Synthesis, Characterization and Evaluation of Some Pyranopyrazoles and Pyranopyrimidines Derivatives as Antioxidants for Lubricating Oils

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Abstract

6-Amino-4-(4-hydroxyphenyl)-5-cyano-3-methyl-1-phenyl-1, 4-dihydropyrano [2,3-*c*] pyrazole (compound 2) was prepared by condensation of 2-(4-hydroxylbenzylidine) malononitrile (compound 1) [which was prepared by Knoevenagel condensation of malononitrile with 4-hydroxy benzaldehyde] with 3-methyl-1-phenyl-2-pyrazolin-5-one. Reactions of compound 2 with different reagents formic acid, formamide, and ammonium thiocyanate under microwave irradiation leads to the synthesis of 4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-4,6-dihydro- pyrazolo [3', 4':5,6] pyrano [2,3-d] pyrimidine-5-one (compound 3), 4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-4, 6-dihydro- pyrazolo [3', 4':5,6]pyrano[2,3-d]pyrimidine-5-imine (compound 4) and N-[4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-7-thioxo-7,8- dihydropyrazolo [3', 4':5,6] pyrano [2,3-d] pyrimidine-5-yl] thiourea (compound 5) respectively. Moreover a series of Schiff bases 6(a-f) were prepared by reaction of compound 2 with different aromatic aldehydes.

The prepared compounds were characterized by FTIR, and most ^{1}HNMR,^{13}CNMR and evaluated as antioxidant additives by blending 1% of each compound with base lubricating oil 60 stock supplied by Midland Refineries Company, Baghdad, Iraq. The formulated blend of compound 6a showed better oxidation stability compared with the base oil (blank), while the oil blend of compound 5 gave higher oxidation stability than the blend with standard antioxidant supplied by Midland Refineries Company.

Keyword: Pyranopyrazol, Pyranopyrimidine, Schiff base, Microwave, Lubricating oil, Antioxidant.

تحضير وتشخيص وتقييم بعض مشتقات البايرنوبايرزل والبايرنوبيرميدين كمضادات أكسدة في زيوت التزييت

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الخلاصة:

حضر المركب (2) 6-Amino-4-(4-hydroxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano [2,3-c]pyrazole من تكاثف 3-methyl-1-phenyl-2-pyrazolin-5-one مع المركب (1) 2-(4-hydroxy-benzylidine) malononitrile [المحضر بوساطة تكاثف]

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Knoevenagel لمشتق 4−hydroxy benzaldehyde مع] malononitrile. تم مفاعلة المركب (2) مع كل من حامض الفورميك والفورمامايد وثايوسيانات الامونيوم باستخدام المايكروويف لتحضير 4−(4-hydroxyphenyl)- 3-methyl-1-phenyl-4,6-dihydro− pyrazolo[3', 4':5,6]pyrano[2,3-d]pyrimidine-5-one (compound 3), 4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-4,6−dihydro- pyrazolo[3', 4':5,6]pyrano[2,3-d]pyrimidine-5-imine (compound 4) and N−[4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-7-thioxo-7,8- dihydropyrazolo [3', 4':5,6] pyrano [2,3-d] pyrimidine-5-yl] thiourea (compound 5) على التوالي. كما حضرت قواعد شيف (a−f)6 من تفاعل المركب (2) مع الديهايدات مختلفة.

شخصت المركبات المحضرة بوساطة مطيافية الاشعة تحت الحمراء وقسم منها بمطيافية الرنين النووي المغناطيسي للبروتون والكربون كما تم تقييمها كمضادات للاكسدة بخلط 1% من كل مركب مع زيت الاساس من نوع 60 stock المجهز من شركة مصافي الوسط. أظهر خليط الزيت مع المركب 6a ثباتية عالية تجاه الاكسدة مقارنة مع زيت الاساس بينما مزيج الزيت مع المركب المحضر 5 اظهر ثباتية تجاه الاكسدة اعلى من مزيج الزيت مع المادة المضادة للاكسدة المستخدمة في شركة مصافي الوسط.

Introduction:

Lubricants are used to prevent damage to the machinery which arises from friction between moving parts in service. Oxidation stability is one of the key requirements of the lubricant because, oxidation produces harmful species, e.g. peroxy radicals, hydroperoxides and organic acids as well as sludge and deposits, which shortens the lubricant service life, and damages the machinery it lubricates [1]. The oxidation is initiated upon exposure of hydrocarbons to oxygen and heat, while engine metal parts acting as effective oxidation catalysts. For the prevention of lubricant oxidation, antioxidants are the additive that protects the lubricant from oxidative degradation [2]. Most of antioxidant additives act as radical scavengers, hydroperoxide decomposers, or through a combination of the functionalities of both of them.

Common antioxidants in lubricants include both sterically hindered phenolic compounds [3,4] and aromatic amines [5- 7], the combination of amine and phenolic moieties in one molecule represents a logic approach to enhance performance. Phenolic imidazolines have been prepared from polyaminophenols and carbonyl compounds [8]. Additives containing sulfur, nitrogen, and phenolic moieties in one molecule have been reported as antioxidant and antiwear [9]. Multifunctional antioxidants, hydroxylamines, and alkyl radical scavengers, can be found in the literature [10]

3-Methyl-1-phenyl-2-pyrazolin-5-one, play an essential role in several biological processes and have considerable pharmacological importance, its pharmacological actions were attributed to its antioxidant activity, as a potent hydroxyl radical scavenger [11]. Some arylidenepyrazolones are used as intermediates in pharmaceuticals and antioxidants [12]. On the other hand, pyran derivatives possess pronounced chemical and biological properties [13,14]. Moreover, pyrimidines present an interesting group of compounds many of which possess wide-spread pharmacological properties [15].
Compounds having a combination of cyclohexylpyran with pyrazolinone and pyrimidine moieties can be expected to possess antioxidant properties. In this work a fused pyrimidine moiety was incorporated with other heterocyclic ring system to obtain new functions in an attempt to improve the antioxidant properties.

