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Synthesis, Characterization and Evaluation of Some Pyranopyrazole Derivatives as Multifunction Additives for Medium Lubricating Oils

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Abstract

The current work involves synthesis of 6-amino-4-(4-hydroxyl-3-methoxyphenyl)-3-methyl-1-phenyl-1,4- dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**2**) by condensation of 2-(4-hydroxyl-3-methoxybenzylidine) malononitrile (**1**) with 3-methyl-1-phenyl-2-pyrazolin-5-one. The product **2** was then reacted with various aldehydes to form a series of Schiff base derivatives **3a-h**. The reaction of the chosen Schiff base derivatives (**3a** and **3b**) with mercaptoacetic acid gave thiazolidinone derivatives (**4a** and **4b**). The structures of prepared compounds were confirmed using FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. They were evaluated as good copper corrosion inhibitors, anti-rust, and antioxidants. This was done by mixing them with the base medium lubricating oil (type 60 stock) provided by the Iraqi Midland Refineries Company/Al-Daura according to the American Society of Testing and Materials ASTM-D130, ASTM-D665, and Institute of Petroleum's testing method, oxidation stability test (IP-280), respectively.

Keywords: Lubricating oil, Pyranopyrazole, Copper corrosion inhibitors, Anti-rust, Antioxidants, Docking,

تحضير وتشخيص وتقييم بعض مشتقات البايرانوبايرازول كمحسنات متعددة الوظائف لزيوت التزييت

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الخلاصة

تم في هذا العمل تحضير المركب 6-amino-4-(4-hydroxyl-3-methoxyphenyl)-3-methyl-1-phenyl-1,4- dihydropyrano[2,3-c]pyrazole-5-carbonitrile (2) من تكاثف 2-(4-hydroxyl-3-methoxybenzylidine) malononitrile (1) مع 3-methyl-1-phenyl-2-pyrazolin-5-one. حضرت سلسلة من مشتقات قواعد شيف (3a-h) من تفاعل مشتق البايرانوبايرازول (2) مع ألديهايدات مختلفة. كما تم تفاعل مشتقات قواعد شيف المختارة (3a و3b) مع mercaptoacetic acid لينتج مشتقات الثايازوليدينون (4a و4b).

شخصت المركبات المحضرة باستخدام التحاليل الطيفية FT-IR و ^{1}H NMR و ^{13}C NMR و تم تقييمها كمثبطات جيدة لتآكل النحاس ومضادات للصدأ ومضادات للأكسدة من خلال مزجها مع زيت الأساس من

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نوع (stock 60) المجهز من شركة مصافي الوسط العراقية / مصفى الدورة اعتمادا على اختبارات ASTM-D130 وASTM-D665 و IP-280 على التوالي.

1. Introduction

A lubricant is a form of oil that is used to reduce wear, friction, and heat between mechanical parts that are in contact. A well-formulated lubricant with chemical additives can help to extend equipment life and conserve energy [1].

Base lubricating oils are blended with different additives to produce different commercial lubricating oils with an improvement in viscosity, viscosity index, pour point, oxidation stability, deterrence, anti-corrosion, and rust resistance [2].

Corrosion inhibitors are lubricating oil additives that protect the engine's non-ferrous metal surfaces from oxygen and moisture, whereas rust inhibitors protect ferrous metal surfaces from oxygen and moisture assault. Antioxidant additives prevent lubricating oil from oxidizing and thickening [3].

Pyranopyrazoles are a fused system of heterocyclic compounds that contain pyran and pyrazol rings with biological activities [4]. Many pyranopyrazoles have been synthesized [5] and have been reported to be antimicrobial [6, 7], antibacterial [8, 9], anti-fungicidal [10], anti-inflammatory [11], anticancer [12, 13], and antioxidant [14, 15]. Additionally, novel pyranopyrazole derivatives have been used as lubricating oil antioxidant additives [16]. Pyranopyrazoles have recently been evaluated as good anti-corrosion lubricants [17].

In this work, new pyranopyrazole compounds will be synthesized with an evaluation of their usage as multifunction additives (anti-corrosion, anti-rust, and antioxidants) for medium-lubricating oils.

