Industrial Oil Blends

Two blends of turbine oil ISO 46 without and with the recommended dosage of international commercial antioxidant additive (IA) according to the performance specifications (0.8% Wt.) were formulated and labeled as B0 and B1. On the other hand blends of compounds 3-6 were prepared by dissolving them in a mixture of toluene and xylene (1:1); dopanol was added for complete solvation and to achieve the required homogeneity of the final blends. Then industrial lubricating oil blends of different dosages (0.8%, 1.2% and 1.6%) of each of the synthesized compounds 3-6 with turbine base oil of viscosity grade ISO 46 were formulated and labeled as B2-B13.

The antioxidant properties of each formulated blend of the synthesized compounds were evaluated by applying the oxidation test (RBOT) according to IP 229 test method. The blend which has the required oxidation stability value was evaluated (Table 1) using the standard international test methods compared to the commercial antioxidant additive.

Table 1: Standard International Test Methods for the Best Formulated Blend

Properties	Test Method
Kinematic Viscosity @ 40 °C, mm^2/s	ASTM-D 445
Kinematic Viscosity @ 100 °C, mm^2/s	ASTM-D 445
Viscosity Index (VI)	ASTM D- 2270
Flash Point (C.O.C), °C	ASTM D-92
Pour Point, °C	ASTM D-97
T.A.N, mg KOH/ gm sample	ASTM D- 664
Foam tendency / stability, ml	IP 146, ASTM D-892
Air Release at 50 °C, min.	IP 313
Demulsibility after steam treatment, min.	IP 19
Copper Corrosion (3 h, 100 °C)	IP 154, ASTM D- 130
Rust protection	D-665 B
Oxidation Stability (RBOT), min.	ASTM D- 2272, IP-229
Oxidation Stability, • AN Value, mg KOH/g. • Sludge Content, %	ISO DP 7624

Results and Discussion

Synthesis of Polyfunctionalized Phenols Linked to Heterocycles

The (4-hydroxyl-3-methoxyphenylmethylene]methane 1,1-dicarbonitril (**1**) was prepared by reaction of molononitrile with 4-hydroxy-3-methoxy benzaldehyde, which upon condensation with 3-ethyl-1-phenyl-2-pyrazolin-5-one (**2**) in presence of piperidine gave 6-amino-3–ethyl-4-(4-hydroxy-3-methoxyphenyl)-1-phenyl-4H-pyrano[3,2-d]pyrazole-5-carbonitrile (**3**). **S**imilarly, compound **1** was condensed with ethyl propionoylacetate, 3-amino-5-methyl pyrazole, β-naphthol to give methyl 6-amino-5-cyano-2-ethyl-4-(4-hydroxy-

