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Synthesis, characterization and antibacterial activity of some novel azo-azoimine dyes of 6-bromo-2-naphthol

Himani N. Chopde[1], Jyotsna S. Meshram*[1], Ramakanth Pagadala[1], Arvind J. Mungole[2]

[1]Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur-440 033, Maharashtra, India

[2]Department of Botany, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur-440 033, Maharashtra, India

Corres.author:drjsmeshram@rediffmail.com; himanichopade@gmail.com

Abstract: [1-((aryl benzylideneamino)(aryl phenyl) methyl)-6-bromo-3-(4-nitrophenyl) diazenyl) naphthalene-2-ol] (**2a-2j**) were synthesized by diazotization of Betti's bases [1-((aryl benzylideneamino) (aryl phenyl)methyl)-6-bromo naphthalen-2-ol] (**1a-1j**). These novel bases were prepared by one-pot Betti's condensation reaction using different aromatic aldehydes in presence of ammonia. The structure of all the synthesized compounds were elucidated by elemental analysis and different spectroscopic techniques (IR, ^{1}H- NMR and Mass spectroscopy). The newly synthesized compounds (IIa-IIj) were screened for their potential antibacterial activities against nine different bacterial species and the results revealed significant activity against the test microorganisms in vitro.
Keywords: Betti's condensation reaction, azo dyes, antimicrobial activities.

Introduction

Study of chemistry of the Betti's bases started at the beginning of the 20th century, when Betti[(1)], a pioneer of asymmetric synthesis, reported that condensation of 2-naphthol, benzaldehyde and ammonia gave a product with the ratio of 1:2:1 respectively. The product was identified as 1, 3-diphenyl-2, 3-dihydro-1H-naphth(1, 2-e)(1, 3)oxazine (**Figure Ia**). Later, on the basis of its reaction in benzene with ethereal ferric chloride, which resulted in an intense reddish-violet color, the isomeric Schiff base structure, N-benzylidine-l-(a-aminobenzyl)-2-naphthol (**Figure Ib**), was proposed. [(2)]

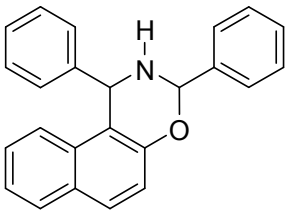


Figure Ia

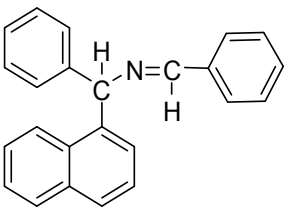


Figure Ib

Preparation of the substituted Betti's base derivatives via the modified Mannich reaction had subsequently become an important area in synthetic chemistry because of C–C bond formation under mild experimental conditions. In later years, attention has been paid to the Betti's reaction, and a similar reaction can be performed by either using other naphthols[3] or quinolinols[4- 5] or by replacing ammonia with alkyl amines.[6–9] In addition, a variety of racemic structures related to the Betti's bases have been prepared recently by addition of naphthols to the preformed imminium salts.[10] In recent years, the effort were done to synthesized the Betti's base derivatives in organic solvents such as EtOH, MeOH, and Et_2O at room temperature or thermally under solventless condition. The literature also reveals that such compounds are gaining interest of chemists who are working in the field of asymmetric synthesis because of utility in preparation of chiral inductors or chiral precursor. Betti's base derivatives have also provided convenient access to many useful synthetic building blocks via the amino and phenolic hydroxy functional groups.[11-12] Optically active Betti's bases have been used as ligands for complexation of dialkyl zinc for enantioselective addition to aryl aldehydes. These ligands showed highly efficient asymmetric induction to give the corresponding alcohols up to 99% yields.[13–15] Moreover, condensation of Betti's base derivatives with aldehydes leads to the formation of the corresponding 1, 3- oxazines with varied biological properties. [16-17]

In the field of azo dyes, phenolic compounds play a major role for synthesizing most of the commercial dyes. Most of the dyes are marketed in the form of azo disperse, azo-vat, azo-acid dyes, *etc*. Most of these commercially available dyes have the naphthols bearing hydroxyl groups as an auxochrome group. Azo compounds have received much attention due to their versatile use in many practical applications such as coloring fiber, photoelectronic applications, printing systems, optical storage technology and in various analytical techniques.[18] The azo compounds also find their wide applications as a polymer additive.[19] The uses of dyes in the various industrial field shows that azo compounds are the largest class of industrial synthesized organic dyes.

