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Imidazole-containing inhibitor-bactericides against corrosive sulfate reducing bacteria in the oil pipelines

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Abstract. Tetrasubstituted phenanthro[9,10-d]imidazoles were obtained from 9,10-phenanthrenequinone, ammonium acetate, aryl amines and substituted aromatic aldehydes in the presence of ionic type N-methyl-2-pyrrolidone acetate catalyst under microwave condition with the yield of 79.8–88.7 %. Structure of synthesized compounds were characterized using ^{1}H and ^{13}C NMR, IR and UV spectroscopy. The obtained imidazole derivatives were tested against sulfate-reducing bacteria as inhibitor-bactericide, the highest result was showed by **S1** in 15 mg/l solution with 100% protective effect.

Keywords: phenanthro[9,10-d]imidazole, microwave, ionic liquid, inhibitor-bactericide, SRB, corrosion.

1. Introduction

Imidazole derivatives are of great interest in bioactive heterocyclic compounds according to various biological and clinical applications. These compounds are used more frequently in the synthesis of medicines and the treatment of various diseases in the last years [1, 2]. The imidazole derivatives having biological activities such as antibacterial, analgetic, anti-allergic, anti-inflammatory, antimalyaria, anti-cancer, anti-HIV [3–10] etc.

In the known source [11], a methodology for the chemoselective synthesis of 2-(1H-indol-3-yl)-1H-benzo[d]imidazole derivatives is presented. Obtained compounds were studied against several bacteria and fungus. Most of compounds (minimum inhibitory concentration (MIC)<1 μg/mL) exhibited excellent antibiofilm activity, inhibiting biofilm formation and killing cells in mature biofilms. Biological activity of azo compounds, along with imidazoles, has been noted in many sources [12].

It is known from literature that imidazole compounds are also used as corrosion inhibitors [13]. Microbiological corrosion is one of the most important factors in the degradation of matter in the oil and gas industry. At present, the major part of oil is mainly derived by filling of various origins water to the oil wells in oil-industry countries. In this case, wells are infected with SRB and other microorganisms. In oil extraction devices, during oil transportation, germs adhere to the surface of the equipment, causing microbiological corrosion by damaging the substrate. The main constituent of microbiological corrosion is sulfate-reducing bacteria. Sulfate-reducing bacteria are bacterial groups that breathe in the anaerobic way, reducing sulfates ($-SO_4^{2-}$) to sulfide (S^{2-}) [14–16].

The fight against the placement of sulfate-reducing bacteria on solid substrate is always a problem. The most effective way to prevent microbiological corrosion is the use of inhibitory-bactericides [17, 18].

In the presented study, azo-group containing 2-aryl-1H-phenanthro[9,10-d]imidazole derivatives were obtained in the presence of ionic liquid N-methyl-2-pyrrolidone acetate (NMPA) catalyst under microwave condition were studied against SRB as inhibitor-bactericides.

2. Experimental Part

Melting points (m.p.) of synthesized compounds were measured on a DSK-Q-20 apparatus. ^{1}H and ^{13}C NMR spectra were acquired on a BRUKER – Fourier (300 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard and acetone-D_6 or chloroform ($CDCl_3$) as solvents

at 20 °C. IR spectra were recorded on a LUMOS FT-IR Microscope spectrometer («BRUKER» Campany of Germany) in the range of 600–4000 sm^{-1}. UV spectra were measured at the 190–1100 nm range in the UV/Vis 6850 (JENWAY) spectrophotometer.

3. Results and discussion

Ethanol 50 ml, 9,10-phenanthrenequinone (10 mmol), ammonium acetate (10 mmol), p-aminoazobenzene (10 mmol), substituted aromatic aldehydes (10 mmol) and NMPA catalyst (3 mol%) were added in triple flask which was equipped thermometer and refrigerator in 10 to 15 min at boiling temperature of ethanol (Fig. 1) under microwave (300 W) condition. After completion of the reaction, the mixture washed with ice water, the solid product recrystallized from ethanol.