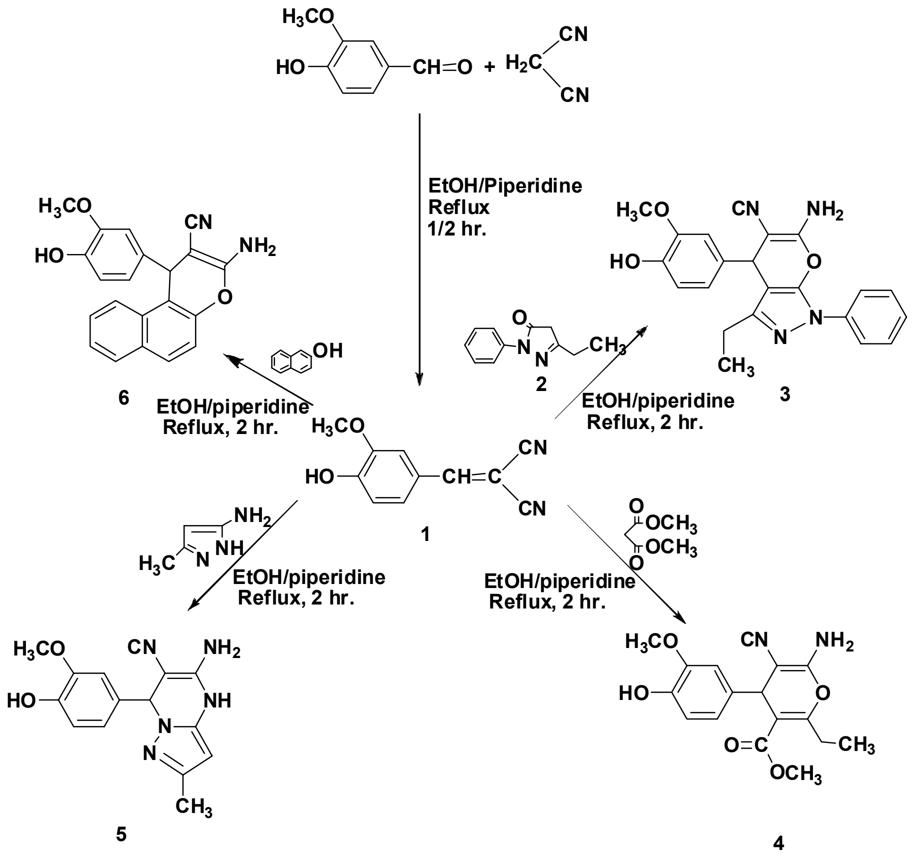
3-methoxyphenyl)-4H-pyran-3-carboxylate (**4**), 5-amino-7-(4-hydroxy-3-methoxyphenyl)-2-methyl-4,7,7a-trihydropyrazolo[1,5a]pyrimidine-6-carbonitrile (**5**) and 3-amino-1-(4-hydroxy-3-methoxyphenyl)benzo[f]4H-chromene-2-carbonitrile (**6**), respectively (scheme 1).

The structure of compounds **2**, **3** and **6** were confirmed by ^{1}H NMR, and IR spectroscopy as well as elemental analysis (table 2).

Evaluation of the formulated industrial lubricating oil blends

The physical, chemical and performance properties of a turbine oil ISO 46 blends B0 and B1, without and with the recommended dosage of the international commercial antioxidant additive (IA), were determined and compared with each other. The evaluation was carried out on each blend according to the international standard test methods as maintained in table 1, and the results were shown in table 3.

While, different turbine oil blends with viscosity grade ISO 46 were formulated using different dosages 0.8%, 1.2 % and 1.6% wt. of each compounds **3-6** which labeled as **B2-B13** and each blend was evaluated, by applying the rotatory oxidation bomb test (RBOT) according to IP 229 which is the main property for the antioxidants. The oxidation stability of the synthesized compounds were measured according ISO 7624 , where, the AN(s) and sludge content were determined for each oxidized blend (table 4) and compared with a blend of 0.8 % wt. of commercial antioxidant additive **IA** (B1).



