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Synthesis and Applications of Pyridazinones for Base Oil Improvement

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THREE pyridazinone derivatives of the type 4,5-dihydropyridazin- 3(2*H*)-ones, N-(4-(6-oxo-5- ((5-phenyl-1,3,4-thiadiazol-2-yl)amino) - 1,4,5,6 – tetrahydropyridazin - 3-yl) phenyl) acetamide (4a), 6-(4-chlorophenyl)-4-((5-phenyl-1,3,4-thiadiazol-2-yl)amino)-4,5-di-hydropyridazin-3 (2*H*)-one (4b) and 6-(4-bromophenyl) -4- ((5-phenyl-1,3,4-thiadiazol-2-yl) amino)-4,5-dihydropyridazin-3(2*H*)-one (4c) were synthesized. They were characterized by the conventional tools of analysis, Elemental analysis, IR and ^{1}H-NMR spectroscopy. The tools of analysis confirmed the structure of the three prepared compounds. These heterocyclic compounds are chemically stable and possess multi actions for base oil improvement. They are tested as antioxidants for local base oil through the change in total acid number (TAN). They gave good results as antioxidants for base oil. Also these three synthesized compounds are tested as corrosion inhibitors for carbon steel in acid medium. The efficiency order for these tested compounds is ranked as follows: 4a > 4b > 4c. Energy of the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}) for the three prepared compounds were calculated via the Ab initio method. Studying of the quantum chemical calculations of the synthesized compounds showed good matching with the experimental results.

Keywords: Pyridazinones, Imidazole, Thiadiazole, Antioxidant, Anticorrosion, Quantum chemical calculations.

Lubricating oils are subjected to deterioration by oxidation at high temperatures [1]. Antioxidants are the main additives that protect the lubricant from oxidative degradation, and be allowing the oil to meet the challenging supplies for use in industrial applications [2]. In order to see the technical economic and environmental requirements, sulfur and phosphorus content are used in the design of lubricating oil with low concentration [3,4]. The compact structure of heterocyclic compounds, lead to possess antioxidant, anticorrosion and anti-wear properties [5-7]. Some functionalized imidazoles and 1,2,4-triazoles are tested as antioxidant additives for industrial lubricating oils [8]. The results explained,

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based on correlating the electron donating and withdrawing abilities of the substituents with the oxidation stability.

Otherwise, the aroyl-prop-2-enoic acids have two electrophilic reactions sites. The reactivity of them toward aromatic hydrocarbon, (under Friedel-Crafts condition), and nitrogen nucleophiles, (under Michael addition) were investigated [9-12]. Because of the stability of the intermediate carbocation they behave as α,β-unsaturated carbonyl rather than α,β -unsaturated acid. The aza-Michael adducts are considered as α-amino acids. They have recognized to show a significant role in the synthesis of novel drug applicants [13-19]. Synthesis of unnatural amino acids is found out cost effective and less time consuming synthetic routes. From this point of view the authors have made an attempt to investigate the reaction of 4-aryl-4-oxo-but-2-enoic acids with 2-amino-1,3,4-thiadiazole, under aza-Michael reaction conditions, which produced adducts as α-amino acid types with acetic anhydride at different conditions and N_2H_4 to give the corresponding furanone, imidazol[2,3-b]1,3,4-thiadiazole, 1,3,4-thiadiazolopyrimidines and pyridazin-one derivatives, respectively. The 2-(3*H*) furanone compounds showed important activities as antioxidants. Beside, they are active as antifungal, antibacterial, antiviral, anti-inflammatory, vasodilation, and anticonvulsant [20-25]. Pyridazinone derivatives incorporated with diazole moieties that exhibit biological activity agents, (Emorfazone and related compounds) [26], for therapeutic intervention of renal urologic [27], respiratory (NIP-502) [28] and dermatologic diseases (FR-1818177) [29] and pyridazinone, (PDE inhibitor developers) [30]. The design of newly prepared compounds based on the structure containing other biological actives heterocycles on the side chains [31]. In our work we used the prepared compounds as antioxidants and corrosion inhibitors for base oil improvement.

Experimental

Preparation of additives

All melting points are approximately correcteded and were determined on a Stuart electric melting point apparatus. Elemental analysis was carried out at the Micro analytical Centre, National Research Centre, Giza, Egypt, by El Germany Viro El Microanalysis, IR spectra (KBr) were recorded on infrared spectrometer FT-IR 400D using OMNIC program and are reported frequency of absorptions in terms of cm^{-1} and ^{1}H-NMR spectra recorded on a Bruker spectro photometer at 400 MHz using TMS as internal standard and with residual signals of the deuterated solvent = 7.26 ppm for $CDCl_3$ and 2.51 ppm for DMSO-d_6. ^{13}C-NMR spectra were recorded on the same spectrometer at 125 MHz MHz and referenced to solvent signals = 77 ppm for $CDCl_3$ and 39.50 ppm for DMSO-d_6. DEPT 135 NMR spectroscopy were used where appropriate to aid the assignment of signals in the ^{1}H and ^{13}C-NMR spectra. The mass spectra were recorded on Shimadzu GCMS-QP-1000 EX mass spectrometer at 70 e.v. using the electron ionization technique Homogeneity of all compounds synthesized was checked by TLC.

Synthesis of the adducts

A solution of 4-aryl-4-oxo-2-butenoic acids (0.01 mol.) and 5-aryl-2-amino-1,3,4-thiadiazole (0.016 mol.) in 30 ml ethanol was refluxed for 3 h. The crude product was washed by petroleum ether (40 – 60 ^{o}C), and then crystallized from the proper solvent to give the following compounds:

4-(4-Acetylaminophenyl)-4-oxo-2-(5-phenyl-2-thiadiazolylamino) butanoic acid (1a)