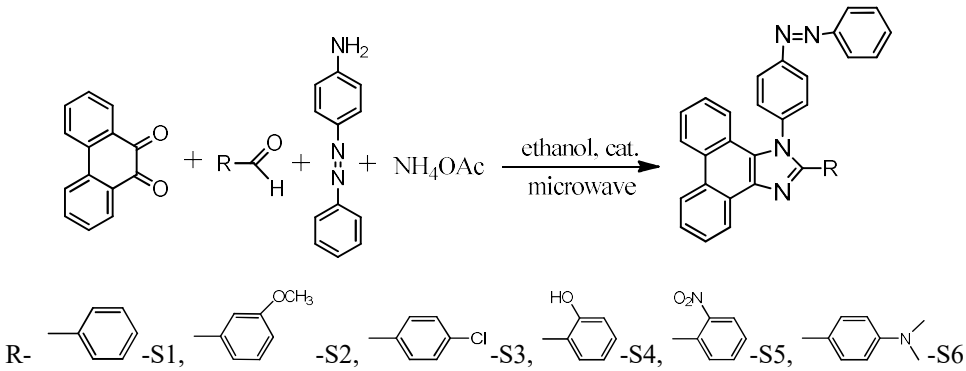

Fig. 1. Synthesis of azo-group containing 2-aryl-1H-phenanthro[9,10-d]imidazole.

Some characterization data of the synthesized compounds were presented in table 1.

Table 1. Characterization data of the synthesized compounds.

Comp.	*t, min*	*t.melt.°C*	*yield, %*
S1	10	184-186	88.7
S2	10	179-181	82.5
S3	13	151.153	83.6
S4	10	141.143	86.4
S5	15	246-248	79.8
S6	12	170-172	80.5

3.1. Spectral and analytical data

2-phenyl-1-(4-(phenyldiazenyl)phenyl)-1H-phenanthro[9,10-d]imidazole (S1): MP. 183–185 °C. $C_{33}H_{22}N_4$. ^{1}H NMR (300 MHz, $CDCl_3$-d), δ, ppm: 7.30-8.17 (m., 19H, CH, Ar.), 8.76 (d.d., 2H, CH, J=8.1, 8.4 Hz), 8.91 (d., 1H, CH, J=7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$-d):120.93, 122.82, 122.91, 123.18, 123.96, 124.22, 124.40, 125.04, 125.72, 126.45, 127.36, 128.02, 128.38, 129.01, 129.32, 129.53, 129.98, 140.63 (C, Ar.), 152.44, 152.74 (C-N). FTIR (cm^{-1}): δ-664, 701, 772, 854, 1468, 1600 and ν-3062, 3163, 3183 (C-H), δ-881 (C=C), ν-1232, 1300 ($C_{arom.}$-N), ν-1648 (C=N), ν-1676 (N=N).

2-(3-methoxyphenyl)-1-(4-(phenyldiazenyl)phenyl)-1H-phenanthro[9,10-d]-imidazole (S2): MP. 178–180 °C. $C_{34}H_{24}N_4O$. ^{1}H NMR (300 MHz, $CDCl_3$-d), δ, ppm: 3.75 (s., 3H, OCH_3), 6.88-8.20 (m., 18H, Ar.), 8.72 (d., 1H, J=8.1 Hz), 8.81 (d., 1H, J=8.4 Hz), 8.91 (d., 1H, J=7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$-d): 55.24 (OCH_3), 114.45, 115.54, 120.94, 121.92, 122.80, 123.19, 123.95, 124.22, 124.43, 125.07, 125.75, 126.44, 127.37, 128.32, 129.31, 129.39, 129.56, 129.98,

130.54, 131.87, 136.02, 140.67 (C, Ar.), 152.49, 152.79 (C-N), 159.38 (C-O). FTIR (cm^{-1}): δ-685, 693, 767, 788, 874, 1452, 1500, 1578, 1609, and ν-3067 (C-H, Ar.), δ-724, 1380, 1482 and ν-2838, 2907, 2939, 2964 (C-H, CH_3) δ-893 (C=C), ν-1048, 1137 (C-O), ν-1226, 1286 ($C_{arom.}$-N), ν-1651 (C=N), ν-1683 (N=N).

