Caspian Corrosion Control

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SYNTHESIS, INHIBITOR-BIOCIDE ACTIVITY OF N, N-DI (9H-FLUOREN-9-YLIDENE) BENZENE-1,4- AND N, N-DI (9H-FLUOREN-9-YLIDENE) NAPHTHALENE-1,5-DIAMINES

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A b s t r a c t

Schiff bases of N1,N4-di(9H-fluoren-9-ylidene)benzene-1,4-diamine (1) and N1,N5-di(9H-fluoren-9-ylidene)naphthalene-1,5-diamine(2) were synthesized by new simple and high yield synthetic procedure. The structures of the synthesized compounds of 1 and 2 were confirmed by elemental, 1H NMR, mass spectroscopic and Single-crystal X-ray analyses. The prepared compounds were evaluated as antibacterial agents against sulfate-reducing bacteria using the serial dilution method, which showed good biocide action. The compounds were tested as corrosion inhibitors against the corrosion of carbon steel in a model of mineralized produced water containing hydrogen sulfide (H_2S) and carbon dioxide (CO_2) using weight loss methods. The results revealed that these compounds have significant inhibiting effects on the corrosion of carbon steel.

Keywords:
Schiff bases;
NMR analysis;
Corrosion inhibition;
Microbial corrosion;
Antibacterial activity.

Introduction

Metals and its alloys are easily undergone to the corrosion when they exposed to harsh condition such acidic, basic, saline water and other corrosion gases like CO_2, SO_2 etc. Corrosion inhibitors were played an important role to prevent corrosion in different corrosive media [1]. The applications of organic compounds have been widely studied as corrosion inhibitors for metals and its alloys [2]. Many organic compounds containing oxygen, nitrogen and sulphur have been studied as corrosion inhibitors for metal. Compounds with π-bonds also generally exhibit good inhibitive properties due to interaction of π-orbital with the metal surface. The corrosion inhibition is a surface which involves the adsorption of the organic compounds on metal surface. Schiff base with –CH=N– linkage (azomethine) have both the above features combined with their structure which make them effective potential corrosion inhibitors. Schiff bases are the condensation products of carbonyls and amines. Although most of the commercial formulations of inhibitors include aldehydes and amines as essential ingredients, Schiff bases have been found to possess more inhibition efficiency than their constituent carbonyls and amines. Certain authors have attributed this considerably stronger inhibition efficiencies to the presence of unoccupied p*-orbitals in the Schiff base molecules, which enable electron back donation from the transition metal d-orbitals and thereby stabilise the existing metal-inhibitor bond, which is not possible with the constituent amines [3]. Several Schiff have been investigated as corrosion inhibitors for the protection of different important metals such as aluminum, carbon steel, iron steel, stainless steel, steel, copper, magnesium and some examples on their alloys [4]. Thus, the synthesis of new Schiff bases, which contains many π-orbitals and an aromatic ring, is of particular importance.

This paper reports the synthesis and characterization of N,N-di(9H-fluoren-9-ylidene) benzene-1,4-diamine (1) and N,N-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamines (2). The effects of these Schiff bases on the corrosion behavior of mild steel in produced water containing hydrogen sulfide (H_2S) and carbon dioxide (CO_2) were studied by weight loss method. Furthermore, antibacterial activities of the synthesized Schiff bases were evaluated against the sulfate reducing bacteria (SRB).

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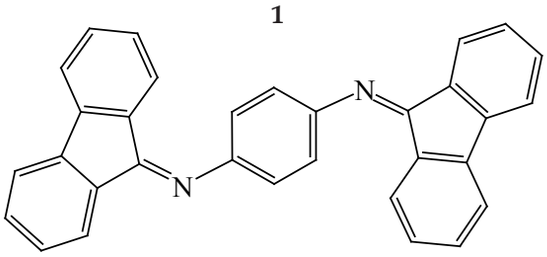

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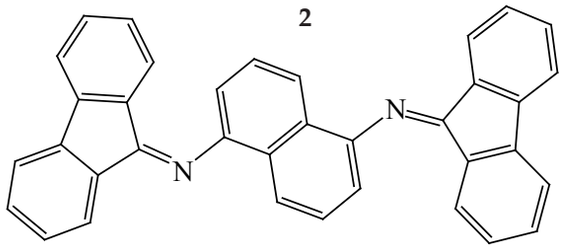


Experimental part

All starting materials were purchased from Aldrich, TCI and Across. ^{1}H NMR spectra were recorded with Bruker AMX400, proton chemical shifts (δ) are reported in parts per million (ppm) relative to the methine singlet at 7.24 ppm for the residual $CHCl_3$ in the deuterio chloroform. Mass spectra were obtained with a FAB JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan). Elemental analyses were done by FlashEA 1112 Series CHNS-O Analyzer. To investigate the molecular structure we performed single-crystal structure analysis using Bruker X8APEX X-ray diffractometer with Mo Kα radiation (λ=0.71073 Å). The data were collected at 100(2) K and the structure was solved by SHELXS-97 program.