Azoimine dyes are used as substrates to prepare a large number of industrial and biologically active compounds via ring closure, cycloaddition and condensation reactions between primary amines and aldehydes.[20] Moreover, azoimine dyes are also known to have biological activities such as antimicrobial[21-24], antifungal[25], antitumour[26-28] and as herbicides.[29] In industries, they have a wide range of application such as it can be used as dyes and pigments with luminescent properties.[30] Azoimine dyes are used as ligand for complexations of metal ions giving the complex compounds of rich physical, chemical and biological properties.[31-32] Namkung and Fletcher[33] reported the use of the azoimine dyes for therapeutic purposes and to exert anti-tumor activity.

Both Schiff bases and azo compounds are important structures in the medicinal and pharmaceutical fields [29] and it has been suggested that the azoimine linkage might be responsible for the biological activities displayed by these Schiff bases. In light of the interesting variety of biological activities seen in compounds containing azo, methoxy groups and azoimine linkages, we thought it worthwhile to examine the effect of having all of above functionalities present simultaneously in one structure. Based on this notion we thus decided to synthesize new azo-azoimine dyes and to test their biological activities against different bacteria. However, very few investigations have been published with respect to synthesis of azo-azoimine dyes from 2-naphthol via Betti's condensation reaction and their further derivatives. In the present communication, we report the synthesis of different Betti's bases (**1a-1j**) via one-pot Betti's condensation reaction of 6-bromo-2-naphthol with different aromatic aldehydes in presence of ammonia as a coupling component (**Scheme 1**). These synthesized compounds were diazotized (**Scheme 2**) to obtain azo-azoimine dyes (**2a-2j**). Structure of all the synthesized compounds was confirmed using elemental analysis and different spectral techniques (IR, Mass and ^{1}H NMR). The biological activities of these compounds against nine different bacterial species have been reported.

Experimental

General: All the chemicals and solvents were obtained from E-Merck, India (AR grade) and were used without further purification. Melting points were taken in an open capillary tube. IR spectra were recorded on a Shimadzu Dr-8031 instrument. Elemental analyses were carried out using a Perkin-Elmer, CHN elemental analyzer model 2400. ^{1}H NMR spectra of the synthesized compounds were recorded on a Bruker-Avance (300 MHz), Varian-Gemini (200 MHz) spectrophotometer using $CDCl_3$ solvent and TMS as the internal standard. EI-MS spectra were determined on a LCQ ion trap mass spectrometer (Thermo Fisher, San Jose, CA, USA), equipped with an EI source.

General procedure for synthesis of 1-((arylbenzylideneamino)(arylphenyl) methyl)-6-bromo-naphthalen-2-ol (1a-1j)

To the mixture of 6-bromo-2-naphthol (1 mol) in ethanol, aldehydes (2 mols) were added. This mixture was slightly warmed, and the solution of ammonia in ethanol was added in slightly excess amount. This

reaction mixture was kept for two hours in stopper conical flask at room temperature. Compounds **(1a-1j)** were obtained after 15 hours standing of the reaction mixtures. These compounds (**1a-1j**) were recrystallized in absolute alcohol.

1-((benzylideneamino)(phenyl)methyl)-6-bromonapthalen-2-ol (1a): Yield: 75 %; m. p.: 100 ^{o}C, IR (KBr): 1655 cm^{-1} (N=C); 3159-3319 cm^{-1} (OH); ^{1}H NMR: δ =5.60 (s, 1H, aliphatic-CH); 6.90 (d, 2H, Ar-CH); 7.20 (d, 2H, Ar-CH); 7.35 (d, 2H, Ar-CH); 7.40(d, 2H, Ar-CH); 7.45 (d, 2H, Ar-CH); 7.52(s, 1H, Ar-CH); 7.80(m, 4H, Ar-CH); 8.10(s, 1H, Ar-CH); 9.60(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{18}NBrO$: C, 69.24; H, 4.36; N, 3.36; Found: C, 69.00; H, 4.20; N, 3.25 ; Mass spectra, m/z = 415.06 (100%).