Experimental:

Materials

All materials and solvents were of analytical reagent grade and supplied from Sigma-Aldrich, Merck, and BDH chemicals. Malononitrile and 4-hydroxy benzaldehyde were supplied from Fluka, AG.

Base oil properties:

Base lubrication oil 60 stock supplied by Midland Refineries Company, was used for preparation of oil blends with the prepared antioxidants. The properties of the oil were listed in table 1.

Table 1- Properties of base lubricating oil 60 stock

No.	Specification	60 stock	Standard test method
1.	Kinematic viscosity at 40 °C, cSt (mm^2/s)	63.0	ASTM-D 445
2.	Kinematic viscosity at 100 °C, cSt (mm^2/s)	8.3	ASTM-D 445
3.	Viscosity index	100	ASTM D- 2270
4.	Specific gravity at 60/60 ^oF	0.884	ASTM D-4052
5.	Pour point,°C	-6	ASTM D-97
6.	Flash Point, °C	250	ASTM D-92
7.	Color	3.0	ASTM D-1500

Instrumentation

Melting points were measured using Stuart. Scientific. SMP1 melting point apparatus and are uncorrected. Infrared spectra were recorded on Shimadzu FTIR-8400S Spectrophotometer as KBr disc, Department of Chemistry, College of Science, Baghdad university. ^1H NMR and ^{13}C NMR spectra were recorded on a Burker model ultra shield at 300 MHz using DMSO- d_6 as solvent and the chemical shifts were expressed in ppm relative to TMS as internal reference, (Middle East Technical university,Ankara, Turkey).

Galanz D90 D25 EL (800W) domestic microwave oven was modified to use as microwave irradiation reactor.

Test methods

Thin-layer chromatography (TLC) was used to monitor the progress of the reaction and to check the purity of the prepared compounds. TLC was performed on aluminum sheets pre-coated with silica gel 60 supplied by Merck. A mixture of ethanol and n-hexane solvent (2:8) was used as elutant. Spots were detected with iodine vapors.

Oxidation stability was determined according to Institute of Petroleum testing method IP 280. 25 g of inhibited oil were blended with 0.25 g of soluble metal catalyst (iron and copper). An oxygen flow was passed through the oil for 164 hours at 120°C. After the test the volatile acids, the acidity of the oil and the precipitated sludge were measured and their values were used to calculate the total oxidation products (TOP).

Synthesis of the Starting Compounds

The 2-(4-hydroxylbenzylidine)malononitrile (compound **1)** was prepared by microwave irradiation of a mixture of 4-hydroxy benzaldehyde (12.2 g, 0.1 mole), malononitrile (6.6g, 0.1 mole) and 5drops of pipridine in ethanol (25 ml) for 1 minute at 160 W. After cooling the mixture, gray precipitate was formed. The precipitate was filtered and recrystalized from ethanol to give the starting compound **1** as gray crystalline; yield 91.3%; mp: 184-186 ^oC; IR(cm^{-1}): 3353.9(OH), 3028(CH), 2227.6(CN), 1610.4(C=C), 1581.5(C=C, Ph).

3-Methyl-1-phenyl-2-pyrazolin-5-one was prepared from ethylacetoacetate and phenylhydrazine according to a reported method in literature [16].

Synthesis of 6-Amino-4-(4-hydroxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydro- pyrano[2,3-c]pyrazole (compound 2)

A mixture of 2-(4-hydroxylbenzylidine) malononitrile (8.5 g, 0.05mol) and 3-methyl-1-phenyl-2-pyrazolin-5-one (8.7g, 0.05mol) in ethanol (25 ml), in the presence of few drops of pipridine was irradiated in microwave for 2 minutes at 160 W. After cooling the solid product was filtered and crystallized from ethanol to give compound **2** as white solid; yield 86%; mp: 208-210 ^oC; IR(cm^{-1}): 3414 and 3317.5(NH_2), 3062.9(CH), 2179.5(CN),1658.7(C=N), 1593.2(C=C, Ph).

Synthesis of 4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-4,6-dihydro- pyrazolo[3', 4':5,6] pyrano[2,3-d]pyrimidine-5-one (compound 3)

A mixture of compound **2** (3.44 g, 0.01 mol) and formic acid (15 mL) was heated for 5 minutes under microwave irradiation at 160 W and then left to cool at room temperature. The reaction mixture was poured onto crushed ice, the solid product was filtered, dried, and crystallized from ethanol to give compound **3** as yellow solid; yield 71%; mp: 230-234 ^oC; IR(cm^{-1}): 3250(OH), 3176.5(NH), 3068.5(CH), 1701.8(C=O), 1654.8(C=N), 1593.09(C=C, Ph).

Synthesis of 4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-4,6-dihydro- pyrazolo[3', 4':5,6] pyrano[2,3-d]pyrimidine-5-imine (compound 4)

A mixture of compound **2** (3.44 g, 0.01 mol) and formamide (10 mL) in dimethylformamide (10 mL) followed by few drops of piperidine. The reaction mixture was heated for 5 minutes under microwave irradiation at 160 W, then cooled and poured into ice cold water and neutralized by dilute hydrochloric acid for complete precipitation. The precipitated solid was filtered, dried and crystallized from aqueous ethanol to give compound **4** as off white solid; yield 63%; mp: 180-184 ^{o}C; IR(cm^{-1}): 3387(NH imine), 3190.2(NH), 3066.8(CH), 1604.7(C=N), 1570(C=C, Ph).

Synthesis of N-[4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-7-thioxo-7,8- dihydro- pyrazolo [3', 4':5,6] pyrano [2,3-d] pyrimidine-5-yl] thiourea (compound 5)

A mixture of compound **2** (3.44 g, 0.01 mol) and ammonium thiocyanate (1.5 g, 0.02mol) in acetic acid (10 mL) was heated for 4 minutes under microwave irradiation at 160 W, the product cooled and poured into ice cold water. The solid product was filtered, dried, and crystallized from ethanol to give compound **5** as yellow solid; yield 76.5%; mp: 154-156 ^{o}C; IR(cm^{-1}): 3344.6 broad(OH and NH_2), 3186.4 and 3167.1(NH), 3066.8(CH), 1585.5(C=C, Ph),1261.4(C=S).