Procedure for synthesis of Schiff bases of 1 and 2.

0.24 mol of 9H-fluoren-9-one, 0.1 mol of benzene-1,4-diamine (or naphthalene-1,5-diamine) and 100 ml glacical acetic acid were placed in a 250 ml two-neck round bottom flack equipped with stirrer, thermometer, reflux condenser and was refluxed for 30 minutes. The reaction mixture was cooled to room temperature; 100 ml of water was added. The solid was filtered off, washed with water (100 ml), 2% Na_2CO_3 solution (100 ml), then again 100 ml of distilled water, ethanol and dried over vacuum, to give Schiff bases of 1 and 2 as an orange solids.

N^1,N^5-di (9H-fluoren-9-ylidene) benzene-1,4-diamine (1). 80% yield. ^{1}H NMR (400 MHz, CDCl3) δ=7.94-7.92(d,J=7.44 Hz, 2H); 7.62-7.60 (d,J=7.54 Hz,4H) ; 7.49-7.45 (t,J=7.44 Hz, 2H); 7.38-7.33 (t,J=7.44 Hz, 4H); 7.09 (s, 4H); 7.01-6.95 (m, 4H); MS (EI, 70 eV) 432.16 (M+, 100%), Elemental Analysis: C, 88.55%; H, 4.43%; N, 6.62%.

N1,N5-di (9H-fluoren-9-ylidene) naphthalene -1,5-diamine(2). 76% yield. 1H NMR (400 MHz, $CDCl_3$) δ=8.17-8.15 (d,J =7.36 Hz, 2H); 7.73-7.71 (d,J=8.48 Hz,2H); 7.64-7.62 (d,J=7.43 Hz, 2H); 7.60-7.58 (d,J=7.46 Hz,2H); 7.54-7.50 (t,J=8.4 Hz,2H); 7.44-7.40 (t,J=7.45 Hz, 2H), 7.40-7.36 (t,J=7.75 Hz,2H); 7.31-7.27 (t,J=8.4 Hz,2H); 7.08-7.06 (d,J=7.11 Hz,2H); 6.79-6.75 (t,J=7.62 Hz, 2H); 6.35-6.33(d,J=7.62 Hz,2H); MS (EI, 70 eV) 482,18 (M+, 100%), Elemental Analysis: C, 89.24%; H, 4.87%; N, 5.46%.

Antibacterial Activity Measurements

The growth inhibition of the two prepared compounds on the SRB was measured using the serial dilution method. SRB-contaminated water was supplied from well No. 3879 of «Bibiheybatneft» OGPD («Azneft» Production Union, SOCAR). This water was used for the microbial inhibition test. The test was conducted according to NACE TM0194-2014 [6]. The tested water was subjected to growth of about 10,000,000 bacteria cells/ml. The prepared compounds were tested as a biocide for the SRB by doses of 50, 100 and 200 ppm. The system was incubated with a contact time of 6.0 h and 24 h; each system was cultured in SRB specific media (Postgate B) for 30 days at 35–40 °C. The amount of bacterial cells is calculated according to the following formula:

$$N = \frac{10^{n-1}}{V} \qquad (1)$$

where:

N - Amount of bacterial cells in the test water;

10 - Dilution coefficient;

n - Serial number of the dilution in the last glass container in which the growth of the bacteria is recorded;

V - Amount of water taken for test (ml).

Activity of synthesized biocides (Z, %) calculated according to the following formula:

$$Z\ (\%) = 100\ (\lg N_0 - \lg N_b) / \lg N_0 \qquad (2)$$

where -

N_0 - amount of bacteria in absence of biocides;

N_b - amount of bacteria in presence of biocides.

Corrosion Measurements

The anticorrosive properties of the synthesized compounds against H_2S and CO_2 corrosion of St 20 steel were performed by weight loss measurements at room temperature according to ГОСТ 9.506-87 [7]. A model of mineralized formation water

with a density of 1.12 g/cm^3 was used as an aggressive medium. Model water is deoxygenated with an inert gas (nitrogen), and hydrogen sulfide (H_2S) is added to the medium after being saturated with carbon dioxide (CO_2). H_2S gas was obtained as a result of the interaction of Na_2S and HCl in a Kipp apparatus.

Corrosion tests were carried out on plates 50×50×0.3 mm size made from samples of steel St 20 according to ГОСТ-9.905-82 (Methods of corrosion tests) [8]. The tests were carried out for 24 hours, provided that the volume of the medium was at least 20 cm^3 for every 1 (one) cm^2 of the sample area.