Yield 80%, m.p. 160-162 ^{o}C, IR for CO for acid and ketone groups (1695 – 1665) cm^{-1}, ^{1}H-NMR (DMSO-d_6) 2.5 (s, 3H, CH_3CO), 3.4 (2dd, CH_2-C=O *J*=15.2, J=7.7, diastereotopic protons), 4.2 (dd, CH-COOH, methine proton), 6.7(s, NH), 7.6-8.1 (m, 9H, Ar-H) , 8.2 (s, 1H, COOH), 8.6 (s, 1H, C=O-NH). ^{13}C NMR (125 MHz, DMSO-d_6), δ 22.3 (CH_3), 48.1 ($\underline{C}H_2$COAr), 72.3 ($\underline{C}$HCOO), 108 (C_1Ar), 114.5 120.3(C_4Ph), 123.2 ($C_{2,6}$Ph), 127.2 ($C_{3,5}$Ph), 130.4 (C_1Ph), 132.1 ($C_{3,5}$Ar), 136.3 ($C_{2,6}$Ar), 143.2 (C_4Ar), 156.2 (SC=N), 168.2 (CONH), 171.2 (NHC=N), 173.5 (COO), 190.30 (CO-Ar). MS: *m/z* 410 (M^+). Anal. Calc. for ($C_{20}H_{18}N_4O_4S$): % C 58.53, H 4.39, N 13.65, S 7.8; Found: % C 58.30, H 4.31, N 13.00, S 7.43.

4-(4-Chlorophenyl)-4-oxo-2-(5-phenyl-2-thiadiazolylamino) butanoic acid (1b)

Yield 80%, m.p. 140-142 ^{o}C, IR for CO for acid and ketone groups (1695) cm^{-1}, ^{1}H-NMR (DMSO-d_6) 3.5 (2 dd, CH_2-C=O, *J*=15.2, *J*=7.7, diastereotopic protons), 4.2 (dd, CH-COOH, methine proton), 6.7(s, NH), 7.6-8.1 (m, 9H, Ar-H), 8.2 (s, 1H, COOH), EIMS: *m/z* 390 (M^++2), 387.5 (M^+). Anal. Calc. for ($C_{18}H_{14}N_3O_3SCl$): % C 55.22, H 3.64, N 10.85, S 8.26, Cl 9.17; Found: % C 55.00, H 3.20, N 10.54, S 8.00, Cl 8.87.

4-(4-Bromophenyl)-4-oxo-2-(5-phenyl-2-thiadiazolylamino) butanoic acid (1c)

Yield 80%, m.p. 128-130 ^{o}C, IR for CO for acid and ketone groups (1693) cm^{-1}, ^{1}H-NMR (DMSO-d_6) 3.5 (2 dd, CH_2-C=O *J*=15.2, *J*=7.7, diastereotopic protons), 4.2 (dd, CH-COOH, methine proton), 6.7(s, NH), 7.6-8.1 (m, 9H, Ar-H), 8.2 (s, 1H, COOH), EIMS: *m/z* 435 (M^++2(2)), 431 (M^+). Anal. Calc. for ($C_{18}H_{14}BrN_3O_3S$): % C 50.01, H 3.26, Br 18.33, N 9.74, S 7.42; Found: % C 49.37, H 3.00, Br 18.09, N 9.53, S 7.11.

Synthesis of furanones 2 and imidazothiadiazole derivatives 3

A mixture of 1a-c (0.005 mol.) and acetic anhydride (9.4 mL) was heated under reflux for 1 h upon water bath. The solid that separated, on cooling, was fractional crystallized from petroleum ether (80-100 ^{o}C) afforded imidazothiadiazoles 3 and from dioxane afforded the furanone derivatives 2.

2-(5-Acetylaminophenyl-2-oxo-furan-3-yl)amino-5-phenyl-1,3,4-thiadiazole (2a)

Yield 50%, m.p. 200-202 ^{o}C, IR: υ NH 3297-3100, CH 3055-2890, and CO at 1767 and 1693 cm^{-1}. ^{1}H-NMR spectrum (DMSO-d_6) exhibits signals at δ

2,1 (s 3H, CH_3CO), 4 (dd, 1H, -CH-NH, *J*=8.5), 6.7 (bs, NH), 7.5-7.9 (m, 9H of Ar), 6.9 (d, 1H, CH furanone moiety, *J*=8.5), 12.7 (s, 1H, –C=O-NH) acidic protons are exchangeable in D_2O. Elem. Anal. For ($C_{20}H_{16}N_4O_3S$) M.wt. 392.43: Calc.: % C 61.21, H 4.11, Cl 9.60, N 14.28, S 8.17; Found % C 60.40, H 3.87, Cl 9.11, N 13.80, S 7.89.

2-(5-Chlorophenyl-2-oxo-furan-3-yl)amino-5-phenyl- 1,3,4-thiadiazole (2b) Yield 50%, m.p. 182-184 ^oC, IR: υ□□CH 3055-2890 and CO at 1772 cm^{-1}. ^1H-NMR spectrum (DMSO-d_6) exhibits signals at δ 4 (dd, 1H, -CH-NH, *J*=8.5), 6.7 (bs, NH), 7.5-7.9 (m, 9H of Ar), 6.9 (d, 1H, CH furanone moiety, *J*=8.5). Elem. Anal. for ($C_{18}H_{12}ClN_3O_2S$): Calc.: % C 58.46, % H 3.27, % N 11.36, % S 8.67; Found % C 58.20, % H 3.00, % N 10.90.8, % S 8.20.

2-(5-Bromophenyl-2-oxo-furan-3-yl)amino-5-phenyl- 1,3,4-thiadiazole (2c) Yield 50%, m.p. 166-168 ^oC, IR: υ□□CH 3055-2890 cm^{-1}, and CO at 1770 cm^{-1}. ^1H-NMR spectrum (DMSO-d_6) exhibits signals at δ 4 (dd, 1H, -CH-NH, *J*=8.5), 6.7 (bs, NH), 7.5-7.9 (m, 9H of Ar), 6.9 (d, 1H, CH furanone moiety, *J*=8.5). ^{13}C NMR (125 MHz, DMSO-d_6), δ 71.4 (CHCOfur), 112.3 (C_1Ar), 115.2 120.3(C_4Ph), 126.1 ($C_{2,6}$Ph), 127.3 ($C_{2,6}$Ar), 128.2 ($C_{3,5}$Ph), 129.7 (C_1Ph), 131.1 ($C_{3,5}$Ar), 139.2 (C_4Ar), 144.3 (=CHfur), 149.3(C fur), 154.2 (SC=N), 169.5 (COfur), 170.2 (NHC=N). Elem. Anal. for ($C_{18}H_{13}BrN_3O_2S$). M wt 414: Calc.: % C 58.20, H 3.80, Br 19.08, N 8.40, S 6.60,; Found % C 58.00, H 3.52, Br 18.87, N 8.11, S 6.23.