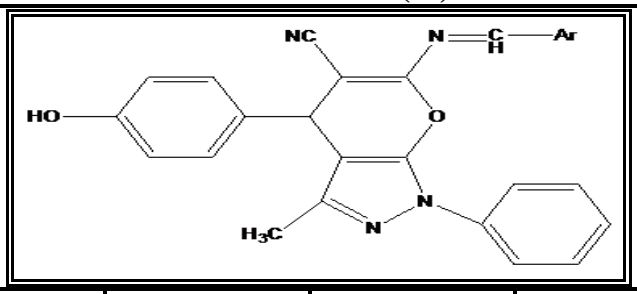
Synthesis of Schiff base derivatives 6(a-f)

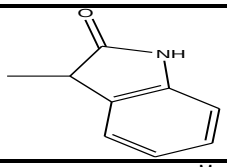
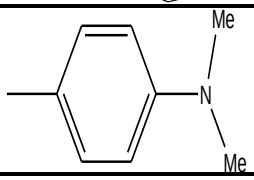
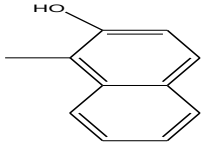
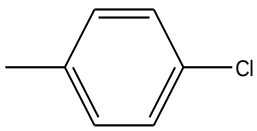
The appropriate aromatic aldehyde (0.005 mol) with two drops of glacial acetic acid in ethanol (10 mL) was added to a solution of compound **2** (3.47 g, 0.01 mol) in ethanol (10 mL), and the reaction mixture was heated for 2-4 minutes under microwave irradiation at 320 W. The product cooled and the separated solid was filtered and crystallized from ethanol.

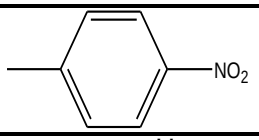
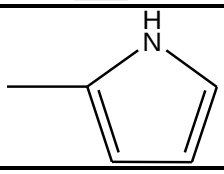
Table 2- lists the physical properties of the Schiff base derivatives 6(a-f).

All the synthesis steps are shown in scheme 1.

Table 2- The physical properties of the Schiff base derivatives 6(a-f)



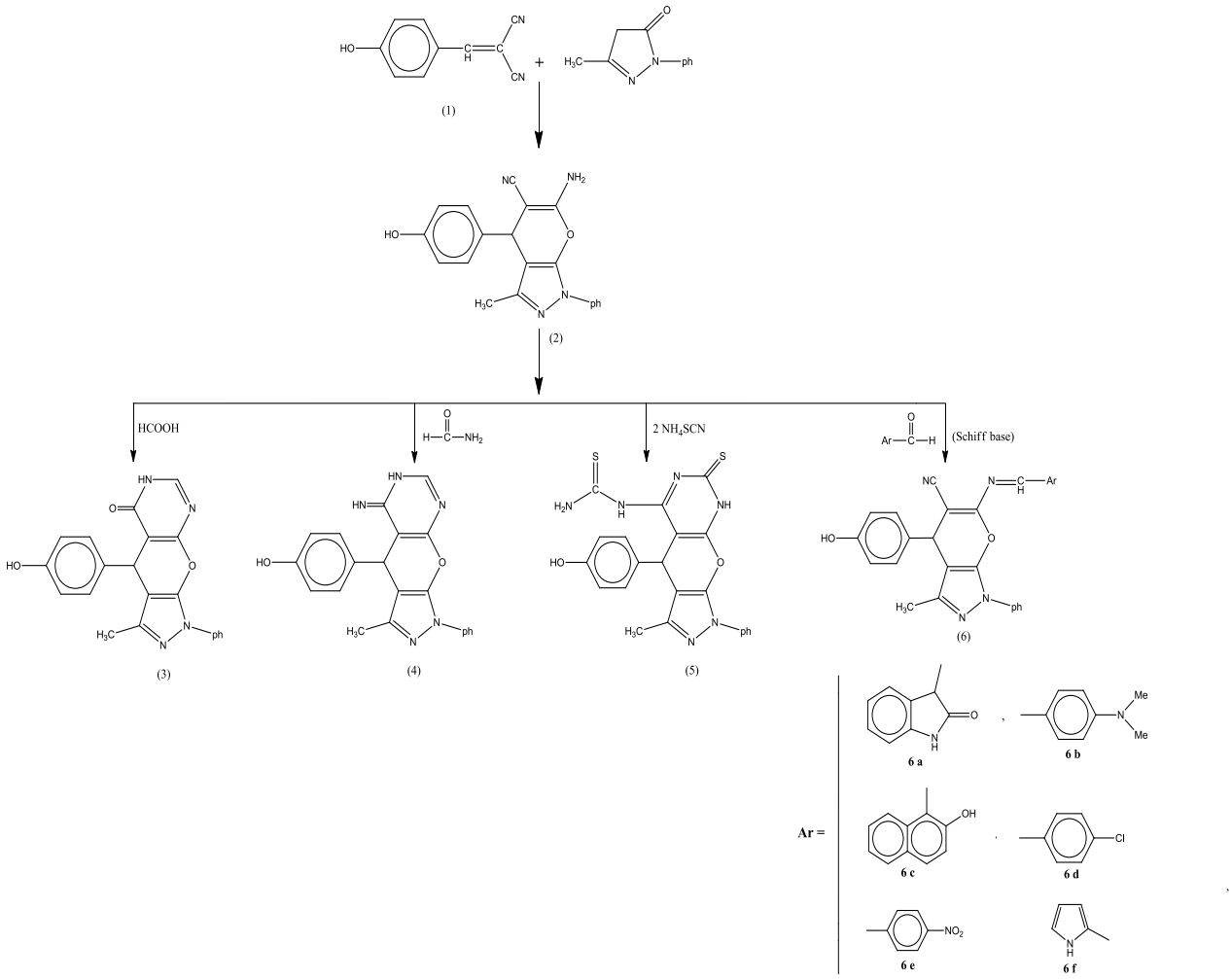
Com. no.	*Ar*	*Formula*	*Molecular weight, g/mol*	*Color*	*Mp., ^{o}C*	*Yield, %*
6a		$C_{29}H_{21}O_3N_5$	487.51	orange	172-174	68.92
6b		$C_{29}H_{25}O_2N_5$	475.54	red		52.57
6c		$C_{31}H_{22}O_3N_4$	498.53	yellow	160-162 Dec.	50.96
6d		$C_{27}H_{19}O_2N_4Cl$	466.92	Off-white	198-200	58.30