The test was repeated three times and the weight loss was their average. The corrosion rate (V) and the inhibition efficiency (Z, %) were calculated using formula 3,4.

$$V = m/S \cdot t \quad (3)$$

$$Z\,(\%) = (V_0 - V) \times 100/V_0 \quad (4)$$

where:

m - average weight loss of three parallel carbon steel plates, gr;

S - total surface area of the specimen, m^2;

t - test time, h;

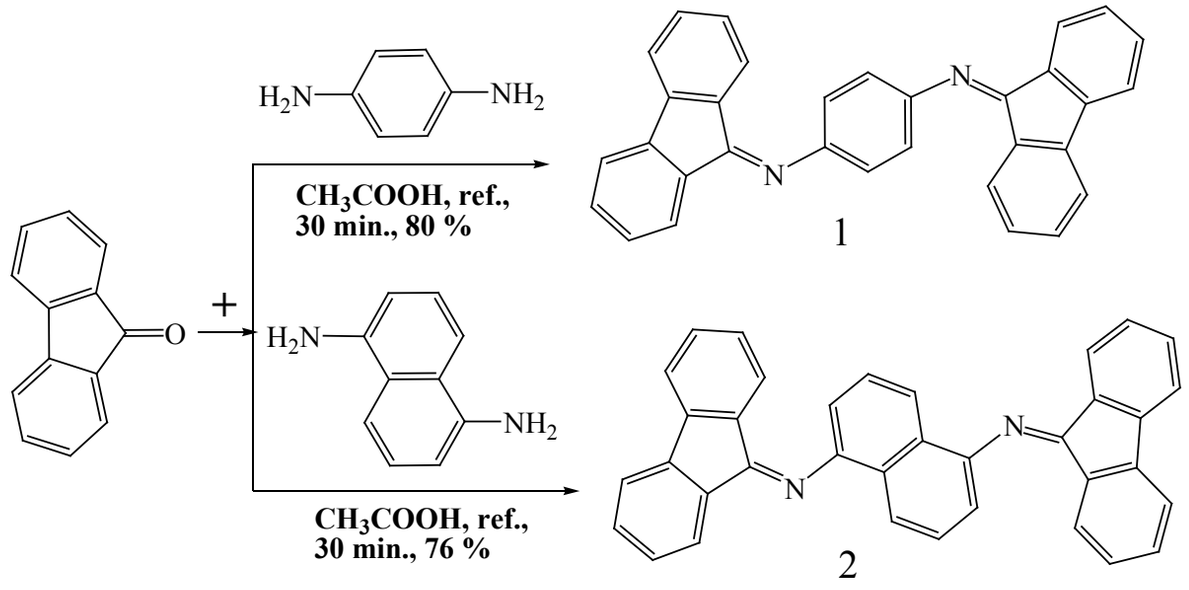
V and V_0 - corrosion rate in presence and absence of inhibitor, respectively.

Results and discussion

Synthesis. In the literature was reported synthetic procedure for compound 1, but proposed method characterized by low yield and complex purification [5]. For synthesis of Schiff bases of N^1,N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine (1) and N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine (2) we introduce new simple and high yield synthetic procedure. Scheme 1 shows synthetic route of compounds 1 and 2.

Reaction of commercial available p-phenylenediamine with 2.4 equivalent 9H-fluoren-9-one in acetic acid at refluxing 30 minutes resulted compound of 1 for 80% yield. The same reaction condition reaction of naphthalene-1,5-diamine with fluoren-9-one N^1,N^5-di(9H-fluoren-9-ylidene) naphthalene-1,5-diamine was obtained for 76% yield. Compounds 1 and 2 characterized by ^{1}H NMR, mass-spectrometric and elemental analysis. Additionally N^1,N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine characterized by Single-crystal X-ray data analyses.

^{1}H MNR spectra. The ^{1}H NMR spectrum of N^1,N^4-di(9H-fluoren-9-ylidene)benzene-1,4-diamine is given in figure 1. The four symmetrical protons present in the central benzene ring designated as '*i*' appeared as a singlet at 7.086 ppm. Since two fluorene-9-ylidene groups in the molecule bonded with nitrogen atoms in the Trans orientation of the benzene ring, there are eight pair of 9H-fluorene protons in the 1H NMR spectrum. Four pair of 9H-fluorene aromatic doublet protons designated as '*a,e,d,h*' appeared in the range 7.92 ppm, 7.60 ppm and 6.97 ppm ppm. Four pair aromatic protons present in the second, third, six and seventh positions in the 9H-fluorene rings designated as '*c,b,f,g*' appeared as a triplets with chemical shifts at 7.45 ppm, 7.33 ppm and 6.95 ppm. The protons of g and h mixed



Scheme 1. Synthetic scheme of compounds 1 and 2

and gives multiplet signals. The peaks at 7.24 ppm are to the deuterio chloroform($CDCl_3$).