5-(4-Acetylaminobenzoylmethyl) -2-phenyl-4 -oxoimidazolo [2,1-b]-1,3,4 thiadiazole(3a)

m.p. 130-132^oC, yield 35%, IR: υ C=O are at 1695 and 1669 cm^{-1}. ^1H-NMR (DMSO-d_6) exhibits signals at 3.2 (s, 2H, CH_3CO), 3.4 (2dd, CH_2-C=O, *J*=7.7) (diastereotopic protons), 3.9 (dd, CH-imidazo, methine proton), 7.2-7.7 (m, 9H, ArH), 11.2 (s, 1H, NH, exchangeable by D_2O). Elem. Anal. For ($C_{20}H_{16}N_4O_3S$) M.wt. 392: Calc.: % C 61.21, % H 4.11, % N 14.28, % S 8.17; Found % C 61.00, % H 3.95, % N 14.00, % S 7.92. The EI-MS shows the molecular ion peak at m/e 395, 392 corresponding to $(M+2)^+$ and $(M^{\cdot+})$ respectively.

5-(4-Chlorobenzoylmethyl)-2-phenyl-4-oxoimidazolo [2,1-b]-1,3,4 thiadiazole (3b)

m.p. 142-144^oC, yield 35%, IR: υ C=O are at 1691 and 1668 cm^{-1}. ^1H-NMR (DMSO-d_6) exhibits signals at 3.31 (2dd, CH_2-C=O, *J*=7.7) (diastereotopic protons), 4.11 (dd, CH-COOH, methine proton), 7.6-7.9 (m, 9H, ArH)). Elem. Anal. for ($C_{18}H_{12}ClN_3O_2S$) M wt 369.5: Calc.: % C 58.46, H 3.27, Cl 9.60, N 11.36, S 8.67; Found % C 58.20, H 3.00, Cl 9.28, N 10.90.8, S 8.20. The EI-MS shows the molecular ion peak at m/e 371, 369 corresponding to $(M+2)^+$and $(M^{\cdot+})$ respectively.

5-(4-Bromobenzoylmethyl)-2-phenyl-4-oxoimidazolo [2,1-b]-1,3,4 thiadiazole (3c)

m.p. 136-138°C, yield 35%, IR: υ C=O are at 1701 and 1672 cm^{-1}. ^{1}H-NMR (DMSO-d_6) exhibits signals at 3.21 (2dd, CH_2-C=O, *J*=7.7) (diastereotopic protons), 3.95 (dd, CH-COOH, methine proton), 7.5-7.9 (m, 9H, ArH)). Elem. Anal. for ($C_{18}H_{13}BrN_3O_2S$). M wt 413: Calc.: % C 58.2, H 3.8, Br 19.08, N 8.4, S 6.6; Found % C 58.4, H 3.5, Br 19.67, N 8.1, S 6.2.The EI-MS shows the molecular ion peak at m/e 415, 413 corresponding to $(M+2)^+$ and $(M^{\cdot+})$ respectively.

Synthesis of pyridazinone derivatives (4a-c).

An equimolar mixture of 1a-c or 2a-c and hydrazine hydrate was refluxed in ethanol for 3 h and the solid separated out was filtered off, dried and crystallized from absolute ethanol.

N-(4-(6-oxo-5-((5-phenyl-1,3,4-thiadiazol-2-yl)amino)-1,4,5,6-tetrahydropyridazin-3-yl) phenyl)acetamide (4a)

Yield 75 %, IR (KBr) υ C=O of 1674, 1708 and (NH) of 3177 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.2(s, 3H, CH_3), 3.7 (2dd, 2H, CH_2-C=N), 4.2 (2 dd, CH, methine proton) 6.7 (s, NH, NH of thiadiazole moiety), 7.43-7.81 (m, 9H, Ar-H), 10.26, 11.59 (brs, 2H, NH of acetamido and pyridazinone moieties). EIMS: *m/z*: 406 (M^+). Anal. Calcd. $C_{20}H_{18}N_6O_2S$: % C 59.11, H 4.46, N 20.69, S 7.88; Found: % C 59. 20, H 4.43, N 20. 10, S 7. 34.

6-(4-Chlorophenyl)-4-((5-phenyl-1,3,4-thiadiazol-2-yl)amino)-4,5 dihydropyridazin -3(2 H)-one (4b)

Yield 80 %, IR (KBr) υ C=O of 1708 and (NH) of 3177 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 3.7 (2dd, 2H, CH_2-C=N), 4.2 (2 dd, CH, methine proton) 6.7 (s, NH, NH of thiadiazole moiety), 7.43-7.81 (m, 9H, Ar-H), 11.59 (brs, 1H, NH pyridazinone moieties). ^{13}C NMR (125 MHz, DMSO-d_6), δ 54.21(CH_2py), 71.4 (CHCOpy), 121.3 (C_1Ar), 127.3(C_4Ph), 128.1 ($C_{2,6}$Ph), 129.3 ($C_{2,6}$Ar), 129.7 ($C_{3,5}$Ph), 131.7 (C_1Ph), 132.1 ($C_{3,5}$Ar), 137.2 (C_4Ar), 147.2 (C py), 153.2 (SC=N), 166.5 (COpy), 170.6 (NHC=N). Anal. Calcd. $C_{18}H_{14}ClN_5OS$. M wt 383.5: % C 58.81, H 4.13, Cl 9.25, N 18.25, S 8.34; Found: % C 58.60, H 4.00, Cl 9.01, N 18.04, S 8.12.

6-(4-Bromophenyl) -4-((5-phenyl -1,3,4 -thiadiazol -2-yl) amino)-4,5 dihydropyridazin-3(2 H)-one (4c)

Yield 70 %, IR (KBr) υ C=O of 1702 and (NH) of 3132 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 3.6 (2dd, 2H, CH_2-C=N), 4.2 (2 dd, CH, methine proton) 6.7 (s, NH, NH of thiadiazole moiety), 7.43-7.81 (m, 9H, Ar-H), 12.09 (brs, 1H, NH pyridazinone moieties). EIMS: *m/z*: 429 (M^++2), 427 (M^+). Anal. Calcd. $C_{18}H_{14}BrN_5OS$: % C 57.21, H 3.82, Br 18.50, N 16.39, S 7.49; Found: % C 57.00, H 3.60, Br 18.24, N 16.13, S 7.19.