6-bromo-1-((2-hydroxybenzylideneamino)(2-hydroxyphenyl)methyl)napthalen-2-ol (1b): Yield: 80 %; m. p.: 110 ^{o}C, IR (KBr): 1645 cm^{-1} (N=C); 2973-3530 cm^{-1} (OH); ^{1}H NMR: δ =5.70 (s, 1H, aliphatic-CH); 6.80-7.00 (m, 7H, Ar-CH); 7.10-7.50 (t, 3H, Ar-CH); 7.65 (s, 1H, Ar-CH); 7.90(s, 1H, Ar-CH); 8.12 (s, 1H, Ar-CH); 8.70(s, 1H, N=CH); 9.60(d, 2H, Ar-OH); 11.20(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{18}NBrO_3$: C, 64.30; H, 4.05; N, 3.12; Found: C, 64.20; H, 4.00; N, 3.00 ; Mass spectra, m/z = 447.00 (100%).

6-bromo-1-((2-nitrobenzylideneamino)(2-nitrophenyl)methyl)napthalen-2-ol (1c): Yield: 85 %; m. p.: 95 ^{o}C, IR (KBr): 1600 cm^{-1} (N=C); 3100-3450 cm^{-1} (OH); ^{1}H NMR: δ =5.60 (s, 1H, aliphatic-CH); 5.90 (s, 1H, Ar-CH); 7.40-7.95 (m, 8H, Ar-CH); 7.98 (m, 4H, Ar-CH); 8.00-8.10(d, 2H, Ar-CH); 8.65(s, 1H, N=CH); 9.65(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{16}N_3BrO_5$: C, 56.93; H, 3.19; N, 8.30; Found: C, 56.80; H, 3.00; N, 8.10 ; Mass spectra, m/z = 505.00 (100%).

6-bromo-1-((3-nitrobenzylideneamino)(3-nitrophenyl)methyl)napthalen-2-ol (1d): Yield: 85 %; m. p.: 105 ^{o}C, IR (KBr): 1635 cm^{-1} (N=C), 3140-3540 cm^{-1} (OH); ^{1}H NMR: δ =5.50 (s, 1H, aliphatic-CH); 6.90 (s, 1H, Ar-CH); 7.50-8.10 (m, 6H, Ar-CH); 7.95 (s, 1H, Ar-CH); 8.12-8.22(m, 4H, Ar-CH); 8.50(s, 1H, Ar-CH); 8.65(s, 1H, N=CH); 9.70(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{16}N_3BrO_5$: C, 56.93; H, 3.19; N, 8.30; Found: C, 56.70; H, 2.90; N, 8.20 ; Mass spectra, m/z = 504.10 (100%).

6-bromo-1-(furan-2-yl)(furan-2-ylmethyleneamino)methyl)napthalen-2-ol (1e): Yield: 75 %; m. p.: 115 ^{o}C, IR (KBr): 1650 cm^{-1} (N=C), 3230-3440 cm^{-1} (OH); ^{1}H NMR: δ =4.30 (s, 1H, aliphatic-CH); 6.08 (s, 1H, Ar-CH); 6.40(s, 1H, Ar-CH); 6.50 (s, 1H, Ar-CH); 6.90(s, 1H, Ar-CH); 6.95(s, 1H, Ar-CH); 7.50(s, 1H, N=CH); 7.65-7.70(d, 2H, Ar-CH); 7.75(s, 1H, Ar-CH); 7.90-8.10(d, 2H, Ar-CH); 9.50(s, 1H, Ar-OH); Anal. Calcd. For $C_{20}H_{14}NBrO_3$: C, 60.62; H, 3.56; N, 3.53; Found: C, 60.40; H, 3.30; N, 3.40 ; Mass spectra, m/z = 395.00 (100%).

6-bromo-1-((4-hydroxybenzylideneamino)(4-hydroxyphenyl)methyl)napthalen-2-ol (1f): Yield: 80 %; m. p.: 110 ^{o}C, IR (KBr): 1660 cm^{-1} (N=C); 3340-3570 cm^{-1} (OH); ^{1}H NMR: δ =5.40 (s, 1H, aliphatic-CH); 6.60 (d, 2H, Ar-CH); 6.85-6.90 (t, 3H, Ar-CH); 7.00 (d, 2H, Ar-CH); 7.60-7.80(m, 4H, Ar-CH); 7.90(s, 1H, Ar-CH); 8.10(d, 2H, Ar-CH); 8.75(s, 1H, N=CH); 9.40(d, 2H, Ar-OH); 9.60(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{18}NBrO_3$: C, 64.30; H, 4.05; N, 3.12; Found: C, 64.20; H, 4.00; N, 3.00 ; Mass spectra, m/z = 447.10 (100%).