6e		$C_{27}H_{19}O_4N_5$	477.47	orange	220-224	82.68
6f		$C_{25}H_{19}O_2N_5$	421.45	yellow		66.32

Formulation of oil blends

Blends of compounds (1-5, 6a, 6b and 6c) were prepared by dissolving 1% of each compound in t-amyl alcohol and mixing with base oil 60 stock at 80 ^{o}C for 1 hour and labeled as B1-B5, B6a, B6b and B6c.

Blend oil with 1% standard antioxidant supplied by Midland Refineries Company was formulated and labeled as B7, while B0 means the blank.

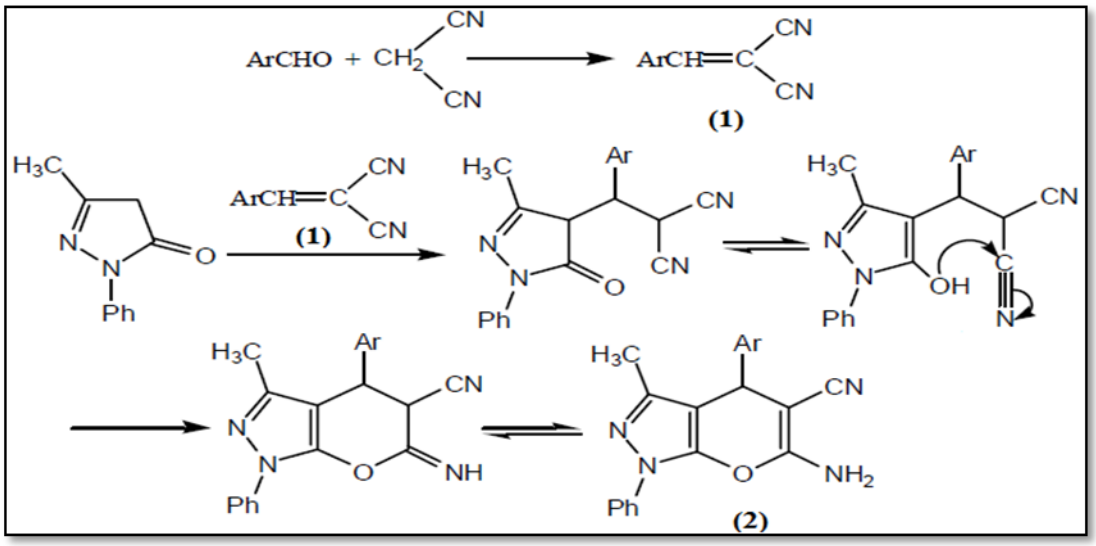


Scheme 1- Synthesis steps

Results and Discussion:

when 2-(4-hydroxylbenzylidine) malononitrile (compound 1) reacted with 3-Methyl-1-phenyl-2-pyrazolin-5-one under microwave irradiation, the 6-amino-4-(4-hydroxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole (compound 2) was obtained according to the mechanism illustrated in scheme 2.

Its IR spectrum showed stretching bands at 3414 and 3317 cm-1 (NH_2), 2179 cm-1 (C≡N), and at 1658 cm^{-1} due to C=N. The 1H- NMR spectrum (δ-ppm) of compound 2 showed signals at δ1.8 (3H- singlet) for CH_3, and δ4.45 (1H- singlet) for 4-H pyrane. The aromatic protons (9H- multiplet) appeared at δ6.73- 7.95, while the NH_2 appeared as singlet at δ7.18.



Scheme 2- Formation mechanism of compound (2)

Reaction of compound 2 with excess formic acid, gave 4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-4,6-dihydro- pyrazolo[3', 4':5,6]pyrano[2,3-d]pyrimidine-5-one (compound 3). IR spectrum of compound 3 showed an absorption bands at 3250 cm^{-1} (OH), and 3176.5 cm^{-1} (NH). The NH_2 and C≡N bands were disappeared, while (C=O) band was appeared at 1701.8 cm^{-1}.

The ^{1}H- NMR spectrum, figure 1- showed the singlet signals at δ10.81 and δ9.14 were assigned for OH and NH protons respectively. Proton of pyrmidone CH appeared at δ 8.6. Aromatic protons appeared as multiplet at δ7.95- δ6.6. The signal at δ4.35 was assigned to pyran proton, while CH_3 protons appeared at δ2.1 as singlet.

^{13}CNMR spectrum, figure 2- showed a characteristic signals at 173.7 ppm for C=O, the carbons of C=N for pyrazol ring appeared at 138.9 ppm, while C-OH and CH of pyrimidone appeared at 152.3 and 148.9 ppm respectively. Carbons of pyran ring (C-O-C) appeared at 163.5 and 162.4 ppm. The aromatic carbons appeared at 129.4-115.3ppm. Carbon of methyl group appeared at 13.6 ppm.