2. Experimental part

Materials

All the used materials and solvents were obtained from Merck, Sigma/Aldrich, and BDH chemicals, while malononitrile and vanillin were purchased from CDH and Reagent World Companies, respectively. Pre-coated aluminum sheets with silica gel 60, provided by Merck Company, were used in thin-layer chromatography (TLC), and iodine vapors were used to mark spots.

Instrumentation

The Electro-Thermal Stuart Scientific (SMP1) melting point device was used to measure melting points. The Shimadzu Fourier Transform Infrared (FTIR-8400S) Spectrophotometer was used to record infrared spectra at the University of Baghdad / College of Science. The Varian model ultra-shield nuclear magnetic resonance spectrometer at 500 MHz and 125 MHz was used to record ^{1}H NMR and ^{13}C NMR spectra, respectively, using deuterated dimethyl sulfoxide solvent (DMSO-d_6). The chemical shifts are measured in parts per million (ppm) relative to the internal reference tetra-methyl silane (TMS) at the University of Tehran in Iran.

*Synthesis of 2-(4-hydroxyl-3-methoxybenzylidine)malononitrile (**1**)*

A mixture of 4-hydroxyl-3-methoxy benzaldehyde (vanillin) (7.6 g, 0.05 mole, 1.0 eq.), malononitrile (3.3 g, 0.05 mole, 1.0 eq.) and piperidine (two drops) in ethanol (25 ml) was heated for two hours. The reaction was monitored by TLC using ethanol: ethyl acetate (8:2), Rf (0.71). The mixture was then left overnight. The formed precipitate was filtered and recrystallized from ethanol to produce pale yellow crystals with 80% yield, and m.p = 134-136 °C [16]. FT-IR (cm^{-1}): 3427.3 (OH), 3026.1 (CH_{aro}), 2223.8 (CN), 1604.7 ($C=C_{alkene}$), 1573.8 and 1508.2 ($C=C_{aro}$); ^{1}H NMR (δ_H, ppm): 10.77 (s, 1H, OH), 8.25 (s, 1H, vinylic), 7.6-6.96 (m, Ar-H), 3.78 (s, 3H, OCH_3); ^{13}C NMR (δc, ppm): 148.6 (C-OH), 154.5, 128.4-115.0 (Ar-H), 113.7 (CN), 56.2 (OCH_3).

*Synthesis of 6-amino-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydro-pyrano [2,3-c]pyrazole-5-carbonitrile (**2**)*

A mixture of compound **1** (2 g, 0.01 mole, 1.0 eq.), 3-methyl-1-phenyl-2-pyrazolin-5-one (1.74 g, 0.01 mole, 1.0 eq.) and pipridine (two drops) in ethanol (10 ml) was heated to reflux for an hour. The reaction was monitored by TLC using petroleum ether: ethyl acetate (6:4), Rf (0.39). The mixture was then left overnight. The precipitate formed was filtered and recrystallized from ethanol to give yellow crystals in 91% yield, m.p = 142 °C [17]. FT-IR (cm^{-1}): 3436.9 (OH), 3373.3 and 3321.2 ($NH_{2asym.\ and\ sym.}$), 3082.0 (CH_{arom}), 2187.1 (CN), 1652.9 (C=N), 1595.0 ($C=C_{aro.}$); ^1H NMR (δ_H, ppm): 8.88 (s, 1H, OH), 7.11 (s, 2H, NH_2), 7.78-6.6 (m, Ar-H), 4.56 (s, 1H, CH pyran), 3.72 (s, 3H, OCH_3), 1.81 (s, 3H, CH_3); ^{13}C NMR (δ_C, ppm): 159.7 and 147.9 (C-O-C), 145.9 (C=N pyrazol), 145.8 (C-OH), 138.1-112.4 (Ar-H), 120.3 (CN), 56.1 (OCH_3), 13.1 (CH_3).

*Synthesis of Schiff's bases **3a-h***

A mixture of appropriate aldehyde or isatin (0.01 mole, 1.0 eq.) in absolute ethanol (10 ml) and glacial acetic acid (three drops) was added to a solution of the pyranopyrazole derivative **2** (3.74 g, 0.01 mole, 1.0 eq.) in absolute ethanol (10 ml). The reaction mixture was then refluxed for 4-20 hours and monitored by TLC using chloroform: diethyl ether (8:2). The mixture was cooled, and the solid that had separated from the ethanol was filtered and crystallized from ethanol to produce the desired Schiff's base derivatives **3a-h** [18]. Table 1 illustrates the physical properties of the Schiff base derivatives **3a-h** in yields 18-64%.