The ^1H NMR spectrum of N^1, N^5-di(9H-fluoren-9-ylidene)naphthalene-1,5-diamine is given in figure 2. 400 MHz^1H NMR spectrum fully characterized structure of this compound. Thus, two aromatic protons present in the second and sixth positions in the naphthalene ring and ortho to nitrogen atoms designated as '*k*' appeared as a doublet at 6.33–6.35 ppm. The protons present at third and seventh positions in the naphthalene ring and metha to nitrogen atoms designated as '*j*' appeared as a triplet at 7.27–7.31 ppm. The protons present in the naphthalene ring para to the nitrogen atoms designated as '*i*' appeared farthest downfield signal as a doublet at 8.15–8.17 ppm. The ^1H NMR spectrum of N^1, N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine molecule eight different signals of sixteen 9H-fluorenone rings protons are clearly visible. The two protons present on the 9H-fluorene rings designated as '*a*' appeared as a doublet signals in the range 7.71-7.73 ppm. The six protons present on the two 9H-fluorene rings designated as '*e, d, h*' gives three different doublet signals

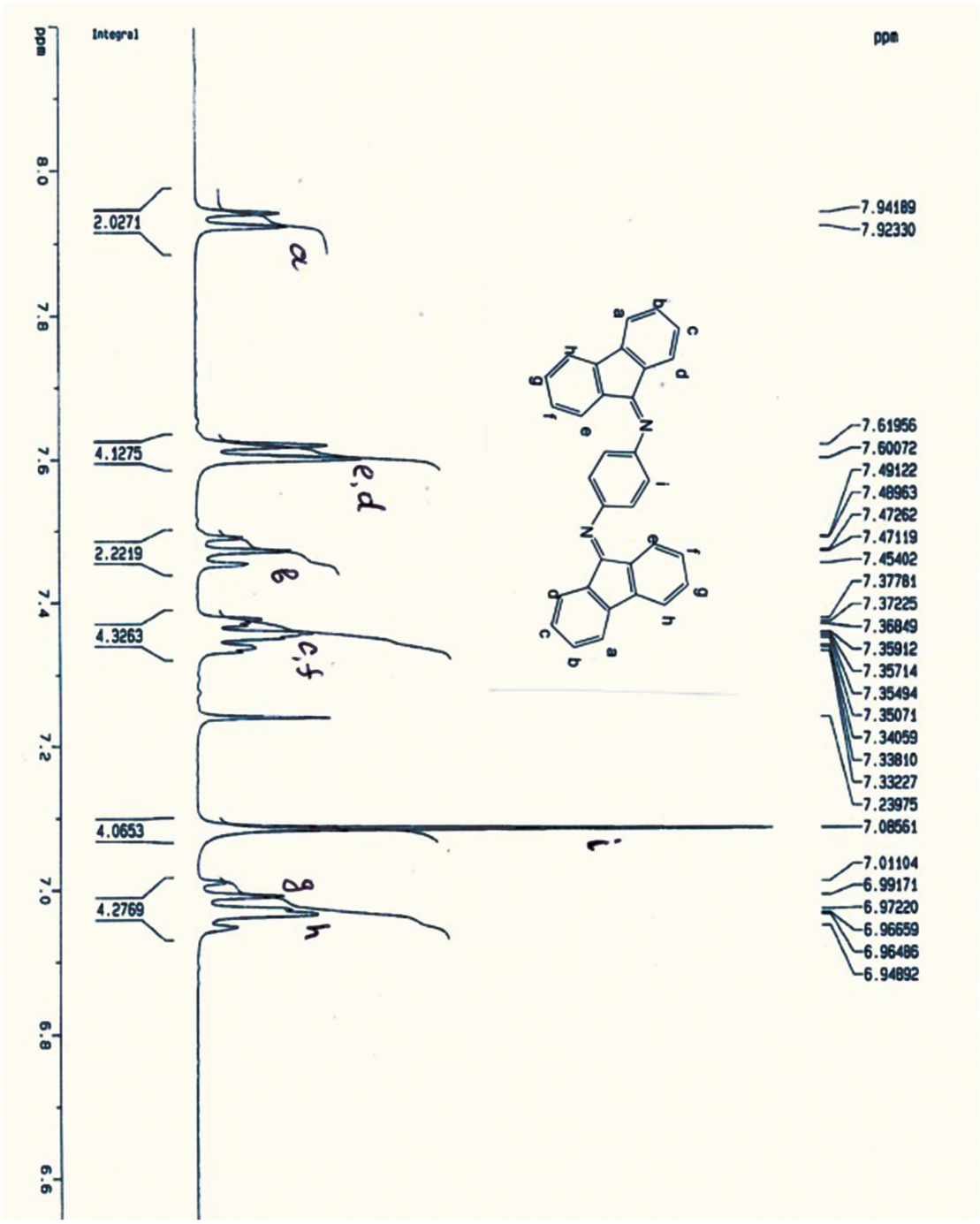


Fig.1. ^1H NMR spectrum of N^1,N^4-di(9H-fluoren-9-ylidene)benzene-1,4-diamine

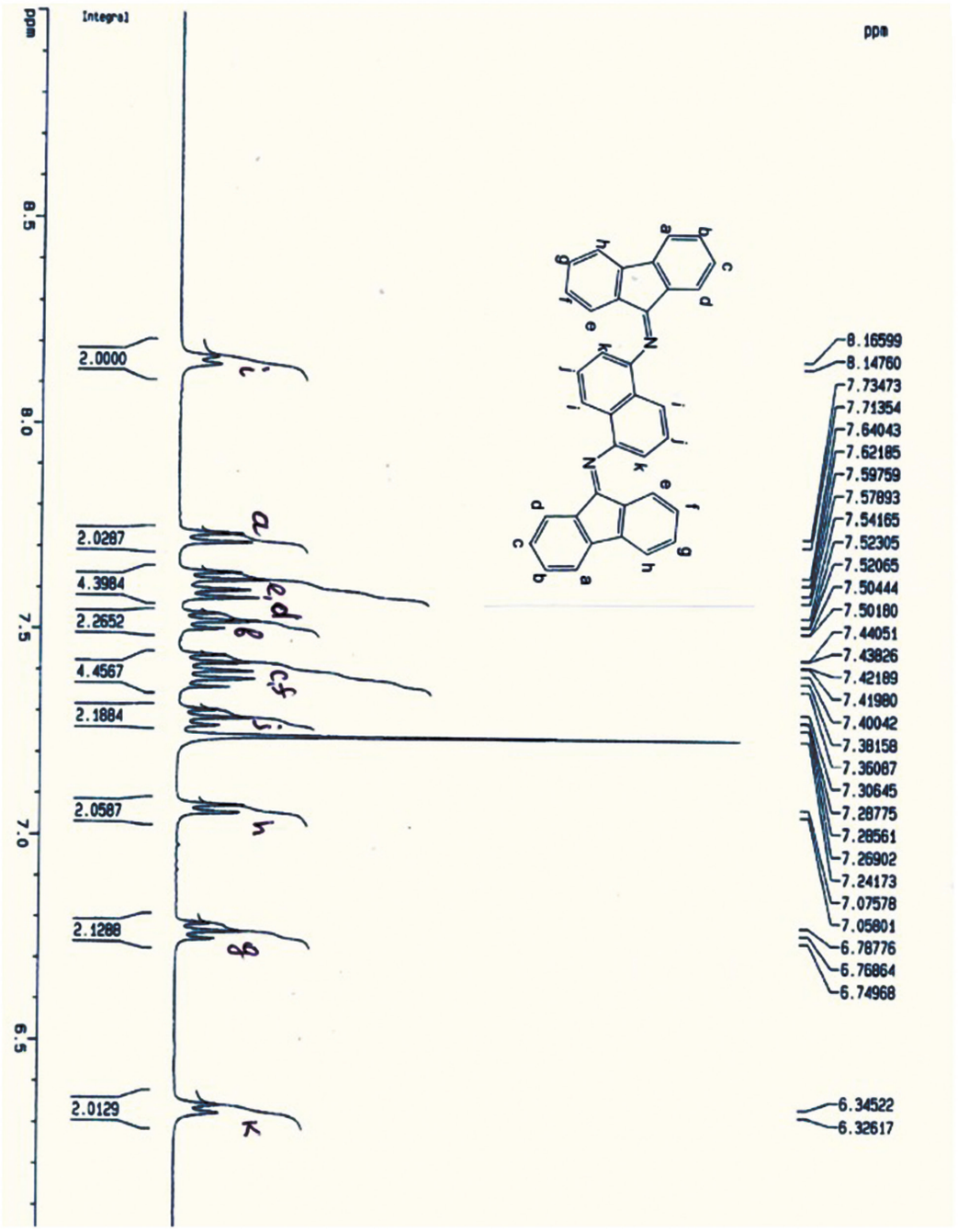


Fig.2. ^{1}H NMR spectrum of N^{1},N^{5}-di(9H-fluoren-9-ylidene)naphthalene-1,5-diamine

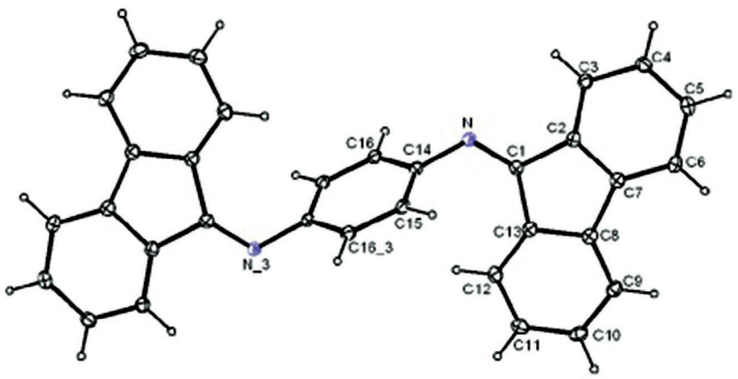


Fig.3. The molecular structure of N^{1},N^{4}-di(9H-fluoren-9-ylidene) benzene-1,4-diamine, thermal ellipsoids drawn at the 50% probability level