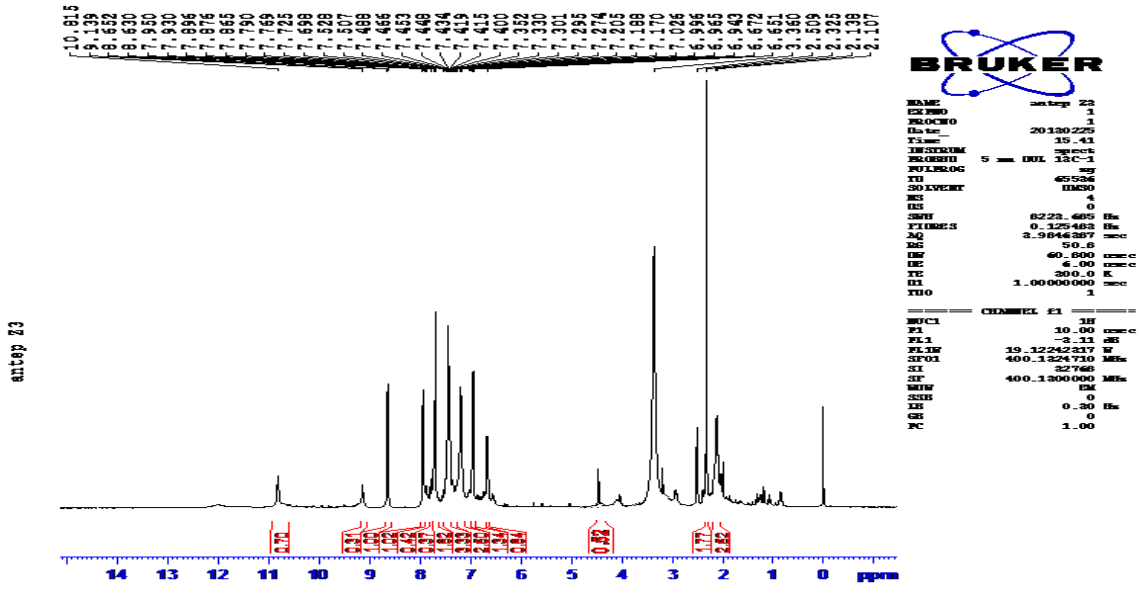


Figure 1- ^{1}HNMR spectrum of (compound 3)

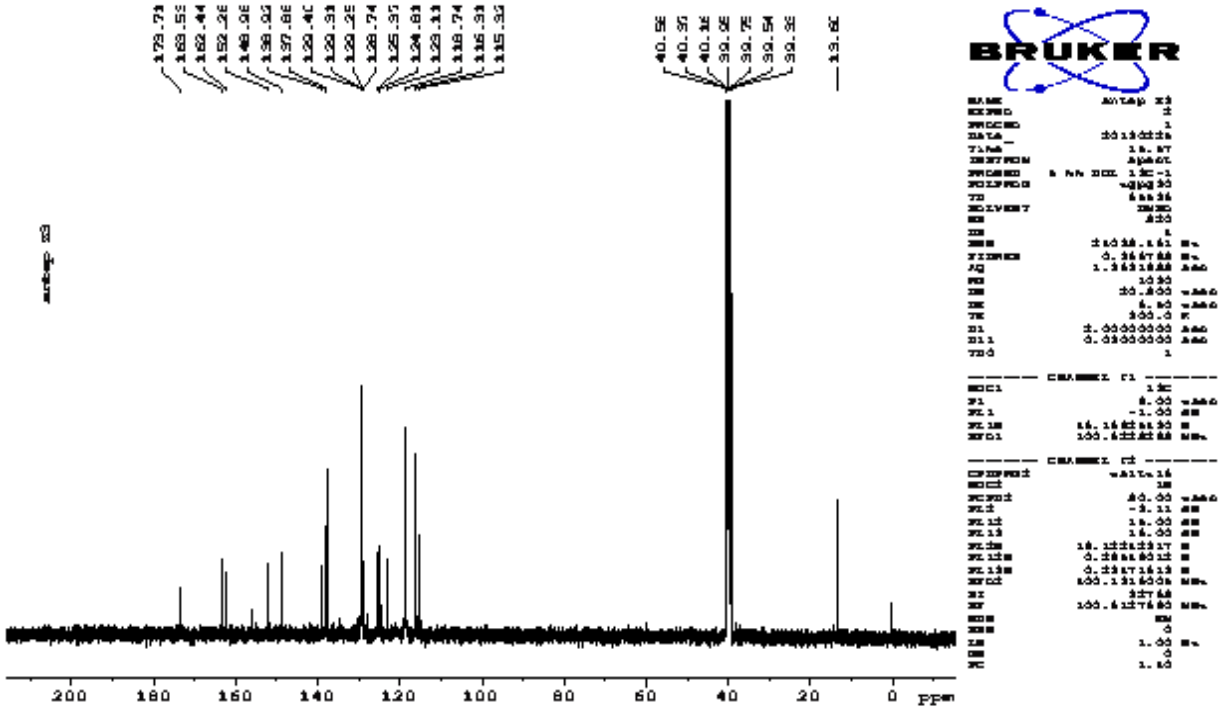
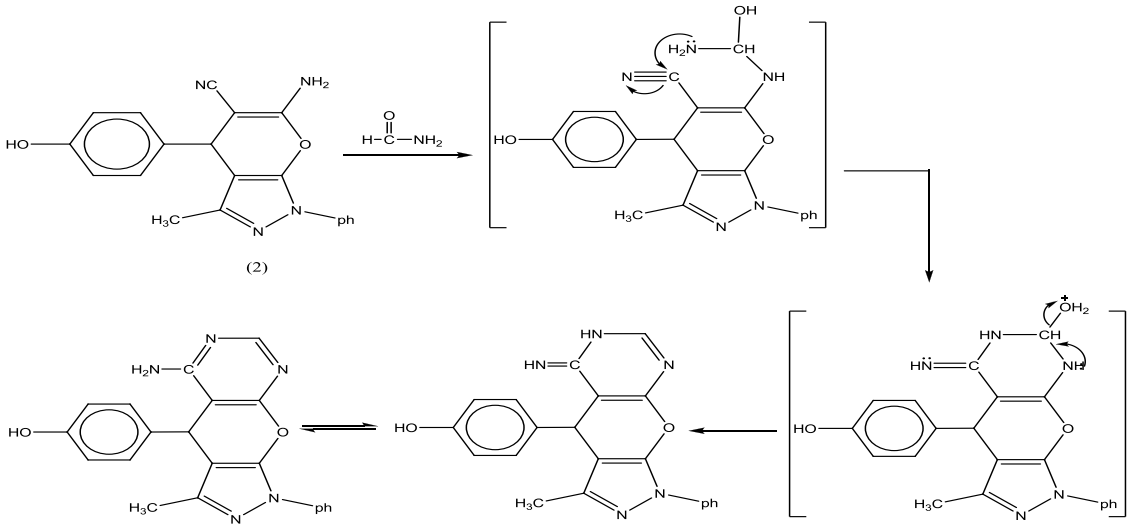