*Synthesis of thiazolidinone derivatives (**4a** and **4b**)*

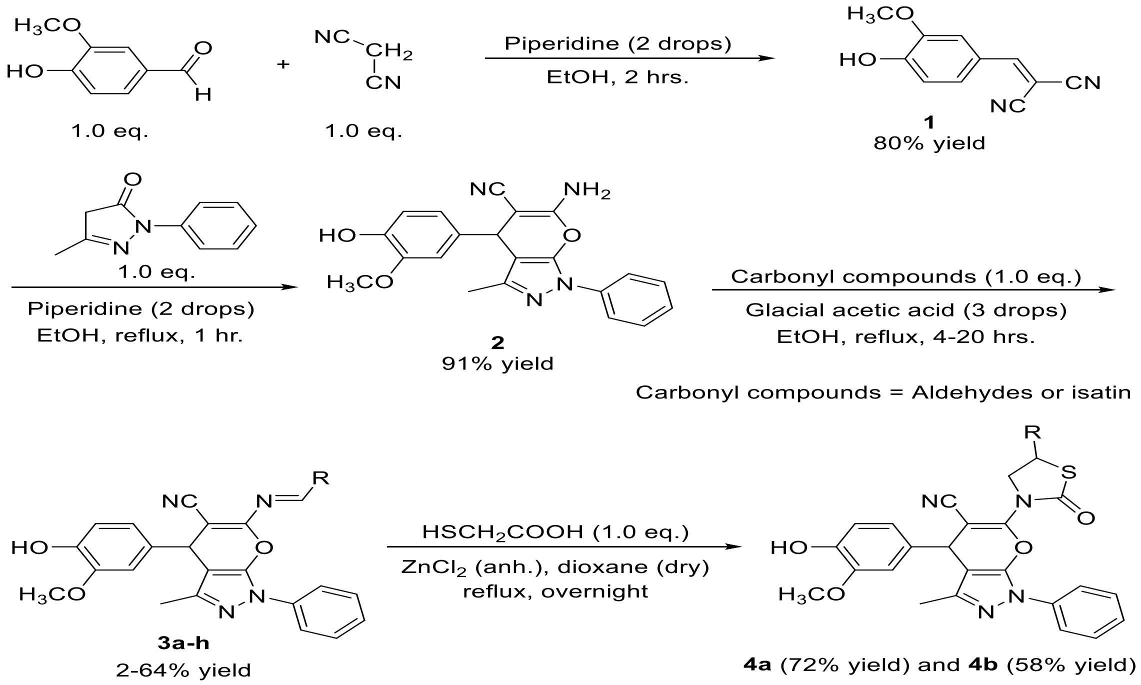
A mixture of Schiff base derivatives **(3a and 3b)** (0.01 mole, 1.0 eq.), mercaptoacetic acid (thioglycolic acid) (0.7 ml, 0.01 mole, 1.0 eq.) and a catalytic amount of anhydrous zinc chloride were dissolved in dry dioxane (20 ml). The mixture was then heated to reflux overnight, and monitored by TLC using petroleum ether: ethyl acetate mixture (6:4) as an eluent. The mixture was cooled, and the solid that had separated from the dioxane was filtered and crystallized from ethanol to afford the title derivatives (**4a and 4b**) [19].

*4-(4-Hydroxy-3-methoxyphenyl)-3-methyl-6-(2-(4-nitrophenyl)-4-oxothiazolidin-3-yl)-1 phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**4a**)*

$C_{30}H_{23}N_5O_6S$, red crystals, m.p = 146-148 °C, 72% yield, Rf (0.66). FT-IR (cm^{-1}): 3423.4 (OH), 3076.3 (CH), 2200.6 (CN), 1714.6 (C=O), 1649.0 (C=N), 1417.5 (CH_2S); ^1H NMR (δ_H, ppm) 8.67 (s,1H,OH), 5.38 (s,1H,CH-S), 8.34-6.66 (m, Ar-H) 4.05 (s, 1H, CH pyran), 3.42 (s, 2H, CH_2), 3.37 (s, 3H, OCH_3);^{13}CNMR (ppm): 165.42 (C=O), 155.95 and 153.20 (C-O-C), 149.66 (C=N for pyrazole), 138.47-112.23 (Ar-C), 121.00 (CN), 56.12(OCH_3), 16.76 (CH_3).