6-Bromo-1-((4-(dimethylamino)benzylideneamino)(4-(dimethylamino)phenyl)methy -l)naphthalen-2-ol (1g). Yield: 90 %; m. p.: 120 ^{o}C; IR (KBr): 1655 cm^{-1} (N=C); 3500-3570 cm^{-1} (OH); ^{1}H NMR: δ =3.10(s, 6H, $N(CH_3)_2$); 5.70 (s, 1H, aliphatic-CH); 6.60 (d, 2H, Ar-CH); 6.80 (d, 2H, Ar-CH); 6.92 (s, 1H, Ar-CH); 7.00(d, 2H, Ar-CH); 7.50(d, 2H, Ar-CH); 7.60-7.70(d, 2H, Ar-CH); 7.90(s, 1H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.65(s, 1H, N=CH); 9.50(s, 1H, Ar-OH); Anal. Calcd. For $C_{28}H_{28}N_3BrO$: C, 66.93; H, 5.62; N, 8.36; Found: C, 66.80; H, 5.40; N, 8.20 ; Mass spectra, m/z = 501.00 (100%).

6-Bromo-1-((2-Chlorobenzylideneamino)(2-Chlorophenyl)methyl)naphthalen-2-ol (1h). Yield: 85 %; m. p.: 110 ^{o}C; IR (KBr): 1645 cm^{-1} (N=C); 3540-3560 cm^{-1} (OH); ^{1}H NMR: δ = 5.40 (s, 1H, aliphatic-CH); 6.90 (s, 1H, Ar-CH); 7.15-7.22 (t, 3H, Ar-CH); 7.40-7.50 (t, 3H, Ar-CH); 7.60-7.80(m, 4H, Ar-CH); 7.90(s, 1H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.70(s, 1H, N=CH); 9.70(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{16}NBrOCl_2$: C, 59.41; H, 3.32; N, 2.89; Found: C, 59.30; H, 3.10; N, 2.60 ; Mass spectra, m/z = 482.90 (100%).

6-Bromo-1-((3-bromobenzylideneamino)(3-bromophenyl)methyl)naphthalen-2-ol (1i). Yield: 77 %; m. p.: 105 ^{o}C; IR (KBr): 1620 cm^{-1} (N=C), 3150-3580 cm^{-1} (OH); ^{1}H NMR: δ = 5.90 (s, 1H, aliphatic-CH); 6.80 (s, 1H, Ar-CH); 7.15-7.20 (d, 2H, Ar-CH); 7.35-7.40 (t, 3H, Ar-CH); 7.55(s, 1H, Ar-CH); 7.60-7.80(m, 4H, Ar-CH); 7.85(s, 1H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.90(s, 1H, N=CH); 9.70(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{16}NOBr_3$: C, 50.21; H, 2.81; N, 2.44; Found: C, 50.10; H, 2.70; N, 2.20 ; Mass spectra, m/z = 570.00 (100%).

6-Bromo-1-((4-Chlorobenzylideneamino)(4-Chlorophenyl)methyl)naphthalen-2-ol (1j). Yield: 77 %; m. p.: 105 ^{o}C; IR (KBr): 1630 cm^{-1} (N=C), 3160-3590 cm^{-1} (OH); ^{1}H NMR: δ = 5.40 (s, 1H, aliphatic-CH); 6.90 (s, 1H, Ar-CH); 7.15 (d, 2H, Ar-CH); 7.30 (d, 2H, Ar-CH); 7.50(d, 2H, Ar-CH); 7.60-7.75(m, 4H, Ar-CH); 7.90(s, 1H, Ar-CH); 8.00(s, 1H, Ar-CH);

8.75(s, 1H, N=CH); 9.80(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{16}NOBrCl_2$: C, 59.41; H, 3.32; N, 2.89; Found: C, 59.10; H, 3.20; N, 2.50 ; Mass spectra, m/z = 484.20 (100%).