Figure 2- ^{13}CNMR spectrum of (compound 3)

Similarly, reaction of compound 2 with formamide, afforded 4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-4,6-dihydro- pyrazolo[3', 4':5,6]pyrano[2,3-d]pyrimidine-5-imine (compound 4) according to the mechanism illustrated in scheme 3.



Scheme 3- Formation mechanism of compound (4)

The IR spectrum of compound (4) showed stretching bands at 3387 cm^{-1} (NH imine), and 3190.2 cm^{-1} (NH), and showed no NH_2 and C≡N bands.

In the ^{1}H- NMR spectrum, figure 3- showed signals for OH and NH as a singlet at δ10.6 and δ9.1 respectively. The appearance of signal at δ7.44 for 2H (NH_2) indicates that compound (4) exist in a tautomeric mixture. Aromatic protons appeared as multiplet at δ7.7- δ6.6. The signal at δ4.7 was assigned to pyran proton, while CH_3 protons appeared at δ1.99.

^{13}CNMR spectrum, figure 4- showed signals at 165.7 and 164.3ppm for carbons of pyran ring (C-O-C), while C=N of pyrazol and imine appeared at 139.7 and 150ppm. The C-OH and carbon of pyrimidin appeared at 155.7 and 148.4ppm respectively. The aromatic carbons appeared at 131.5-118.4ppm, while the signals at 27.0 and 11.5ppm were attributed to pyrane CH and CH_3.

In reacting one mole of compound 2 with two mole ammonium thiocyanate in acetic acid gave N-[4-(4-hydroxyphenyl)- 3-methyl-1-phenyl-7-thioxo-7,8- dihydropyrazolo [3', 4':5,6] pyrano [2,3-d] pyrimidine-5-yl] thiourea (compound 5), the structure of this compound was confirmed by FTIR and ^{1}H-NMR.

The IR spectrum showed a broad at 3340 which was attributed to overlap NH_2 and OH bands. Stretching NH bands appeared at 3186.4 and 3167.1 $cm^{-1.}$ The IR spectrum also showed the disappearance of C≡N band, and appearance of C=S at 1261.4 cm^{-1}.

^{1}H-NMR spectrum of compound **5**, figure 5- showed signals at δ10.8 for OH, and δ8.65 for NH. Protons of NH_2 appeared at δ7.3, while the proton of pyran appeared at δ5.3. Protons of methyl group appeared as singlet at δ2.3 [17].

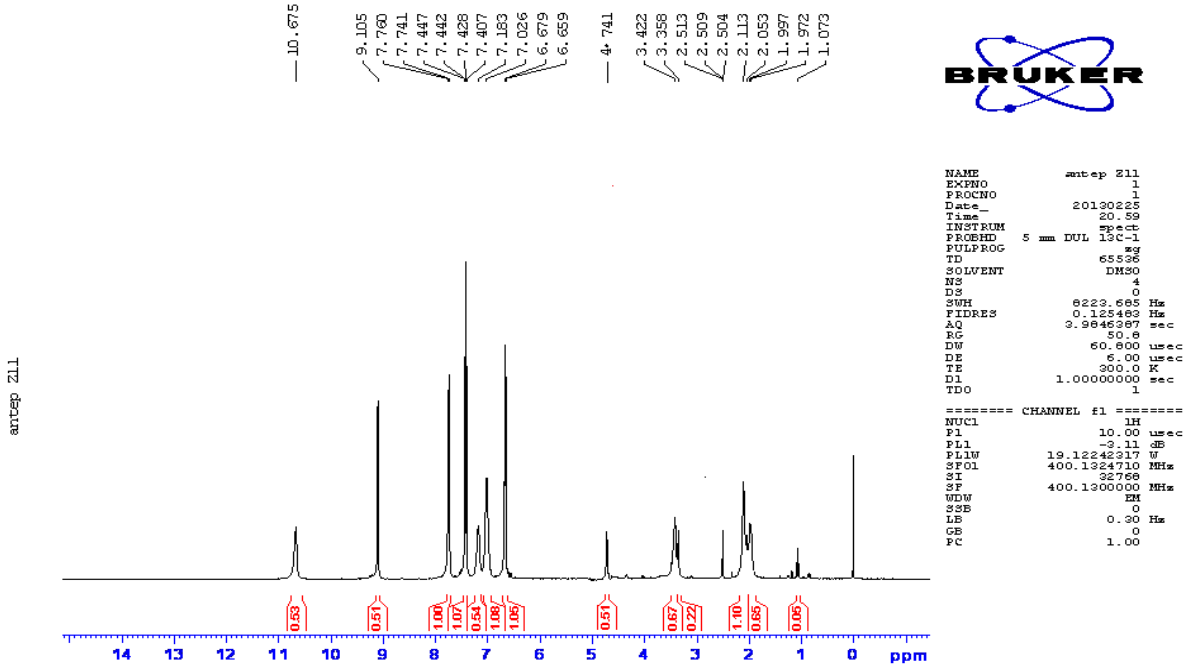


Figure 3- ^{1}HNMR spectrum of (compound 4)