Table 1

Crystal data of 1

Empirical formula		$C_{32}H_{20}N_2$	
Formula weight		432.50	
Temperature		100(2) K	
Wavelength		0.71073 Å	
Crystal system		Monoclinic	
Space group		P2(1)/n	
Unit cell dimension	a = 5.0791(2) Å	α= 90°.	
	b = 14.4635(5) Å	β= 96.192(2)°.	
	c = 14.6089(5) Å	γ = 90°.	
Volume		1066.93(7) Å^3	
Z		4	
Density (calculated)		1.346 Mg/m^3	
Absorption coefficient		0.079 mm^{-1}	
F(000)		452	
Crystal size		0.14×0.12×0.08 mm^3	
Theta range for data collection		1.99 to 25.03°.	
Index range		-6<=h<=6, 0<=k<=17, 0<=l<=17	
Reflections collected		1877	
Independent reflections		1877 [R(int) = 0.0353]	
Completeness to theta = 25.03°		100.0%	
Absorption correction		None	
Refinement method			
Full-matrix least-squares on		F^2	
Data / restraints / parameters		1877/2/163	
Goodness-of-fit on F^2		1.073Final	
R indices [I>2sigma(I)]		R1=0.0308, wR2=0.0763	
R indices (all data)		R1=0.0406, wR2=0.0804	
Extinction coefficient		0.013(2)	
Largest diff. peak and hole		0.212 and -0.138 e.Å^{-3}	

with chemical shifts at 7.62-7.64 ppm, 7.58-7.60 ppm, 7.06-7.08 ppm respectively. Eight aromatic protons present 9H-fluorene rings designated as '*b,c,f,g*' appeared as a four triplets with chemical shifts at 7.50-7.54 ppm, 7.40-7.44 ppm, 7.36-7.40 ppm and 6.75-6.79 ppm respectively. The peaks at 7.24 ppm are to the deuterio chloroform($CDCl_3$).

Crystal structure. In the range of ~0.6–0.5 sm long and ~0.10-0.06 mm wide needle like bright orange single-crystals of N^1,N^4-di(9H-fluoren-9-ylidene)benzene-1,4-diamine (1) were obtained by recrystallization from $CHCl_3$-ethyl ether solution. Single-crystal X-ray analyses of (I) revealed that a Trans orientation of the fluoren-9-ylidene groups attached to the central ring (fig.1).

The crystal data for compound 1 are listed in Table 1 and the selected bond lengths and angles are listed in table 2.

Anti-bacterial performance. The evaluation of biocide activity of the synthesized 1 and 2 Schiff bases against planktonic bacteria was tested on their 50, 100, və 200 mg/dm^3 concentrated solutions. For this purpose 5 sterile serum vials with 200 mL nominal capacity and maintaining an inert gas atmosphere (e.g., nitrogen or argon) were prepared. Three of these vials were filled with 1, 2 and 4 ml of the studied 1 and 2 compounds solution in 10 g/l ethanol consistently by using a sterile syringe. To evaluate the influence of ethanol the fourth vial was filled with 4 ml of ehtanol, the fifth vial was filled with 4ml of distilled water for comparison. Produced water supplied from the well No. 3879 of «Bibiheybatneft» OGPD («Azneft» Production Union, SOCAR) was added to all the vials to the measuring line. To prevent oxigen contact special screens (septium seals) were used. The vials were sealed with stoppers and shaked up well. To evaluate the exposure time of the prepared biocides 1ml of this well-mixed broth was withdrawn from each vial after 6 and 24 h and cultured in SRB specific media within 30 days by serial dilution method. Then the amount of survived bacteria was determined. The results of laboratory studies for the compounds of 1 and 2 were shown in table 3.

As seen from the carried studies (tabl.1) no biocide effect of ethanol was determined. In a control sample of produced water in absence of inhibitor the rapid growth of bacteria in corresponding growth mediums was observed and the amount of SRB was 107 cell/ml. The addition of N^1,N^4-di(9H-fluoren-9-ylidene) benzene-1,4-diamine (1) reagent in 50 mg/l concentration to the system showed 28.6% of inhibition efficiency in first 6 h and 57.1% in 24 h. When the concentration of this reagent is increased to 100 mg/l and 200 mg/l the inhibition efficiency was 85.7% and 100%, respectively in 24 hours for SRB bacteria.

The addition of N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine (2) reagent in 50 mg/l concentration to the system showed 42.9% of inhibition efficiency in the first 6h and 85.7% in 24h. When the concentration of this reagent is increased to 100 mg/l the inhibition efficiency was 100%.

It should be noted that the obtained results show that the biocide properties of N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine (2) reagent is higher than that of N^1,N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine (1) reagent. That is, 100% killing of SRB bacteria was in 200 mg/l of concentration for the first compound, whereas it was obtained in 100 mg/l of concentration for the second compound. It