General procedure for synthesis of 1-((arylbenzylideneamino) (arylphenyl) methyl)-6-bromo-3-(4-nitrophenyl) diazenyl) naphthalene-2-ol (2a-2j)

p-Nitroaniline (1 mol) was added in concentrated HCl (5ml, 1:1 ratio) and boiled for 10 minutes. This solution was then cooled to 0-5^{o}C in ice water bath. Aqueous sodium nitrite (1 mol, 10 ml) solution in cold condition was then added to this solution dropwise with vigorous stirring. The temperature of the reaction mixture was kept to 0-5^{o}C for 1 hour to give diazonium chloride solution. Then the resulting diazonium solution was poured dropwise with vigorous stirring to a suspension of compounds (**1a-1j)** in water (10ml, 1 mol) at 0-5^{o}C. The pH of the reaction mixture was maintained at 8 to 9 by simultaneous addition of 10% aqueous sodium hydroxide solution. After complete addition, the coloured azo-azoimine dyes **(2a-2j)** were precipitated. The precipitated product separated upon dilution with water (100ml) was filtered off, washed with water several times, dried and crystallized in absolute ethanol.

1-((Benzylideneamino)(phenyl)methyl)-6-bromo-3-((4-nitrophenyl)diazenyl) naphthalen-2-ol (2a). Yield: 80 %; m. p.: 120 ^{o}C; IR (KBr): 1655 cm^{-1} (N=C), 3159-3319 cm^{-1} (OH), 1433 cm^{-1} (N=N); ^{1}H NMR: δ = 4.20 (s, 1H, aliphatic-CH); 6.00 (s, 1H, Ar-CH); 6.40 (s, 1H, Ar-CH); 6.50 (s, 1H, Ar-CH); 6.90(s, 1H, Ar-CH); 7.40(s, 1H, N=CH); 7.50(s, 1H, Ar-CH); 7.70-7.90(m, 5H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.35(d, 2H, Ar-CH); 8.40(s, 1H, Ar-CH); 10.50(s, 1H, Ar-OH); Anal. Calcd. For $C_{24}H_{16}NOBrCl_2$: C, 59.41; H, 3.32; N, 2.89; Found: C, 59.10; H, 3.20; N, 2.50 ; Mass spectra, m/z = 484.20 (100%).

6-Bromo-1-((2-hydroxybenzylideneamino)(2-hydroxyphenyl)methyl)-3-((4-nitrophenyl) diazenyl) naphthalen-2-ol (2b). Yield: 91 %; m. p.: 155 ^{o}C; IR (KBr): 1645 cm^{-1} (N=C), 2973-3530 cm^{-1} (OH), 1460 cm^{-1} (N=N); ^{1}H NMR: δ = 5.30 (s, 1H, aliphatic-CH); 6.85 (d, 2H, Ar-CH); 7.00-7.10 (m, 4H, Ar-CH); 7.50 (s, 1H, Ar-CH); 67.70(d, 2H, Ar-CH); 7.80-7.90(t, 3H, Ar-CH); 8.00(s, 1H, Ar-CH); 8.10(d, 2H, Ar-CH); 8.30(s, 1H, Ar-CH); 8.60(s, 1H, N=CH); 9.60(s, 1H, Ar-OH); 10.30(s, 1H, Ar-OH); 11.20(s, 1H, Ar-OH); Anal. Calcd. For $C_{30}H_{21}N_4O_5Br$: C, 60.31; H, 3.54; N, 9.38; Found: C, 60.20; H, 3.30; N, 9.10 ; Mass spectra, m/z = 590.00 (100%).

6-Bromo-1-((2-nitrobenzylideneamino)(2-nitrophenyl)methyl)-3-((4-nitrophe- nyl) diazenyl) naphthalen-2-ol (2c). Yield: 95 %; m. p.: 150 ^{o}C, IR (KBr): 1600 cm^{-1} (N=C), 3100-3450 cm^{-1} (OH), 1416 cm^{-1} (N=N); ^{1}H NMR: δ = 5.75 (s, 1H, aliphatic-CH); 7.50-7.90 (m, 5H, Ar-CH); 7.70 (d, 2H, Ar-CH); 7.80-7.90 (m, 4H, Ar-CH); 8.00-8.10(d, 2H, Ar-CH); 8.30(d, 2H, Ar-CH); 8.45(s, 1H, Ar-CH); 8.75(s, 1H, N=CH); 10.20(s, 1H, Ar-OH); Anal. Calcd. For $C_{30}H_{19}N_6O_7Br$: C, 54.98; H, 2.92; N, 12.82; Found: C, 54.70; H, 2.80; N, 12.60 ; Mass spectra, m/z = 654.00 (100%).