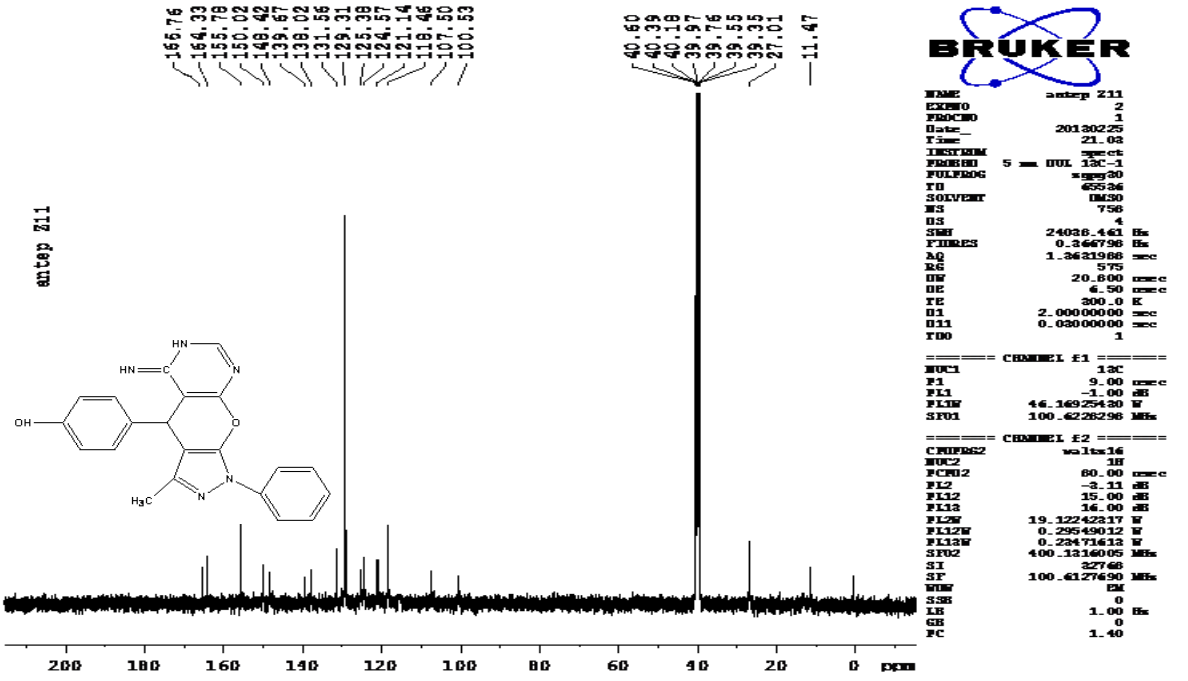


Figure 4- ^{13}CNMR spectrum of (compound 4)

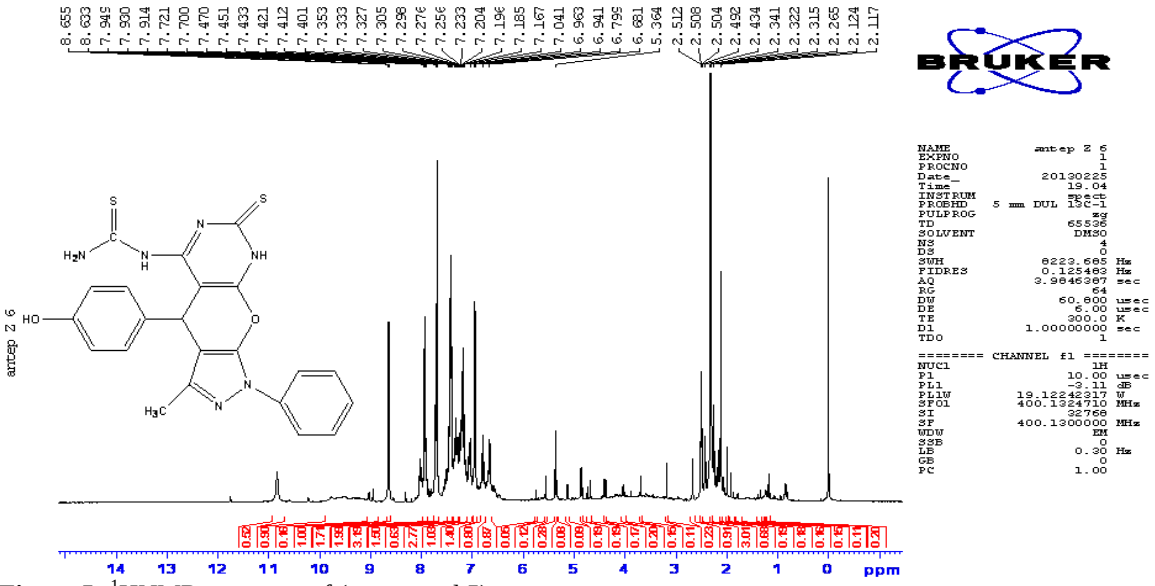
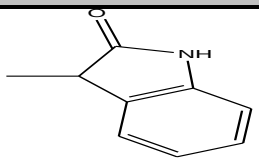
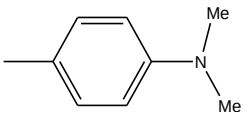
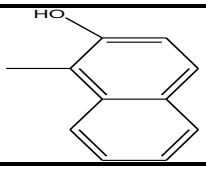
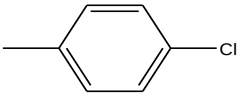
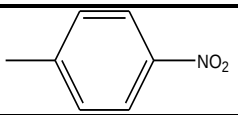
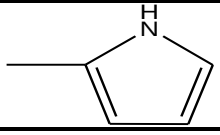


Figure 5- ^{1}HNMR spectrum of (compound 5)

Moreover, condensing compound 2 with the appropriate aldehyde or ketone gave rise to the corresponding Schiff-bases 6(a-f), which were identified by IR spectrum. The characteristic absorption bands are listed in table 3.