2-(4-chlorophenyl)-1-(4-(phenyldiazenyl)phenyl)-1H-phenanthro[9,10-d]imidazole (S3). MP. 150–152 °C. $C_{33}H_{21}N_4Cl$. ^1H NMR (300 MHz, $CDCl_3$-d), δ, ppm: 7.32-8.02 (m., 19H, Ar), 8.18 (d.d., 2H, J=7.5, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$-d): 121.62, 122.83, 123.96, 124.14, 129.10, 129.18, 129.56, 130.18, 130.51, 130.91, 131.01, 134.47, 135.83, 136.02, 137.81 (C, Ar.), 150.85, 153.98 (C-N), 159.47 (C-Cl). FTIR (cm^{-1}): δ-667, 701, 765, 852, 1473, 1594 and ν-3065, 3189 (C-H), δ-854 (C=C), ν-1231, 1298 ($C_{arom.}$-N), ν-1650 (C=N), ν-1677 (N=N), 687 (C-Cl).

2-(1-(4-(phenyldiazenyl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)phenol (S4). MP. 141–143 °C. $C_{33}H_{22}N_4O$. ^1H NMR (300 MHz, aseton-d_6), δ, ppm: 6.98-8.41 (m., 21H, Ar.), 9.02 (s., 1H, OH). ^{13}C NMR (75 MHz, aseton-d_6): 116.88, 119.17, 119.36, 122.35, 122.69, 124.06, 124.38, 129.31, 129.48, 131.27, 133.18, 133.64, 135.72 (C, Ar.), 150.95, 152.62 (C-N), 164.83 (C-O). FTIR (cm^{-1}): δ-671, 719, 771 and ν-3057 (C-H, Ar.), δ-850 (C=C), ν-1225 (C-O), ν-1291, 1328 ($C_{arom.}$-N), ν- 1598 (C-C, Ar.) ν-1653 (C=N), ν-1672 (N=N), ν-3419 (O-H).

2-(2-nitrophenyl)-1-(4-(phenyldiazenyl)phenyl)-1H-phenanthro[9,10-d]imidazole (S5). MP. 245–248 °C. $C_{33}H_{21}N_5O_2$. ^1H NMR (300 MHz, $CDCl_3$-d), δ, ppm: 7.32-8.80 (m., 20H, Ar.), 8.81 (d., 1H, J=8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$-d): 120.98, 122.65, 123.13, 124.17, 124.78, 125.39, 125.85, 126.41, 127.05, 128.42, 129.26, 129.47, 130.71, 131.87, 133.06, 133.43, 137.78, 139.11 (C, Ar.), 147.52 (C-NO_2), 152.38, 152.56 (C-N). FTIR (cm^{-1}): δ-665, 718, 770, 852 and ν-3058 (C-H, Ar.), δ-825 (C=C), ν-1299, 1324 ($C_{arom.}$-N), ν-1527 (C-NO_2), ν-1598 (C-C, Ar.) ν-1648 (C=N), ν-1676 (N=N).

N,N-dimethyl-4-(1-(4-(phenyldiazenyl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)aniline (S6). MP. 170–172 °C. $C_{35}H_{27}N_5$. ^1H NMR (300 MHz, $CDCl_3$-d), δ, ppm: 2.94 (s., 6H, CH_3), 6.62 (d., 1H, J=9.3 Hz), 6.83 (d., 1H, J=9.0 Hz), 7.47-8.92 (m., 19H, Ar.). ^{13}C NMR (75 MHz, $CDCl_3$-d): 40.14 (CH_3), 111.63, 111.68, 122.94, 123.15, 123.97, 124.41, 125.44, 126.31, 127.18, 128.63, 129.27, 129.56, 130.15, 130.34, 130.54, 131.01, 131.78, 135.86, 136.03 (C, Ar.), 149.79, 150.62, 151.04 (C-N). FTIR (cm^{-1}): δ-668, 688, 722, 737, 755, 771, 821, 860, 1448, 1611 and ν-3066 (C-H, Ar.), δ-1381, 1480 and ν-2801, 2933 (C-H, CH_3), ν-1223, 1284 ($C_{arom.}$-N), ν-1657 (C=N), ν-1675 (N=N).