6-Bromo-1-((3-nitrobenzylideneamino)(3-nitrophenyl)methyl)-3-((4-nitrophenyl) diazenyl)naphthalen-2-ol (2d). Yield: 90 %; m. p.: 140 ^{o}C; IR (KBr): 1635 cm^{-1} (N=C), 3140-3540 cm^{-1} (OH), 1400 cm^{-1} (N=N); ^{1}H NMR: δ = 5.75 (s, 1H, aliphatic-CH); 7.50-7.90 (m, 5H, Ar-CH); 7.70 (d, 2H, Ar-CH); 7.80-7.90 (m, 4H, Ar-CH); 8.00-8.10(d, 2H, Ar-CH); 8.30(d, 2H, Ar-CH); 8.45(s, 1H, Ar-CH); 8.75(s, 1H, N=CH); 10.20(s, 1H, Ar-OH); Anal. Calcd. for $C_{30}H_{19}N_6O_7Br$: C, 54.96; H, 2.90; N, 12.82; Found: C, 54.90; H, 2.70; N, 12.50. Mass spectra, m/z = 654.00 (100%).

6-Bromo-1-(furan-2-yl(furan-2-ylmethyleneamino)methyl)-3-((4-nitrophenyl) diazenyl)naphthalen-2-ol (2e). Yield: 85 %, m.p.: 130 ^{o}C; IR (KBr): 1650 cm^{-1} (N=C), 3230-3440 cm^{-1} (OH), 1430 cm^{-1} (N=N); ^{1}H NMR: δ = 4.20(s, 1H, aliphatic-CH); 6.00 (s, 1H, Ar-CH); 7.70 (d, 2H, Ar-CH); 7.80-7.90 (m, 4H, Ar-CH); 8.00-8.10(d, 2H, Ar-CH); 8.30(d, 2H, Ar-CH); 8.45(s, 1H, Ar-CH); 8.75(s, 1H, N=CH); 10.20(s, 1H, Ar-OH); Anal. Calcd. for $C_{26}H_{17}O_5N_4Br$: C, 57.24; H, 3.11; N, 10.27; Found: C, 57.19; H, 3.00; N, 10.00. Mass spectra, m/z = 546.00 (100%).

6-Bromo-1-((4-hydroxybenzylideneamino)(4-hydroxyphenyl)methyl)-3-((4-nitro phenyl)diazenyl)naphthalen -2-ol (2f). Yield: 75 %; m. p.: 160 ^{o}C; IR (KBr): 1660 cm^{-1} (N=C), 3340-3570 cm^{-1} (OH), 1445 cm^{-1} (N=N); ^{1}H NMR: δ = 5.20 (s, 1H, aliphatic-CH); 6.60 (d, 2H, Ar-CH); 6.80 (d, 2H, Ar-CH); 7.00 (d, 2H, Ar-CH); 7.70-8.00(m, 6H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.35(d, 2H, Ar-CH); 8.40(s, 1H, Ar-CH); 8.60(s, 1H, N=CH); 9.40(d, 2H, Ar-OH); 10.50(s, 1H, Ar-OH); Anal. Calcd. for $C_{30}H_{21}N_4O_5Br$: C, 60.30; H, 3.50; N, 9.30; Found : C, 60.18; H, 3.49; N, 9.29.Mass spectra, m/z = 596.00 (100%).