Scheme 1. Synthesis of some polyfunctionalized phenol linked to heterocycles

Table 2: Properties of Synthesized Compounds **1-6**

Compd. No.	m.p.◦ C	Yield %	Mol. Formula	Mol. wt.	Calcd./ Found(%) C	H	N	Spectral Date
1	130	88	$C_{11}H_8N_2O_2$	200	66.60 66.31	4.00 4.09	14.00 14.05	IR (KBr) ν: 3427 (OH), 2222 (CN), 1611, 1566 and 1515 cm-1 (aryl –H)
2	98	85	$C_{11}H_{12}N_2O$	188	70.21 70.32	6.38 6.45	14.89 14.99	IR (KBr) ν: 2970, 2936 and 2877 (CH3 and CH2), 2561 (NH), 1720 (CO), 1591, 1545 cm-1 (aryl-H)
3	169	83	$C_{22}H_{20}N_4O_3$	388	68.04 68.23	5.10 5.22	14.43 14.51	IR (KBr) ν: 3428-3213 (OH), 2186 cm-1 (CN), cm-1,; HNMR (DMSO-d6): δ 0.93 (t, 3H, CH3), 2.17 (q, 2H, CH2), 2.50 (s, 3H, OCH3), 3.72 (s, 1H, CH), 4.59 (s, 1H, Ar OH), 6.61-7.81 (m, 10H,8 ArH,
4	170	89	$C_{17}H_{18}N_2O_5$	330	61.81 61.92	5.45 5.57	8.48 8.33	IR (KBr) ν: 3490-3330 (OH), 2193 (CN), 1694 and 1677 cm^{-1} (CO and C=C)
5	> 320	89	$C_{15}H_{15}N_5O_2$	297	66.60 66.72	5.05 5.15	23.56 23.68	IR (KBr) ν: 3366-3218 (OH), 2209 cm-1 (CN).
6	101	87	$C_{21}H_{16}N_2O_3$	344	73.25 73.32	4.65 4.86	8.14 8.21	IR (KBr) ν: 3436 (OH), 2185 (CN), 1650 cm^{-1} (C=C); ^{1}HNMR (DMSO-d_6): δ 2.50 (s, 3H, OCH_3), 3.40 (s, 1H, CH), 5.18 (s, 1H, Ar OH), 6.4 (m,11H, 9 Ar H, NH_2).

Table 3: Physical, chemical and performance properties of turbine oil blends, with and without the recommended dosage of commercial additive **(IA).**

Properties	Standard Specifications According to HTGD 90 117 V0001 R (may 2000)	Turbine Oil Blend ISO 46	
		Without Additive **B0**	With 0.8 %Wt. (IA), **B1**
Kinematic Viscosity @ 40°C, cSt.	46±10% (41.4-50.6)	46.3	47.00
Kinematic Viscosity @ 100°C, cSt.		6.65	6.75
Viscosity Index, VI	90 (min.)	94	96
Flash Point (C.O.C) °C.	185 (min.)	188	189
Pour Point, ° C	-6 (min.)	-3	-6
Foam tendency, ml. Sequence I Sequence II Sequence III	 450/0 50/0 450/0	 190/0 20/0 340/0	 60/0 0/0 50/0
Copper Corrosion (3 h, 100° C)	2 (max.)	1 A	1A
TAN, mg KOH/ gm sample	0.3 (max.)	0.015	0.04
Demulsibility after steam treatment.	5 (max.)	1	1.35
Rust protection	None	None	None
AIR Release, at 50°C.	4 (max.)	1.19	1.39
Oxidation Stability, (RBOT), minutes	300 (min.)	30	302
Oxidation Stability, • A.N. value,mg KOH/g. • Sludge Content, %	 1.8 max. 0.4 max.	 1.7 2.25	 1.75 0.39

Table 4: Evaluation of the polyfunctionalized phenols as antioxidant additives for turbine oil **ISO 46**

Blend No.	**Additive %wt.**	Oxidation Stability (RBOT), minutes IP 229	Oxidation Stability ISO 7624	
			A.N value, mg KOH/g.	Sludge Content %.
B1	**0.8 % of IA**	**302**	**1.75**	**0.39**
B2	0.8% of **3**	155	0.75	0.25
B3	0.8% of **4**	105	0.50	0.20
B4	0.8% of **5**	140	0.65	0.22
B5	0.8% of **6**	109	0.52	0.23
B6	1.2% of **3**	270	1.45	0.37
B7	1.2% of **4**	200	1.35	0.29
B8	1.2% of **5**	250	1.39	0.35
B9	1.2% of **6**	235	1.39	0.30
B10	1.6% of **3**	305	1.65	0.38
B11	1.6% of **4**	245	1.37	0.33
B12	1.6% of **5**	264	1.48	0.35
B13	1.6% of **6**	272	1.47	0.36

The percentage of 0.8% wt of each of compounds **3-6** at blends (**B2**-**B5)** did not obey the HTGD 90 117 V0001 R specifications, since the oxidation test (RBOT) according to IP 229 values were 155,105,140 and 109 minutes, respectively, whereas the standard specification value is 300 minutes minimum. When the percentage of the compounds was raised to 1.2% wt (blends **B6-B9),** the oxidation test values were 270, 200, 250 and 235 minutes, respectively. On the other hand, when the percentage of the compounds were raised to 1.6% wt. (blends **B10-B13**).