Table 3- FTIR spectral data (cm^{-1}) of Schiff base derivatives 6(a-f)

Com. no.	Ar.	νCH arom.	νC≡N	νC=N & νC=C	γ C-H arom.	Other bands
6a		3066.8	2194.9	1654.9 1612.5	813.9	ν N-H 3201.8 νC=O 1728.2
6b			2210.3	1668.3 1614.3	817.6	-
6c		3068.5	2200.1	1654.8 1618.2	817.7	-
6d			2175.7	1647.2 1612.5	810.1	ν C-Cl 678.9
6e		3072	2216	1647.1 1612.4	808.2	ν NO_2 1514asym. 1342.3sym.
6f		3058.9	2181.3	1656.7	813.9	ν N-H 3315.4

Oil oxidation at elevated temperatures normally leads to the formation of acidic components which are responsible for the sludge deposition metal corrosion and fatigue. The oxidation stability of the

blended oils was tested by IP 280. This method has been used for determination of the resistance to oxidation under specified conditions of unused inhibited mineral turbine oils. The value of the total oxidation products (TOP) was determined, the lower the TOP value the better the oxidation stability. Total sludge (wt%), volatile acidity and soluble acidity (mg KOH/g oil) are measured, a low result indicates good performance [18].

The evaluation results of oil blends are shown in figures (6 and 7). The results showed that blend B6a has higher oxidation stability compared with the blank B0 and the same oxidation stability as the blend with standard antioxidant B7, while blend B5 has higher oxidation stability than the blend with standard antioxidant B7. According to the structure of compound 6a, which has isatine ring, an active scavenger of radicals[19]. While compound 5 an additive to blend oil B5 is fused pyranopyrimidine moiety with thiourea, and thiourea derivatives are autooxidation inhibition and have a decomposition effect of hydroperoxide [20].

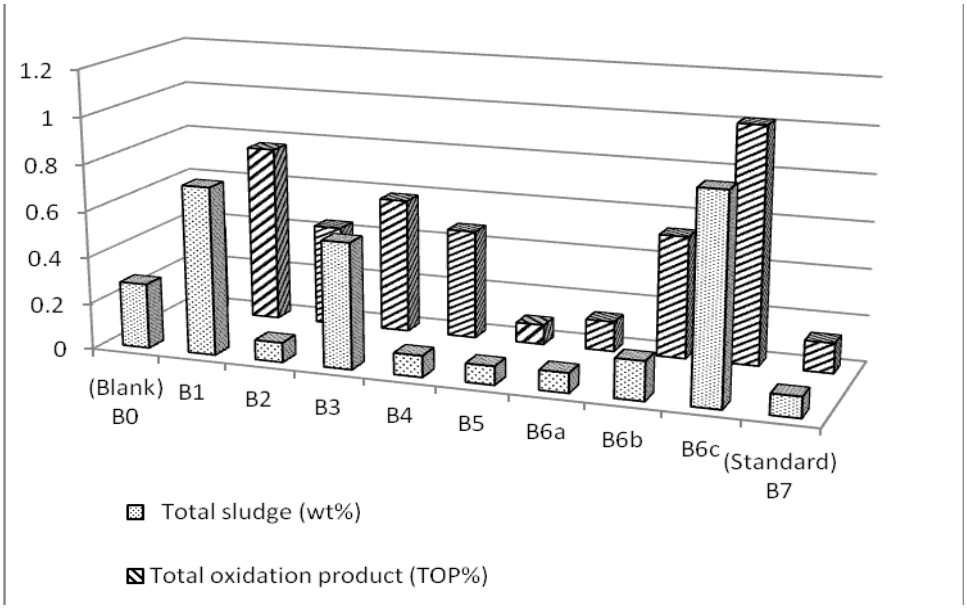


Figure 6- Total sludge and TOP% of oil blends

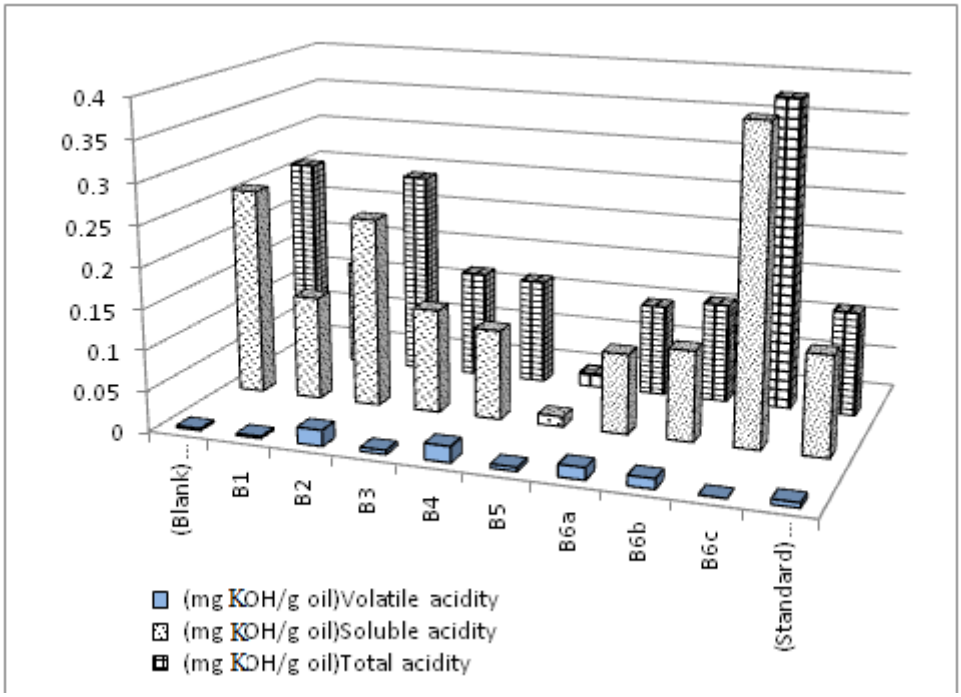


Figure 7- Volatile, soluble and total acidity of oil blends

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