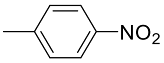
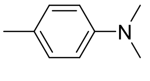
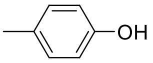
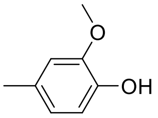
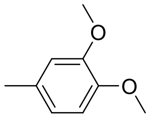
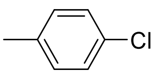
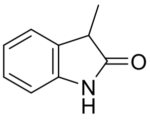
*4-(4-Hydroxy-3-methoxy-phenyl)-3-methyl-6-(2-(4-(dimethylamino)phenyl)-4-oxothiazolidin-3-yl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4b)***

$C_{32}H_{29}N_5O_4S$, reddish oily, 58% yield, Rf (0.78). FTIR (cm^{-1}): 3442.7 (OH), 3058.9 (CH), 2208.3 (CN), 1712.7 (C=O), 1415.6 (CH-S); ^1H NMR (δ_H, ppm): 8.66 (s, 1H, OH), 8.02-6.69 (m, ArH), 5.50 (s, 1H, CH-S), 4.11 (s, 1H, CH pyran), 3.66 (s, 2H, CH_2), 3.14 and 3.12 (s, 6H, $N(CH_3)_2$), 3.51 (s, 3H, OCH_3), 1.15 (s, 3H, CH_3);^{13}C NMR (ppm): 162.9 (C=O), 154.3 and 152.0 (C-O-C), 148.6 (C=N pyrazol), 139.3-111.8 (Ar-C), 118.8 (CN), 60.6 (OCH_3), 13.7 (CH_3). The synthetic route of various pyranopyrazole derivatives is shown in Scheme 1.



Scheme 1 - Synthetic route of pyranopyrazole derivatives

Table 1 - The physical properties of Schiff base derivatives **3a-h**

Comp. no.	**R**	**Molecular formula**	**Molecular weight g/mole**	**Color**	**m.p. (°C)**	**Time (hour)**	**Yield (%)**	**Rf**
3a		$C_{28}H_{21}N_5O_5$	507.15	Yellow	76-78	14	20	0.61
3b		$C_{30}H_{27}N_5O$	505.58	Red	144-146	5	30	0.86
3c		$C_{28}H_{22}N_4O_4$	478.51	Orange	138-142	14	64	0.56
3d		$C_{29}H_{24}N_4O_5$	508.53	Orange	161-163	9	62	0.67
3e		$C_{30}H_{26}N_4O_5$	522.56	Orange	116-120	8	29	0.77
3f		$C_{28}H_{21}ClN_4O$	496.95	Pale yellow	156-158	12	20	0.66
3g	$CH_3(CH_2)_6$-	$C_{28}H_{3}0N_4O_3$	470.57	Brown	120-123	21	18	0.42
3h		$C_{30}H_{23}N_5O_4$	517.55	Deep brown	115-117	22	43	0.45

Formulation of oil blends

Blends of the synthesized compounds were made by dissolving and mixing 0.2 percent weight/ weight of each compound in medium base oil (type 60 stock) at 75 °C, followed by an hour of stirring at room temperature [20]. The base lubricating oil (type 60 stock) properties are illustrated in Table 2.