6-Bromo-1-((4-(dimethylamino)benzylideneamino)(4-(dimethylamino)phenyl)Meth -yl-3-((4-nitrophenyl) diazenyl) naphthalen-2-ol (2g). Yield: 95 %; m. p.: 125 ^{o}C; IR (KBr): 1655 cm^{-1} (N=C), 3500-3570 cm^{-1} (OH), 1455 cm^{-1} (N=N); ^{1}H NMR: δ = 3.10(s, 6H, $N(CH_3)_2$); 5.10 (s, 1H, aliphatic-CH); 6.70 (d, 2H, Ar-CH); 6.90 (d, 2H, Ar-CH); 7.20 (d, 2H, Ar-CH); 7.50(d, 2H, Ar-CH); 7.70(s, 1H, Ar-CH); 7.80(d, 2H, Ar-CH); 7.90(s, 1H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.30(d, 2H, Ar-CH); 8.40(s, 1H, Ar-CH); 8.60(s, 1H, N=CH); 10.70(s, 1H, Ar-OH); Anal. Calcd. for

$C_{34}H_{31}O_3N_6Br$: C, 61.97; H, 4.85; N, 13.14; Found: C, 60.99; H, 4.78; N, 13.00. Mass spectra, m/z = 650.00 (100%).

6-bromo-1-((2-Chlorobenzylideneamino)(2-Chlorophenyl)methyl)-3-((4-Nitrophen-yl)diazenyl)napthalen-2-ol (2h). Yield: 90 %; m. p.: 125 ^oC; IR (KBr): 1645 cm^{-1} (N=C); 3540-3560 cm^{-1} (OH); 1465 cm^{-1} (N=N); ^1H NMR: δ = 5.70 (s, 1H, aliphatic-CH); 7.20-7.25 (t, 3H, Ar-CH); 7.40-7.50 (t, 3H, Ar-CH); 7.60-7.90 (m, 6H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.30(d, 2H, Ar-CH); 8.60(s, 1H, Ar-CH); 8.90(s, 1H, N=CH); 10.50(s, 1H, Ar-OH); Anal. Calcd. for $C_{30}H_{19}O_3N_4BrCl_2$: C, 56.81; H, 3.02; N, 8.83; Found: C, 56.60; H, 3.00; N, 8.50. Mass spectra, m/z = 633.70 (100%).

6-bromo-1-((3-bromobenzylideneamino)(3-bromophenyl)methyl)-3-((4-nitrophe-nyl) diazenyl)naphthalen-2-ol (2i). Yield: 87 %; m. p.: 120 ^oC; IR (KBr): 1620 cm^{-1} (N=C), 3150-3580 cm^{-1} (OH), 1415 cm^{-1} (N=N); ^1H NMR: δ = 5.20 (s, 1H, aliphatic-CH); 7.20-7.30 (t, 3H, Ar-CH); 7.35-7.40 (t, 3H, Ar-CH); 7.55 (s, 1H, Ar-CH); 7.70-7.85(m, 5H, Ar-CH); 7.90(s, 1H, Ar-CH); 8.20(s, 1H, Ar-CH); 8.30(d, 2H, Ar-CH); 8.50(s, 1H, Ar-CH); 8.70(s, 1H, N=CH); 10.90(s, 1H, Ar-OH); Anal. Calcd. for $C_{30}H_{19}O_3N_4Br_3$: C, 49.79; H, 2.62; N, 7.74; Found: C, 49.01; H, 2.59; N, 7.70. Mass spectra, m/z = 721.00(100%).

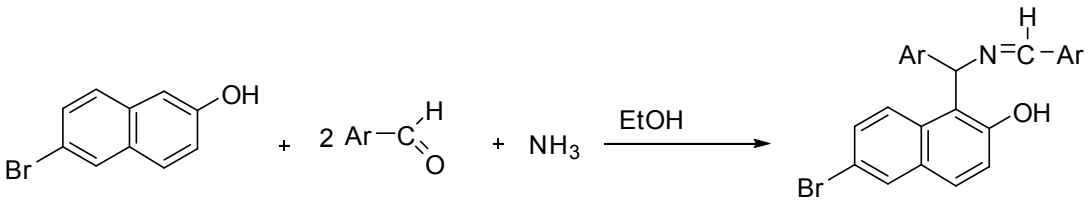
6-Bromo-1-((4-chlorobenzylideneamino)(4-chlorophenyl)methyl)-3-((4-nitro phenyl) diazenyl) naphthalen-2-ol (2j). Yield: 80 %; m. p.: 115 ^oC; IR (KBr): 1640 cm^{-1} (N=C), 3550-3580 cm^{-1}(OH), 1465 cm^{-1} (N=N); ^1H NMR: δ = 5.50 (s, 1H, aliphatic-CH); 7.10 (d, 2H, Ar-CH); 7.35 (d, 2H, Ar-CH); 7.50 (d, 2H, Ar-CH); 7.70-7.90(m, 6H, Ar-CH); 8.10(s, 1H, Ar-CH); 8.20(d, 2H, Ar-CH); 8.50(s, 1H, Ar-CH); 8.65(s, 1H, N=CH); 9.90(s, 1H, Ar-OH); Anal. Calcd. for $C_{30}H_{19}O_3N_4Cl_2Br$: C, 56.78; H, 2.99, N, 8.83; Found: C, 56.69; H, 2.89; N, 8.80. Mass spectra, m/z = 634.00(100%).