Physicochemical properties of the base stock

The tested base stock was delivered from Co-operative Petroleum Company, Cairo, Egypt. The physicochemical characteristics of the base stock are tabulated in Table 1, showed that wax content 0.86%, total Sulfur 0.36%, carbon residue 0.75% , total acid number 0.07 mg KOH/ gram sample Viscosity 7.42 cSt at 100 ^{o}C, has high flash point 221 ^{o}C and it has low pour point -3 ^{o}C. The oxidation test methods were carried out according to the standard test method ASTM D- 943.

TABLE 1. Base Stock properties.

Test	Result	Standard Test Method
Density at 15.56 ^{O}C, g /cm^{3}	0.8818	ASTM D – 1298
Pour Point, ^{O}C	-3	ASTM D – 97
Viscosity at 40 ^{O}C at 100 ^{O}C	52.34 7.42	ASTM D – 445
Viscosity Index (VI)	92	ASTM D – 2270
Total Acid Number (TAN)	0.07	ASTM D – 664
Sulfur Content, wt %	0.36	ASTM D – 4294
Color	2.5	ASTM D – 1500
Ash Content, wt %	0.003	ASTM D – 482
Copper Corrosion	1 a	ASTM D – 130
Flash Point, ^{o}C	221	ASTM D – 92
Aniline Point	100.6	ASTM D – 611

Corrosion inhibitor study

1.0 M HCl solution is prepared by dilution of 37% HCl A.R. grade with distilled water and the examined inhibitors is 0.025 - 0.075 mmol dm^{-3}.The composition of carbon steel bar presented in Table 2.

TABLE 2. Carbon steel composition in wt. %.

Element	Si	C	Mn	P	S	Cu	Ni	Cr	Al	Mo	V
(wt.%)	0.22	0.09	1.52	0.01	0.05	0.02	0.04	0.02	0.04	0.004	0.002

Electrochemical measurements

Electrochemical measurements are performed with a traditional three-electrode cell using Volta lab 40 (Tacussel-Radiometer PGZ402) potentiostat controlled by Tacussel corrosion analysis software (model: Voltamaster 4) under static condition. All experiments are performed at 25 ^{o}C. Potentiodynamic polarization measurements have been achieved by changing the electrode from −700 to − 400 mV versus SCE. The inhibition efficiency percentage (η_p %) was calculated using the following equations:

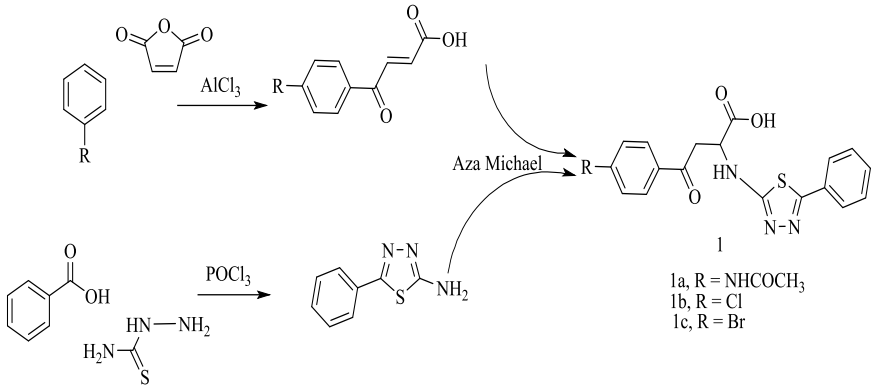
$$\eta_p \% = (1 - I/I_o) \times 100,$$

where I_o and I are the corrosion current densities in the absence and presence of the inhibitor, respectively.

Results and Discussion

Chemistry

The authors reported the behavior of 4-aryl-4-oxo-but-2-enoic acids (1) that were permitted to react with novel nitrogen nucleophile *e.g.* 2-amino-5-phenyl-1,3,4-thiadiazole in boiling ethanol (neutral medium) afforded the aza-Michael products 4-(4-acetylamino/chloro/bromophenyl)-2-(5-phenyl-1,3,4thiadiazol-2-yl) amino-4-oxo-butan-oic acids (1). The 2-aminothiadiazole derivative could be synthesized from treatment of aromatic acid with thiosemicarbazide in the presence of $POCl_3$ under reflux 0.5h (Scheme 1).

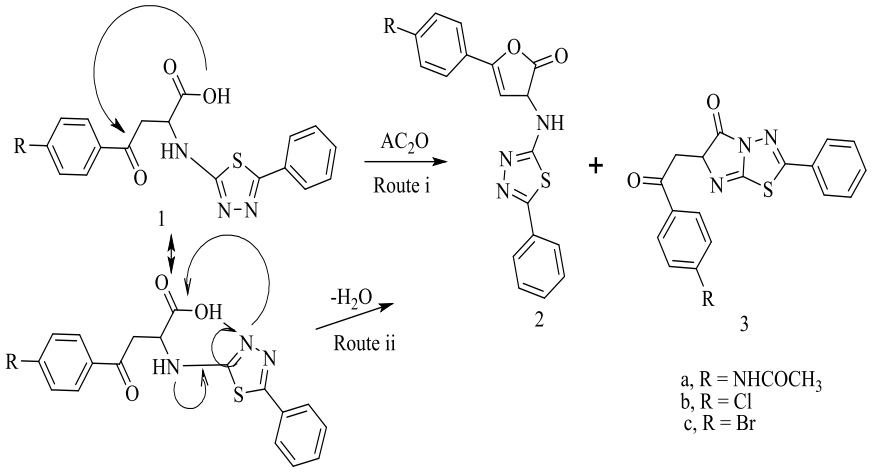


Scheme 1.