Table 2 - The base lubricating oil properties

No.	Specification	Properties	Standard test method
1	Kinematic viscosity at 40°C, (mm^2/s)	58.02	ASTM D445
2	Kinematic viscosity at 100°C, (mm^2/s)	8.07	ASTM D445
3	Viscosity index(V.I)	106	ASTM D2270
4	Specific gravity	0.8842	ASTM D4052
5	Pour point, °C	0.0	ASTM D97
6	Flash Point, °C	242	ASTM D92
7	Total oxidation product, %	0.4152	IP 280
8	Color	1.5	ASTM D1500
9	Copper corrosion	2a	ASTM D130
10	Rust preventing	Fail	ASTM D665

3. Results and Discussion

According to the Knovenagel mechanism, 6-amino-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydro-pyrano [2,3-c]pyrazole-5-carbonitrile (**2**) was synthesized by a reaction between 2-(4-hydroxyl-3-methoxybenzylidine)malononitrile (**1**) and 3-methyl-1-phenyl-2pyrazolin-5-one using a piperidine catalyst [21]. The prepared pyranopyrazole derivative **2** was reacted with various aldehydes and isatin in the presence of glacial acetic acid as a catalyst to produce the desired Schiff bases **3a-h** as shown in Scheme 1. Schiff bases **3a-h** were identified by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopies.

The FT-IR spectra revealed stretching bands of the imine group in the region 1635.5-1676.0 cm^{-1} (C=N), while the NH_2 band had disappeared [22]. The detailed absorption bands are listed in Table 3.

^{1}H NMR spectra of the products **3a-h** showed a singlet signal due to the imine proton in the region between 7.66 and 8.32 ppm, while the signal of the NH_2 had disappeared. The characteristic ^{1}H NMR signals of **3a-h** are listed in Table 4. ^{13}C NMR spectra of **3a-h** showed signals at 162.3-159.3 ppm for C=N imine, and 140.0-110.36 ppm for C=C aromatic [23]. The characteristic ^{13}C NMR signals are listed in Table 5.

The derivatives **3a** and **3b** were reacted with mercaptoacetic acid in the presence of anhydrous zinc chloride as a catalyst to furnish the thiazolidinone derivatives **4a** and **4b**, which were characterized using FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopies.

FT-IR data of compounds 4a and 4b showed stretching bands at 1714.6 and 1712.7 cm^{-1} belonging to the C=O amide, and bands at 1417.6 and 1415.7 cm^{-1} are attributed to the CH_2-S, while the bands of C=N imine had disappeared.

^{1}H NMR spectra of compounds **4a** and **4b** showed singlet signals at 8.67 and 8.66 ppm for OH proton, signals at 5.50 and 5.35 ppm due to CH-S proton, and signals at 4.11 and 4.05

ppm for CH pyran ring, respectively. On the other hand, the signal of the imine proton disappeared. ^{13}C NMR spectra of compounds **4a** and **4b** showed signals at 165.4 and 162.9 ppm (C=O), respectively, while the signal of imine carbon disappeared [24].

Table 3 - FTIR spectra data (cm^{-1}) of Schif base derivatives **3a-h**

Comp. no.	**ν OH**	**ν C-H aromatic**	**ν C-H aliphatic**	**ν C≡N**	**ν C=N**	**ν C=C**	**δ (o-o-p)**	**Others (ν)**
3a	3445	3028	2972	2220	1651	1605	Mono-subs. 741 692 Para-subs. 816	NO_2 1348 1572
3b	3466	3076	2916	2208	1668	1614	Mono-subs. 727 692 Para-subs. 814	–
3c	3404	3078	2982	2226	1655	1608	Mono-subs. 737 691 Para-subs. 814	OH 3404
3d	3416	3082	2976	2224	1653	1612	Mono-subs. 729 689 Tri-subs. 820 847	OH 3416
3e	3447	3082	2963	2222	1676	1641	Mono-subs. 739 690 Tri-subs. 818 849	–
3f	3433	3034	2922.0	2227.6	1636	1585	Mon-subs. 683 708 Para-subs. 827	C-Cl 617
3g	3443	3071	2929.7	2187.1	1651	1597	Mono-subs. 729 691	-
3h	3433	3080	2871.8	2196.8	1653	1618	Mono-subs. 731 685 Ortho-subs. 854	N-H 3296 C=O 1703