Table 2

Bond lengths [Å] and angles [°] for 1

C(1)-N	1.2824(15)	C(5)-C(4)-C(3)	120.50(12)
C(1)-C(2)	1.4796(17)	C(5)-C(4)-H(4)	119.7
C(1)-C(13)	1.4979(17)	C(3)-C(4)-H(4)	119.7
C(2)-C(3)	1.3830(18)	C(4)-C(5)-C(6)	121.52(12)
C(2)-C(7)	1.4004(17)	C(4)-C(5)-H(5)	119.2
C(3)-C(4)	1.3891(18)	C(6)-C(5)-H(5)	119.2
C(3)-H(3)	0.9300	C(7)-C(6)-C(5)	118.09(12)
C(4)-C(5)	1.3870(18)	C(7)-C(6)-H(6)	121.0
C(4)-H(4)	0.9300	C(5)-C(6)-H(6)	121.0
C(5)-C(6)	1.3942(19)	C(6)-C(7)-C(2)	120.13(12)
C(5)-H(5)	0.9300	C(6)-C(7)-C(8)	131.95(11)
C(6)-C(7)	1.3860(18)	C(2)-C(7)-C(8)	107.91(11)
C(6)-H(6)	0.9300	C(9)-C(8)-C(13)	120.67(12)
C(7)-C(8)	1.4743(18)	C(9)-C(8)-C(7)	130.17(12)
C(8)-C(9)	1.3856(18)	C(13)-C(8)-C(7)	109.15(11)
C(8)-C(13)	1.4079(17)	C(8)-C(9)-C(10)	118.63(12)
C(9)-C(10)	1.3906(19)	C(8)-C(9)-H(9)	120.7
C(9)-H(9)	0.9300	C(10)-C(9)-H(9)	120.7
C(10)-C(11)	1.3882(19)	C(11)-C(10)-C(9)	120.93(12)
C(10)-H(10)	0.9300	C(11)-C(10)-H(10)	119.5
C(11)-C(12)	1.3932(18)	C(9)-C(10)-H(10)	119.5
C(11)-H(11)	0.9300	C(10)-C(11)-C(12)	120.72(12)
C(12)-C(13)	1.3892(18)	C(10)-C(11)-H(11)	119.6
C(12)-H(12)	0.9300	C(12)-C(11)-H(11)	119.6
C(14)-C(16)	1.3912(17)	C(13)-C(12)-C(11)	118.74(12)
C(14)-C(15)	1.3941(18)	C(13)-C(12)-H(12)	120.6
C(14)-N	1.4130(15)	C(11)-C(12)-H(12)	120.6
C(15)-C(16)#1	1.3815(18)	C(12)-C(13)-C(8)	120.23(11)
C(15)-H(15)	0.963(11)	C(12)-C(13)-C(1)	131.69(11)
C(16)-C(15)#1	1.3815(18)	C(8)-C(13)-C(1)	107.97(11)
C(16)-H(16)	0.977(11)	C(16)-C(14)-C(15)	119.11(12)
N-C(1)-C(2)	121.43(11)	C(16)-C(14)-N	120.12(11)
N-C(1)-C(13)	133.26(12)	C(15)-C(14)-N	120.54(11)
C(2)-C(1)-C(13)	105.30(10)	C(16)#1-C(15)-C(14)	120.83(12)
C(3)-C(2)-C(7)	121.60(11)	C(16)#1-C(15)-H(15)	120.7(8)
C(3)-C(2)-C(1)	128.65(11)	C(14)-C(15)-H(15)	118.5(8)
C(7)-C(2)-C(1)	109.61(11)	C(15)#1-C(16)-C(14)	120.03(12)
C(2)-C(3)-C(4)	118.15(12)	C(15)#1-C(16)-H(16)	121.2(8)
C(2)-C(3)-H(3)	120.9	C(14)-C(16)-H(16)	118.7(8)
C(4)-C(3)-H(3)	120.9	C(1)-N-C(14)	120.65(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+2

Table 3

The amount of bacteria in different concentrations of N^1, N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine (1) and N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine (2) reagents in formation water and their inhibition efficiency (Z, %)

$C_{ing.}$ mg/l \ Biocides	Compound 1		Compound 2	
	cell/ml	Z, %	cell/ml	Z, %
6 (six) hours				
0	10^7	-	10^7	-
0 (Ethanol)	10^7	-	10^7	-
50	10^5	28.6	10^4	42.9
100	10^4	42.9	10^3	57.1
200	10^3	57.1	10^2	71.4
24 (tventy four) hours				
50	10^2	71.4	10^1	85.7
100	10^1	85.7	-	100
200	-	100	-	100

Table 4

Corrosion effects (Z,%) of N^1,N^4-di(9H-fluoren-9-ylidene)benzene-1,4-diamine (1) and N^1,N^5-di(9H-fluoren-9-ylidene)naphthalene-1,5-diamine(2) reagents in the formation water model with different H_2S concentrations.

C_{H_2S}, mg/l / $C_{ing.}$, mg/l	250 mg/l		500 mg/l	
	K, g/m²h	Z, %	K, g/m²h	Z, %
N^1,N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine				
0	0.8576	-	1.3387	-
50	0.4401	48.7	0.4632	65.4
100	0.0832	90.3	0.1178	91.2
200	0.0292	96.6	0.0211	98.4
N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine				
50	0.5368	37.4	0.5850	56.3
100	0.1861	78.3	0.1981	85.2
200	0.0798	90.7	0.0905	93.2

can be explained that the biocide properties of the naphthalene nucleus in N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine (2) compound is higher that the biocide properties of the benzene nucleus in N^1,N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine (1) compound.