The UV/Vis 6850 spectrophotometer produced by JENWAY has been used to study the structure of compounds in terms of quality. High sensitivity, binary spectrophotometry operating range is 190–1100 nm, and the optical discharge rate of the device is 0.1 nm. Mercury and incandescent lamps are used as a source of excitement. The researches were carried out at room temperature and ethalon chloroform was used as the solvent. The obtained solution and etalon were poured into 1 cm rectangular quartz tubes and inserted in front of appropriate windows in UV-spectrophotometer, spectra of samples were acquired. One of the two absorption strips of the imidazole ring in the UV spectrum of the S3 sample was observed at 215 nm with a small intensity. Low intensity is associated with groups that connected imidazole. Thus, this absorption strip belongs to the π-π * transition of the nuclear electronic system. The second absorption strip for the n-π transition of the undivided electron pair of nitrogen was recorded at 330 nm with high intensity. The connection of chlorine to the aromatic ring causes the boat chromium to slide, which has essentially been shown on the 2nd absorption strip. The C_6H_4Cl group was at 200 and 235 nm, and the absorption strips belonging to the phenanthrene group were determined at a wavelength of 260, 345 and 360 nm. The absorption strips of the diphenyldiazo group were observed in the visible region (535 nm). One of the factors influencing sliding is that the solvent is polyar.

3.2. Biological activity against SRB

Postgate B was used for study the bactericidal effect of compounds:

Bactericidal properties of inhibitors are determined using OCT 39-234-89. In practice, the desulfovibrio desulfuricans type of the SRB was used in 1143 stamp. The experiment was conducted in a 20 ml sterilized test bottles [19]. The bactericidal effect of the reagents was investigated by observing for 14 days and eventually calculating the amount of H_2S. The formation of H_2S is determined by the method of iodometric titration [20].

Quality indicators of synthesized compounds have been estimated by the change in the amount of bacteria during SRB checking. In practice, solutions of bactericides were taken in isopropanol.

The results of bactericidal tests for S1, S2, S4, and S5 samples are given into table 2:

Table 2. Bactericidal tests of S1, S2, S4, and S5 against SRB.

Sample	*Concentration, mg/l*	*Amount of H_2S, mg/l*	*Protective effect, Z-%*
S1	150	–	100
	75	–	100
	15	–	100
	5	45	83.6
S2	150	58	79
	75	72	73.8
	15	98	65
S4	150	–	100
	75	–	100
	15	29	89.4
S5	150	27	90.1
	75	31	88.7
	15	69	74.9
Control-I, amount of H_2S without SRB			24-32 mg/l
Control-II, amount of H_2S with SRB			275 mg/l

As can be seen from the table, sample S1 showed the highest results with a 100% preservative effect in 150, 75 and 15 mg/l solutions, relatively high result recorded in sample S4.

4. Conclusion

Azo-group containing 2-aryl-1H-phenanthro[9,10-d]imidazole derivatives were obtained in the presence of NMPA catalyst under microwave condition, were tested against SRB as bactericide. The highest result was a 100% protective effect of 2-phenyl-1-(4-(phenyldiazenyl) phenyl)-1H-phenanthro[9,10-d]imidazole in 15 mg/l solution.

Synthesized 2-phenyl-1-(4-(phenyldiazenyl)phenyl)-1H-phenanthro[9,10-d]imidazole may be offered against SRB as bactericide.

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