Table 4 - ^{1}H NMR spectra data (δ ppm) of Schiff base derivatives **3a-h**

Comp. no.	O-H singlet	=C-H singlet	C-H Aromatic multiplet	C-H Pyran singlet	OCH_3 (3H) singlet	CH_3 (3H) singlet	Other
3a	8.26	8.20	8.26-6.95	4.90	3.83	1.78	-
3b	8.64	8.03	7.95-6.82	3.11	2.49	2.27	3.09 and 3.08 s, 6H, $N(CH_3)_2$
3c	8.84	8.25	8.28-6.9	3.84	3.71	1.04	1H, OH singlet 10.53
3d	8.84	7.66	7.97-6.93	3.87	3.43	1.06	3.84, s, 3H, OCH_3 10.51, s, 1H, OH
3e	8.83	8.32	8.06-7.14	4.32	3.78	1.05	3.88 and 3.85 s, 6H, $2OCH_3$
3f	8.54	7.95	7.93-7.70	4.33	3.79	1.05	-
3g	-	8.017	7.61-6.43	4.503	3.591	1.981	1.70-0.63 m, 15H, $CH_3(CH_2)_6$-
3h	8.9	-	8.20-6.96	3.918	3.817	1.598	10.809 1H, s, NH

Table 5 - ^{13}C NMR spectra data (δppm) of Schiff base derivatives **3a-h**

Comp. no.	C-O-C	C=N imine	C=N Pyrazol	C-O Phenolic	CN nitrile	Aromatic carbons	O-CH_3	CH_3	Others
3a	161.0 154.0	160.2	147.0	146.1	120.2	137.9-120.5	57.3	13.0	_
3b	162.9 154.8	159.3	152.0	148.6	118.5	139.3-111.8	56.5	13.6	$(CH_3)_2$ 40.1 40.3
3c	163.5 153.4	162.5	149.4	148.9	118.9	138.9-116.0	56.1	13.6	C-OH 162.4
3d	162.5 153.4	160.9	149.4	147.7	118.9	138.9-116.0	56.1	13.6	O-CH_3 56.5 C-OH 152.2
3e	162.4 154.1	161.1	149.1	148.6	118.9	138.8-111.2	56.0	13.6	2O-CH_3 56.5 56.3
3f	163.0 156.0	160.6	149.7	147.5	119.6	140.0-113.5	56.6	14.3	-
3g	172.5 157.7	160.9	147.6	145.9	119.4	139.3-112.4	56.1	14.4	CH_3 13.2 $6CH_2$ 36.9-21.5
3h	162.5 153.4	160.9	149.2	148.6	118.5	137.7-110.4	56.6	13.6	C=O 139.0 C-N 153.6

Evaluation of the prepared derivatives as anti-corrosion additives

Blends of the synthesized compounds were evaluated for their anti-corrosion activity according to the ASTM D130 method, which involved dipping a polished copper strip in the blend oil heated at 100 °C for three hours. When the heating time was over, the strip was removed, cleaned, and the tarnish level was considered against the standard ASTM classification and color-match scale [25, 26].

The prepared derivatives were found to be good anti-corrosion lubricating oil additives, causing slight tarnish (1b) as compared with moderate tarnish (2a) on the base oil (blank) as shown in Table 6.

Evaluation of the prepared derivatives as anti-rust additives

Blends of the synthesized derivatives were evaluated for their anti-rust properties according to the ASTM D-665 method, which entails dipping a polished steel rod in a sample of blended oil mixed with water and heated at 60 °C for four hours. The test rod was then examined for signs of rust. This test was run in duplicate, and to be considered successful, both test rods had to be rust-free [27].

Most of the oil blends of the synthesized derivatives passed the rust-preventing test as shown in Table 6.

Evaluation of the prepared derivatives as antioxidants

The oxidation stability of the prepared blends was determined using the Institute of Petroleum's testing method. The oxidation stability test (IP 280), which includes mixing an oil sample with a copper-iron metal catalyst and passing an oxygen gas through it for three days at 120 °C. At the end of the period test, both the total sludge (T.S) and acidity (T.A) levels in the oil were measured while the total oxidation products (TOP%) were calculated using the following Equation [28]:

$$TOP\% = T.S + 180\,(T.A)/561$$

The evaluation results of oil blends which were subjected to severe oxidation conditions are shown in Table 6 and Figure 1. According to these results, all blends of compound **2** and Schiff base derivatives **3b-h** have higher oxidation stabilities than the base oil (blank), low total sludge (T.S), and low total oxidation product (TOP%), which were in the acceptable range. The oil blend with compound **3h** gave approximately the same oxidation stability as the standard antioxidant (hindered phenol HP) oil blend, because the structure of compound **3h** bearing an isatin ring, which is known as an active scavenger of radicals [29].