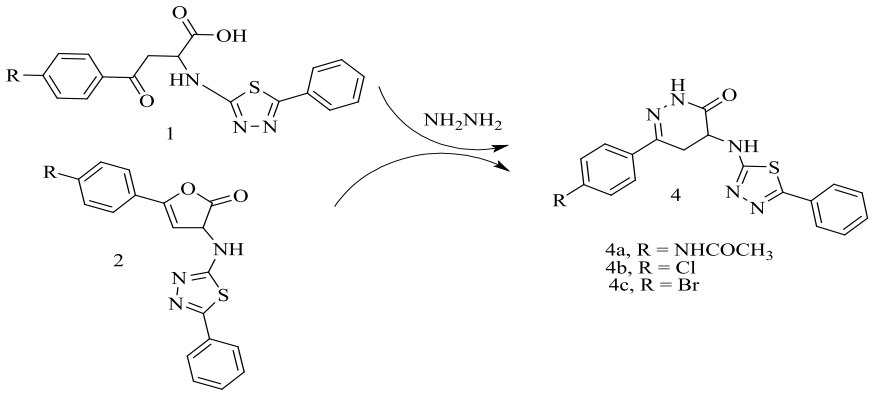
The recent efforts made for the development of new ascorbic acid analogues in obtaining antioxidant [16-20], antitumor [21] agents have resulted 2(3H)-furanones as a new anti-inflammatory and antioxidant agents [20]. Some 3,5-diaryl-2(3H)furanone possess significant anti-inflammatory and antioxidant activities. So, the current work describes the synthesis of 2(3H)-furanone with expected anti-antioxidant activity [2,5] yielded the corresponding furanone 2 that is confirmed chemically by interaction with hydrazine hydrate to afford the corresponding pyridazinone 4 (Scheme 2). Moreover, the another product could be isolated imidazolo [2,1-b]1,3,4-thiadiazole derivative. There may be a competitive reaction in dehydration followed by cyclization via route [i] carboxylic group within enol of the aroyl group affording the foranone 2 and/or via route[ii] carboxylic group within imino of the thioguanidino group affording imidazolothiadiazole derivative 3(Scheme 2).

When the acids 1 and their furanone were submitted to react with hydrazine hydrate in boiling ethanol, afforded pyridazin-3-(2H)one 4 (Scheme 3). It's well-known and found out the important the 6-aryl pyridazin-3(2H)-one in

medicinal fields [22-28]. The newly route apply and study the target compounds in petro chemistry as antioxidant, and anti-corrosion additives. In addition to study some characterization of substituent group effect upon the active site of pyridazinone nucleus (Scheme 3).



Scheme 2.



Scheme 3 .

where: R = $NHCOCH_3$, N-(4-(6-oxo-5-((5-phenyl-1,3,4-thiadiazol-2-yl)amino)-1,4,5,6-tetrahydropyridazin- 3-yl)phenyl)acetamide (4a).

R = Cl, 6-(4-Chlorophenyl)-4-((5-phenyl-1,3,4-thiadiazol-2-yl)amino)-4,5-dihydropyridazin-3(2H)-one (4b).

R = Br, 6-(4-Bromophenyl)-4-((5-phenyl-1,3,4-thiadiazol-2-yl)amino)-4,5-dihydropyridazin-3(2H)-one (4c).

Estimation of the synthesized compounds (4a-c) as antioxidants for base stock

Effect of compounds 4a-c on Total Acid Number (TAN) on base stock

The oxidation process of engine lubricants progressed by two mechanisms, namely oxidation and thermal decomposition. Mineral oil is very complex in nature due to the presence of large range of molecular types and functional groups. This complex structure makes the oxidation reactions extremely hard to understand. The test is carried out at 24, 48, 72 and 96 hours. The results showed that the oxidative products (acidic, ketonic and alcoholic compounds) increased with time. Therefore, in the absence of antioxidants, the TAN values of the base stock increased from 0.07 mg KOH/g to 2.02 mg KOH/g after 96. Also viscosity increased from 52.38 to 77.71 cSt, at 40^{o}C (Table 3). Consequently, after adding the prepared antioxidants the efficiency of them as inhibitors is studied.

TABLE 3. Acid numbers (ANs) and viscosity of the base oil without antioxidants.

Oxidation time interval (h)									
Total Acid numbers, KOH mg /g Sample					**Viscosity (cst), at 40^{o}C**				
Blank	24 h	48 h	72 h	96 h	Blank	24 h	48 h	72 h	96 h
0.07	0.94	1.02	1.20	2.02	52.38	59.39	64.35	68.49	77.71

Effect of additives concentration on TAN values

Three concentrations (200, 400, and 500 ppm) of each prepared antioxidant were added to the blank sample.

The results obtained in Table 4 illustrated the following:

- After 24 h, by adding 200 ppm of antioxidant 4a to the blank sample, total acid number value decreased from 0.94 to 0.069 KOH mg/g. After 48 h, the value decreased from 1.02 to 0.083 KOH mg/g. A marked decrease is observed in the third day of oxidation (72 h), from 1.2 to 0.441 KOH mg/g. Consequently, after 96 h the value decreased from 2.02 down to 0.778 KOH mg/g.
- In the case of blank with 400 ppm of 4a, the values of TAN decreased during the oxidation period (24 – 96 h) as follows: (0.94 – 2.02 down to 0.075 – 0.916 KOH mg/g).
- Increasing concentration of 4a to 500 ppm gave the following results of the TAN values (0.94 – 2.02 down to 0.164 – 1.003 KOH mg/g).
- Addition of 4b to blank sample (200, 400 and 500 ppm) during the oxidation period illustrate the following:

a) With 200 ppm, TAN changed (from 0.94 – 2.02 down to 0.082 – 0.936 KOH mg/g) respectively.
b) After adding 400 ppm the values gradually changed from (0.94 – 2.02 down to 0.116 – 1.007 KOH mg/g) respectively.

c) The effect of adding 500 ppm of 4b on the plank sample decreases the TAN by the following values, (from 0.94 – 2.02 down to 0.235 – 1.260 KOH mg/g) respectively.