Anti-corrosive inhibition performance. Anti-corrosive effect of the sythesised compounds was tested and determined on their 50, 100, və 200 mg/dm³ concentrated solutions. The corrosion rate was evaluated for the weight loss of the samples for three parallel tests. Corrosion effects (Z, %) of the compounds 1 and 2 of the model produced water in 250 mg/l and 500 mg/l concentrations of H_2S on St 20 steel samples were shown in the table 4.

As seen from the table, corrosion effects of 100 mg/l of N^1,N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine and N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine reagents in the model produced water with 250 mg/l concentration of H_2S were 90.3% and 78.3%, respectively. When the concentration of H_2S was increased to 500 mg/l corrosion effects were 91.2% and 85.2% respectively. 200 mg/l concentration of both compounds in both concentrations of H_2S (250 mg/l and 500 mg/l) show high inhibition performance (>90%) against H_2S and CO_2corrosion in carbon steel.

Conclusions:

Schiff bases of N^1,N^4-di (9H-fluoren-9-ylidene) benzene-1,4-diamine (1) and N^1,N^5-di (9H-fluoren-9-ylidene) naphthalene-1,5-diamine(2) were synthesized by new synthetic methods. The structures of the synthesized compounds were confirmed by elemental, ^{1}H NMR, mass spectroscopic analyses. In additional N^1,N^4-di(9H-fluoren-9-ylidene)benzene-1,4-diamine (1) were characterized by Single-crystal X-ray diffraction analyses. The prepared compounds were evaluated as antibacterial agents against sulfate-reducing bacteria using the serial dilution method, which in 100 ppm doses N^1,N^5-di (9H-fluoren-9-ylidene)naphthalene-1,5-diamine killed all the bacteria within 24 h (as contact time), but N^1,N^4-di(9H-fluoren-9-ylidene)benzene-1,4-diamine shoes 85.7% efficiency at the same condition. The compounds were tested as corrosion inhibitors against the corrosion of carbon steel in a model of mineralized produced water containing hydrogen sulfide (H_2S) and carbon dioxide (CO_2) using weight loss methods. The results revealed that these compounds have significant high (90.7- 98.4%) inhibition efficiency on the corrosion of carbon steel at the 200 ppm concentration.

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Синтез, ингибиторно-биоцидная активность N, N-di (9h-флуоренилиден-9) бензол-1,4-диамина и N, N-di (9h-флуоренилиден-9) нафталин-1,5-диамина

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Реферат

Основания Шиффа N^1, N^4-ди (9H-флуорен-9-илиден) бензол-1,4-диамина (1) и N^1, N^5-ди (9H-флуорен-9-илиден) нафталин-1,5-диамин (2) синтезированы по новой простой и высокопроизводительной методике синтеза. Структуры синтезированных соединений 1 и 2 подтверждены элементным, ^{1}H ЯМР, масс-спектроскопическим и рентгеноструктурным анализами. Полученные соединения были оценены как противомикробные средства против сульфатредуцирующих бактерий с использованием метода серийных разведений, который показал хорошее биоцидное действие. Синтезированные соединения также были испытаны в качестве ингибиторов коррозии углеродистой стали на модели минерализованной пластовой воды, содержащей сероводород (H_2S) и диоксид углерода (CO_2), с использованием гравиметрического метода. Результаты показали, что эти соединения обладают значительным ингибирующим эффектом на коррозию углеродистой стали.

Ключевые слова: основания Шиффа; ЯМР анализ; ингибирование коррозии; микробиологическая коррозия; антибактериальная активность.

N, N-di (9h-fluoren-9-iliden) benzol-1,4-diamin və N, N-di (9h-fluoren-9-iliden) 1,5-naftalin-diaminin sinthezi və inhibitor-biosid xassəsi

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Xülasə

Yeni sadə və yüksək çıxımlı sintez metodu ilə N^1, N^4-di (9H-fluoren-9-iliden) benzol-1,4-diamin (1) və N^1, N^5-di (9H-fluoren-9-iliden) nafalin-1,5-diamin (2) Şiff əsasları sintez edilmişdir. Sintez edilmiş 1 və 2 birləşmələrinin strukturları element analizi, ^{1}H NMR, kütlə spektroskopiyası və rentgenquruluş analizləri ilə təsdiqlənmişdir. Ardıcıl durulaşma metodu ilə alınan birləşmələrin, sulfatreduksiyaedici bakteriyalara qarşı antibakterial xassələri öyrənilmiş və müəyyən olunmuşdur ki, bu birləşmələr yüksək biosid xassəsinə malikdir. Eyni zamanda sintez olunmuş birləşmələr qravimetrik metoddan istifadə edərək hidrogen sulfid (H_2S) və karbon dioksid (CO_2) olan minerallaşdırılmış lay suyu modelində karbonlu poladın korroziyasına qarşı inhibitor kimi sınaqdan keçirilmişdir. Nəticələrdən müəyyən olunmuşdur ki, bu birləşmələr karbonlu poladın korroziyasında yüksək mühafizə effektinə malik olur.

Açar sözlər: Shiff əsasları; NMR analizi; korroziyanın inhibirə olunması; mikrobioloji korroziya; antibakterial aktivlik.