Table 6 - Copper corrosion, rust prevention, and oxidation stability results of oil blends

Comp. no.	**Copper corrosion test**	**Rust preventing test**	**T.A**	**T.S**	**TOP %**
Blank	2a	Failed	0.2685	0.3291	0.4152
2	1b	Passed	0.1611	0.2138	0.2127
3b	1b	Passed	0.1194	0.1847	0.2230
3c	1b	Passed	0.1360	0.1645	0.2081
3d	1b	Passed	0.1096	0.1023	0.1374
3e	1b	Failed	-	-	-
3g	1b	Passed	0.2013	0.1346	0.1992
3h	1b	Passed	0.1081	0.0992	0.1338
Standard (HP)	-	-	0.1306	0.0886	0.1305
4b	1b	Passed	-	-	-

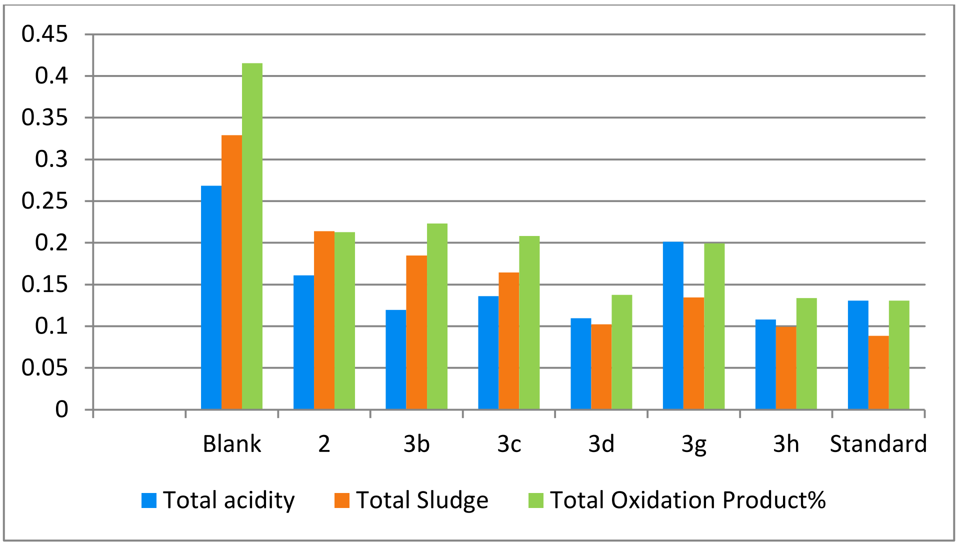


Figure 1 - Total sludge, total acidity and total oxidation product of blend oils

Molecular docking study of the Schiff base derivative 3b

Molecular docking is used to discover the interaction mechanism and to explore suitable binding models of the prepared Schiff base derivative **3b** on the active site of rubredoxin protein from *desulfovibrio gigas* bacteria.

Desulfovibrio gigas (D. gigas) is a sulfate reducing bacteria (SRB), which is one of the microbial-induced corrosion (MIR) in oil pipelines [30].

Version 15.6 of the Auto Dock Vina program is used for molecular docking [31] of the crystal structure of *desulfovibrio gigas* rubredoxin protein (2DSX), which was obtained from the Research Collaborator for Structural Bioinformatics (RCSB) protein data bank (PDB: 2DSX) [32].

The lowest binding energy of the Schiff base derivative **3b** was calculated to be -6.2 Kcal/mole compared to the 2DSX receptor, which had a good docking score for hydrogen bonding interaction. Figure 2 depicts the minimization energy structure of the compound **3b**.