- Finally, by studying the effect of antioxidant 4c (200, 400 and 500 ppm) on the blank sample during the oxidation time interval we noticed that:

a) With 200 ppm, TAN changed (from 0.94 – 2.02 down to 0.109 – 0.968 KOH mg/g) respectively.
b) With increasing concentration up to 400 ppm, the values have changed, (from 0.94 – 2.02 down to 0.152 – 1.201 KOH mg/g) respectively.
c) At last, after adding 500 ppm of 4c, the values changed from 0.94 – 2.02 down to 0.246 – 1.343 KOH mg/g during the time interval respectively.

Effect of electron donating and withdrawing groups

As it is clear from Scheme 3, the data shown in Table 4, we noticed that the most effective substituted groups are shown with donating group (4a) than withdrawing groups (4b and 4c) This may be attributed to the electron donating nature group (4a) that facilitates the break of the hydrogen-bonded to the nitrogen to produce a stable free radical but in case of electron withdrawing groups(4b,4c) that may increase the difficulty of the N–H bond breaking whereby it has a much lower oxidation stability.

TABLE 4. Variation of TAN with oxidation time at changed additive concentrations .

Compound	Total Acid number, KOH mg / g Sample				
	Concentration (ppm)	Time (h)			
		24	48	72	96
4a	200	0.069	0.083	0.441	0.778
	400	0.075	0.098	0.631	0.917
	500	0.164	0.246	0.756	1.003
4b	200	0.082	0.138	0.532	0.936
	400	0.116	0.172	0.698	1.007
	500	0.235	0.361	0.799	1.260
4c	200	0.109	0.195	0.586	0.968
	400	0.152	0.236	0.739	1.201
	500	0.246	0.404	0.854	1.343

The data showed in Fig. 1, 2 and 3 represented the correlation between the oxidation periods and TAN of blank sample without and with additive concentrations of 200, 400 and 500 ppm, for compounds 4a, 4b and 4c, respectively. The order of increasing inhibition efficiency is ranked as follows:

4a > 4b > 4c > blank. Thence, increasing the additive concentration from 200 to 500 ppm lead to an increase in the TAN values. This may be attributed to high sulphur percent which retard the inhibition efficiency [32] .

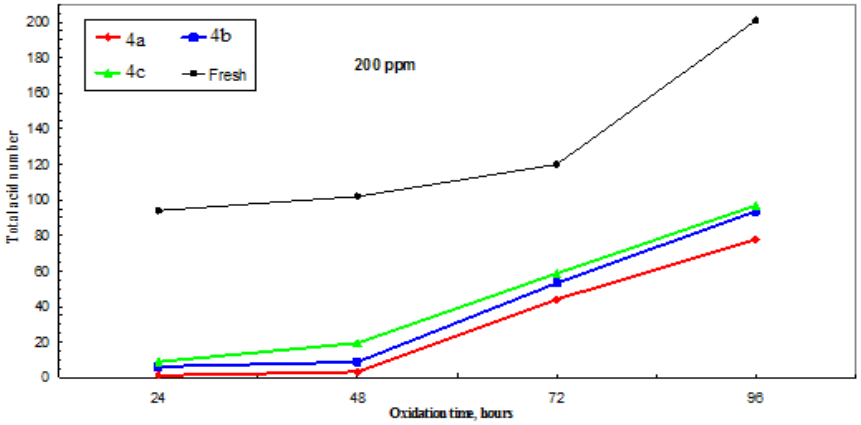


Fig.1. TAN variation of the base stock without and with 200 ppm of 4a, 4b and 4c.

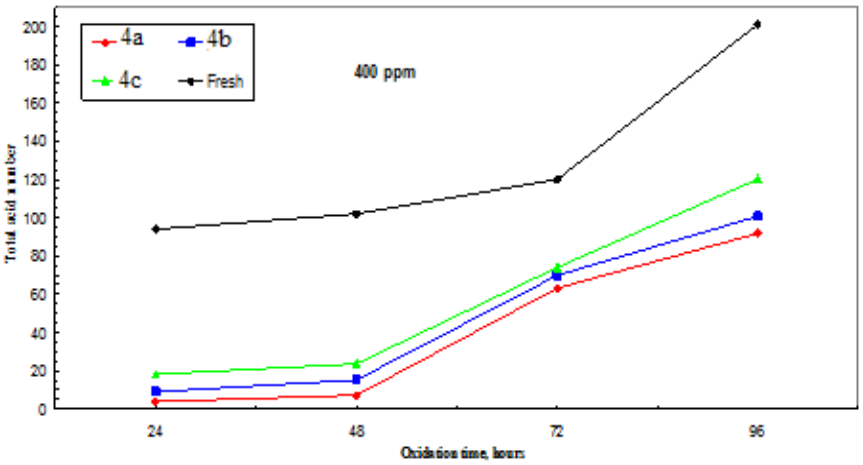


Fig. 2. TAN variation of the base stock without and with 400 ppm of 4a, 4b and 4c .

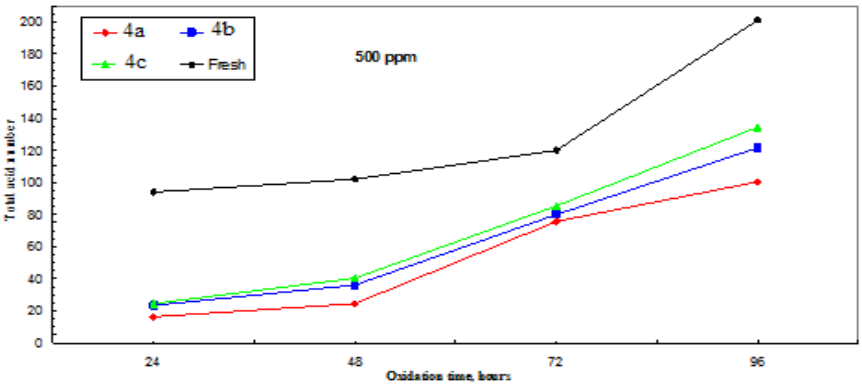


Fig. 3. TAN variation of the base stock without and with 500 ppm of 4a, 4b and 4c .