It was found that the blend **B10** containing 1.6 % of 6-amino-3-ethyl-4-(4-hydroxy-3-methoxyphenyl)-1-phenyl-4H-pyrano[3,2-d]pyrazole-5-carbonitrile **3** was the only one that meet the oxidation requirements according to the standard specifications where it resisted oxidation for 305 minutes. It was even higher than the oxidation stability of the blend containing 0.8%wt of commercial antioxidant additive **IA**, **B1**. Thus, compound **3** has the best antioxidant property for turbine oil with viscosity grade ISO 46**.**

The chemical, physical and performance properties of blend **B10** were determined and compared with the data by using the optimum dosage of an international commercial antioxidant additive (IA) and the international specifications of HTGD 90 117 V0001R (table 5).

Table 5: Chemical, physical and performance properties of turbine oil blends ISO 46 with optimum dosage. of compound **3** compared with the standard specifications.

Properties	HTGD 90 117 V0001 R	Turbine Oil Blend ISO 46	
		B1 (0.8 %Wt. IA)	**B10** (1.6%Wt.)
Kinematic Viscosity @ 40°C, cSt.	46±10% (41.4-50.6)	47.00	48.67
Kinematic Viscosity @ 100°C, cSt.		6.75	6.79
Viscosity Index, VI	90 (min.)	96	95
Flash Point (C.O.C) °C	185 (min.)	189	187
Pour Point, ° C	-6 (min.)	-6	-3 -6*
Foam tendency / stability, ml, max. Sequence I Sequence II Sequence III	 450/0 50/0 450/0	 60/0 0/0 50/0	 270/0 40/0 140/0
Copper Corrosion (3 h, 100 °C)	2 (max.)	1A	1A
TAN, mg KOH/ gm, sample	0.3 (max.)	0.04	0.02
Demulsibility after steam treatment, min.	5 (max.)	1.35	1.5
Rust protection	None	None	None
AIR Release, at 50C, min.	4 (max.)	1.39	2.50
Oxidation Stability (RBOT) , minutes	300 (min.)	302	305
Oxidation Stability, • A.N. value,mg KOH/g. • Sludge Content, %	 1.8 max. 0.4 max.	 1.75 0.39	 1.65 0.38

• with 50 ppm of commercial pour point depressant additive.

The results indicated that the blend has all the standard specifications of HTGD 90 117 V0001 R with exception of high pour point property which covered by adding 50 ppm of a pour point depressant additive.

The efficiency of the phenolic derivative **3** can be due to the known establishment of such compounds to be efficient antioxidants as a result of their ability to quench radicals produced by autoxidation of industrial lubricating oils.

Economical feasibility study

The production cost of the synthesized compound 6-amino-3-ethyl-4-(4-hydroxy-3-methoxyphenyl)-1-phenyl-4H-pyrano[3,2-d]pyrazole-5-carbonitrile (**3**) and its blending with a concentration of 1.6 % wt in a ton of turbine oil ISO 46 has been compared with the cost of blending the commercial antioxidant additive (IA) with a concentration of 0.8 % wt (Table 6). The data indicated that the cost of the synthesized compound was higher than the commercial one.

Table 6. The feasibility study of blends with compounds **3** compared with a blend with **IA**

Additive	IA	Compound 3
Cost of additive in one ton of Turbine oil ISO 46, L.E	208.71	398.80
Oxidation Stability Test, (RBOT), minutes	302	305

Conclusions

In conclusion compound **3** with a percentage of 1.6 %wt in the final blend gave higher oxidation stability than that which given by the international commercial additive (IA). The efficiency of the phenolic derivative **3** can be due to the known establishment of such compounds to be efficient antioxidants as a result of their ability to quench radicals produced by autoxidation of industrial lubricating oils. The results are encouraging and further studies are required to evaluate more compounds in this series to get more economical products.

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