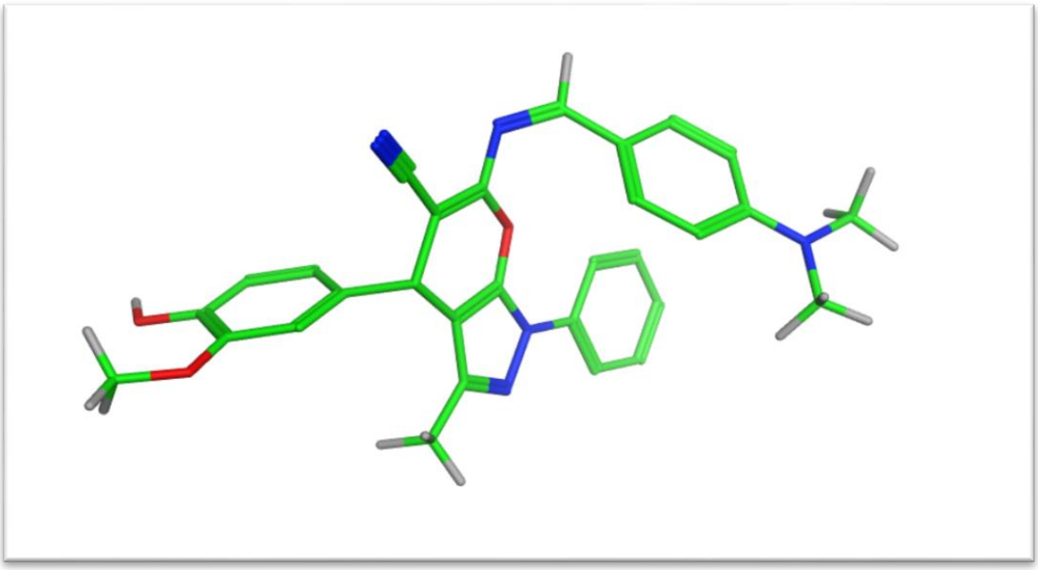


Figure 2 - Minimization energy structure of compound **3b**

The Schiff base derivative **3b** interacts with the active site of 2DSX through three interactions: the benzene ring bearing *N*,*N*-dimethyl group interacts with lysine (LYS A: 17).

On the other hand, the benzene ring bearing hydroxyl and methoxy groups interact with glutamic acid (GLU A: 12). While the pyran ring interacts with tyrosine (TYR A: 11) at the lowest binding energies, in order to imagine these interactions in a better vision, two-dimensional and three-dimensional interactions are shown in Figure 3.

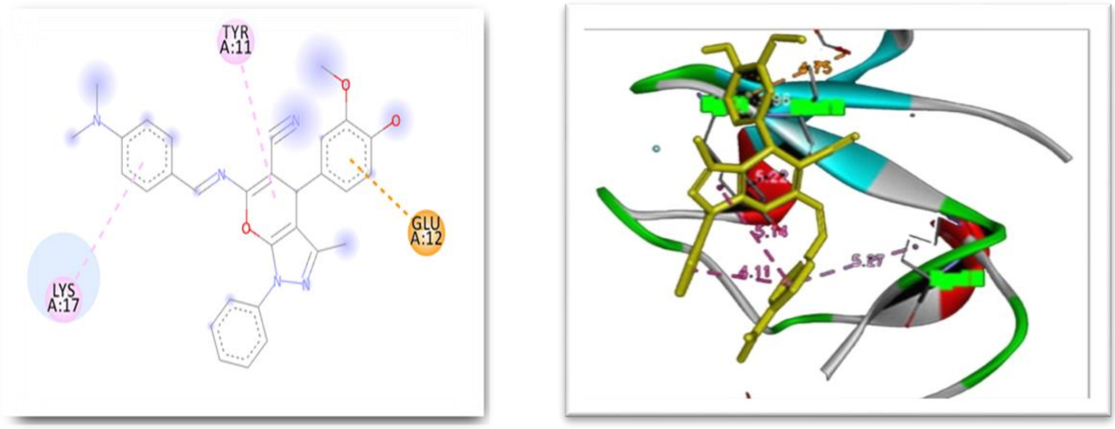


Figure 3 - 2D and 3D interactions pose of compound **3b** with amino acids of the active site

4. Conclusions

New pyranopyrazole derivatives have been successfully synthesized and shown to be effective multifunction additives (antioxidants, anti-rust, and corrosion inhibitors) for medium-lubricating oils.

Schiff's base derivative **3b** was theoretically verified as an anti-microorganism influenced corrosion (MIC) against *desulfovibrio gigas* bacteria.

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