Effect of antioxidants on viscosity of blank sample

The most important physical properties for the categorization of base stock is Viscosity. As the oxidative products increased lead to the formation of sludge and other higher molecular weight compounds so causing the increasing in viscosity. The data shown in Table 3 obtained that the viscosity of the blank sample increased from 52.38 up to 77.71 cSt after oxidation for 24 to 96 hours. The data of the viscosity values are tabulated in Table 5 and graphically represented in Fig. 4 - 6, the results of the viscosities are given after oxidation time intervals for (24, 48, 72 and 96 hours). The viscosity decreased by increasing the additive concentration from 200 ppm up to 500 ppm. Among the three base compounds (4a, 4b and 4c), the order of these compounds towards decreasing viscosity is ranked as follows 4a > 4b > 4c.

Correlation of the antioxidants activity with their structures

The program Ab initio (HF/3-21G) can be used for correlation between the structure of the prepared compounds and their antioxidant activity. The more values of the E_{HOMO} simplify adsorption and then restraint by the effect of transported process through the adsorbed layer . Low energy gap (ΔE) gives good antioxidant efficiencies . The results of the calculations, for the synthesized compounds 4a,4b and 4c are given in Table 6. The results obtained by Ab initio HF/3-21G method showed that (4a; ΔE = 4.963), (4b; ΔE = 5.304), (4c; ΔE = 5.344). According to these values, the efficiency order is as follows 4a > 4b > 4c. The HF/3-21G calculations agreed with the experimental data.

TABLE 5. Variation of viscosity with oxidation time and different additive concentrations.

Compound	Viscosity, cst at 40 °C× 10^2				
	Concentration (ppm)	Oxidation time (hr)			
		24	48	72	96
4a	200	5239	5243	5370	5736
	400	5242	5247	5702	6011
	500	5253	5264	5722	6075
4b	200	5245	5263	5854	6013
	400	5257	5298	5988	6032
	500	5266	5314	6018	6154
4c	200	5251	5272	5901	6025
	400	5268	5321	6035	6121
	500	5278	5333	6066	6371

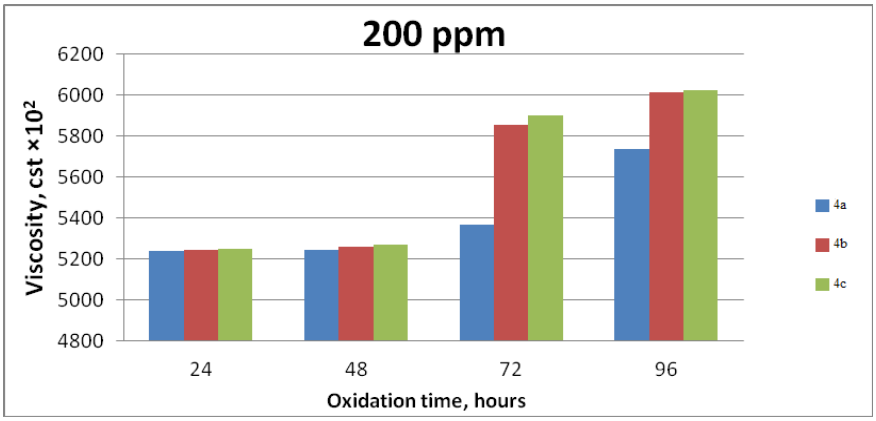


Fig. 4. Variation of viscosity of the base oil with 200 ppm of antioxidants 4a , 4b and 4c.

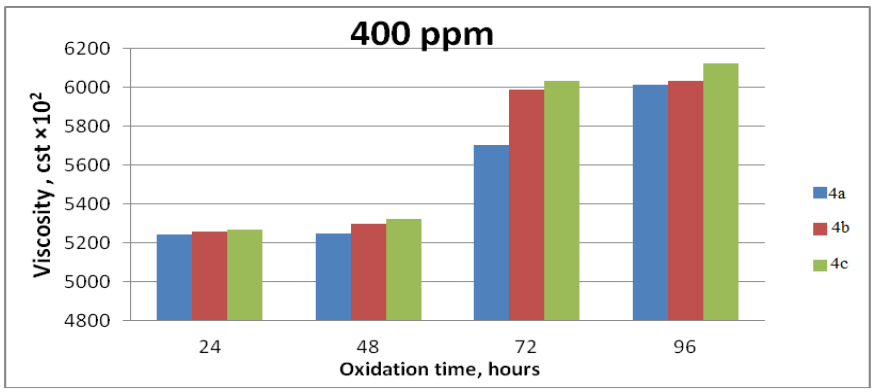


Fig. 5. Variation of viscosity of the base oil with 400 ppm of antioxidants 4a, 4b and 4c.

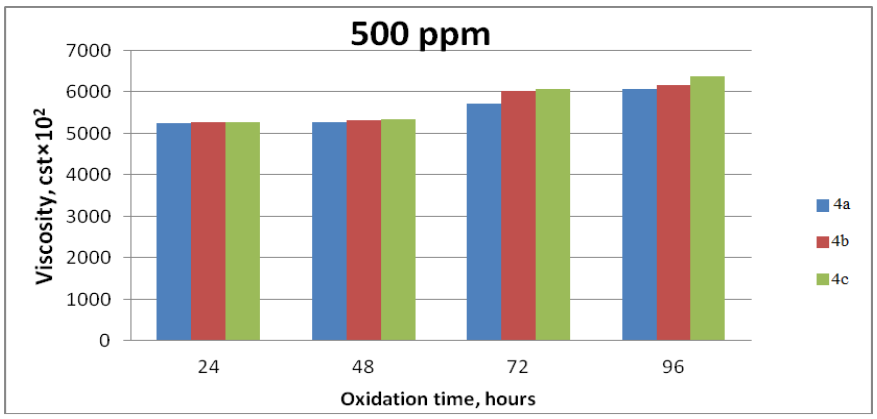


Fig. 6. Variation of viscosity of the base oil with 500 ppm of antioxidants 4a, 4b and 4c.

TABLE 6. Quantum Chemical Parameters.

Compound	Quantum Parameters				
	Dipole Moment (Debye)	**Total energy (Kcal/mole)**	**E_{LUMO} eV**	**E_{HOMO} eV**	**ΔE eV E_{LUMO} - E_{HOMO}**
Ab Initio HF/3-21G					
4a	3.11	7.736	-2.924	-7884	4.963
4b	3.74	12.548	-2.594	-7898	5.304
4c	3.36	12.384	-2.595	-7.939	5.344

Evaluation of the synthesized compounds as corrosion inhibitors for carbon steel in acid medium

Potentiodynamic polarization measurements are performed for carbon steel immersed in 1 M HCl in absence and presence of the synthesized compounds to evaluate their effectiveness as corrosion inhibitors. From Table 7 and Fig. 7, the

efficiency order of these compounds towards corrosion inhibition is ranked as follows: 4a > 4b > 4c with value 76.1 > 68.8 > 56.0%, respectively and the Data reveal the following:

1- Addition of any of the three compounds resulted in a significant reduction in the corrosion current density (I_{corr}) in comparison to that measured in the blank acid solution. On increasing the concentration of these inhibitors, I_{corr} decreases continuously indicating that their molecules adsorb on Carbon steel surface forming a physical barrier against the corrosion attack via blocking the active sites on the steel surface[33].

The maximum displacement in E_{corr} measured in the presence of corrosion inhibitors , with respect to that measured in the blank acid solution, is +99, +46, +31 mV for 4a, 4b and 4c, respectively. According to Riggs [34] an inhibitor can be classified as anodic or cathodic-type inhibitor if the E_{corr} displacement is at least ±85 mV relative to the value of E_{corr} measured for the blank solution. Therefore, 4a can act as anodic-type inhibitor while 4b and 4c act as mixed-type inhibitors with major effectiveness on anodic reactions. This behavior supports the adsorption of inhibitor onto the metal surface and caused a barrier effect for mass and charge transfer of anodic and cathodic reactions [35].

TABLE 7. Electrochemical polarization parameters for the corrosion of carbon steel in 1 M HCl containing various concentrations of the investigated inhibitors.

Inhibitor	Concentration (mmol dm-3)	-Ecorr (mV vs. SCE)	Icorr (mA cm-2)	ηp (%)
Blank	0	558	1.2235	---
4a	0.025	480	0.3618	70.4
	0.050	459	0.3507	71.3
	0.075	504	0.2926	76.1
4b	0.025	562	0.4590	62.5
	0.050	512	0.4216	65.5
	0.075	528	0.4067	68.8
4c	0.025	553	0.7639	37.6
	0.050	527	0.5581	54.4
	0.075	544	0.5383	56.0

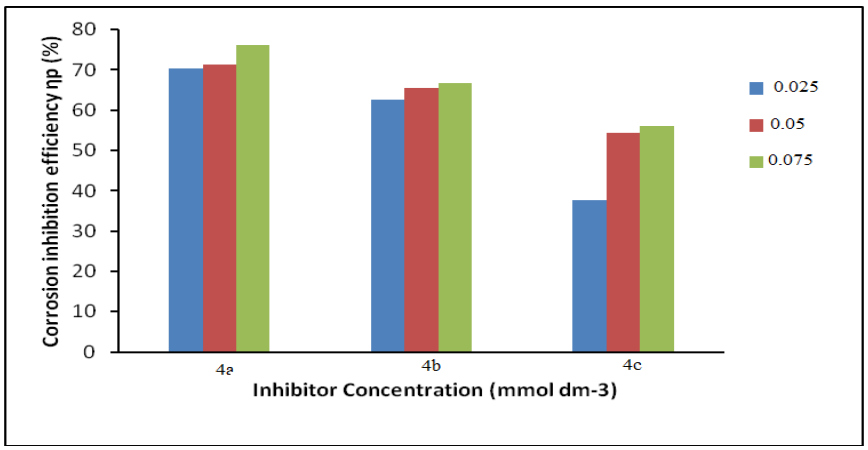


Fig.7. Relationship between corrosion inhibition efficiency (ηp, %) and different concentrations of the investigated inhibitors in 1 M HCl .

Conclusion

The newly prepared compounds were examined as antioxidant and anticorrosion the compounds 4a, 4b (high E_{HOMO}) were showed high antioxidant activities and anticorrosion. There are relationships between anticorrosion and antioxidant agents from point of view quantum chemical parameter. Increasing in the E_{HOMO} values refer to high antioxidant activity that was identical to identical to the experimental results.

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توليف وتطبيقات بيريدازينونات لتحسين خواص الزيوت الاساسية

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ثلاثة مشتقات للبيريدازينون من نوع ٤،٥-ديهيدروبيريدازين- ٣)٢one- (H، 6) -4) -N-أوكسو -٥- ((٥-فينيل-١،٣،٤-ثياديزول-٢-يل) الأمينية) - ١،٤،٥،٦ - تيترايدروبيريدازين - ٣-يل) فينيل) أسيتاميد (٤(a، 4) -6-كلوروفينيل) -٤ - ((٥-فينيل-١،٣،٤-ثياديازول-٢-يل) أمينو) -٤،٥-دي-هدروبيريدازين- ٣ (٢ 4b) one- (H) و ٦ - (٤-بروموفينيل) -٤- ((٥-فينيل-١،٣،٤-ثياديازول-٢-يل) الأمينية) -٤،٥- ديهيدروبيريدازين-٣ (٢C4) one- (H) تم تحضيرها. وقد تم التاكد من تركيبها البنائى من خلال الأدوات التقليدية للتحليل، التحليل العنصري، الأشعة تحت الحمراء والرنين المغناطيسى الهيدروجينى. وأكدت أدوات التحليل المركبات الثلاثة المخلقة. هذه المركبات الاروماتية غير المتجانسة مستقرة كيميائيا ولها خواص متعددة لتحسين مواصفات زيوت التزييت الاساسية. لقد تم اختبارها كمضادات الأكسدة للزيت المحلي من خلال التغيير في عدد الحمض الكلي (تان). وقد أظهرت نتائج جيدة كمضادات الأكسدة لزيت الأساس. كما تم اختبار هذه المركبات الثلاثة كمثبطات تآكل للصلب الكربوني في وسط حامضى. و قد تم ترتيب كفاءة هذه المركبات المختبرة على النحو التالي: a٤ > b٤ > c٤ . تم حساب الطاقة من أعلى المدار الجزيئي المحتل (هومو) وأقل المداري الجزيئية غير المأهولة (لومو) للمركبات المحضرة الثلاثة عبر طريقة أب إنيشيو. وأظهرت دراسة الحسابات الكيمائية الكيمياوية للمركبات المركبة تطابقا جيدا مع النتائج التجريبية.