Antimicrobial activity of compounds 2a-2j

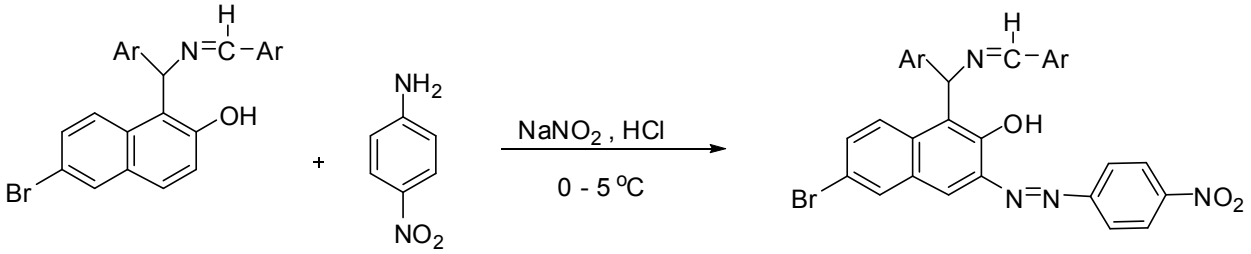
The antimicrobial activity of the newly synthesized azetidinone moities **2a-2j** were evaluated using well diffusion method against the panel of nine different bacterial strains. Different bacterial strains used for the screening were *Staphylococcus aureus*, *Bacillus subtillis*, *Bacillus streaothermophilus*, *Rhodococci* sp., *Proteus valgaris*, *Escherichia coli*, *Pseudomonas* sp., *Escherichia coli* (positive strain) and *Salmonella* sp. (MTCC). The petri dishes and nutrient agar medium was sterilized by autoclaving. To this sterilized nutrient medium, 10 ml of one day old bacterial cultures were added. Culture were inoculated and stirred well, this media were poured in petri dishes and allowed to set. Two well were created using a 5 mm cork borer. In this well 100 µl of extracts/standards were filled. All the nutrient agar plates were incubated at 37 ^oC for 24 hrs and the plates were observed for clear zone of inhibition. Then diameters of the zone of inhibition for these compounds **2a-2j** were measured. The extracts of 3-chloro-4-aryl-1-(4-(phenyldiazenyl) phenyl) azetidin-2-one were prepared using ethanol as solvent. The antimicrobial test was carried out for at least three times for all the compounds **2a-2j** against all microorganisms. The mean values of diameters of the zone of inhibition for these compounds **2a-2j** are reported in **Table 1**.

Result and Discussion

General. In the present work, 1-((benzylideneamino)(aryl)methyl)-6-bromonaphthalen-2-ol **(1a-1j),** was used as the key intermediate for further synthesis. These compounds were prepared by the reaction of 6-bromo-2-naphtol, aldehydes and ammonia via Betti's condensation reaction **(Scheme 1). C**ompound (**1a-1j**) in alkaline medium were diazotized by treating with *p*-nitro aniline in the presence of $NaNO_2$ and HCl **(Scheme 2)**. Thus compound 2(1-((benzylideneamino)(phenyl)methyl)-6-bromo-3-((4-nitrophenyl)diaze nyl) naphthalen-2-ol) (**2a-2j**) were obtained. In **Table 1,** the physical parameters of newly synthesized azo-azo-imine dyes (**2a-2j**) are reported.



Scheme 1. Synthesis of 1-((arylbenzylideneamino)(arylphenyl)methyl)-6-bromo naphthalen-2-ol (1a-1j)



Scheme 2. Synthesis of 1-((aryl benzylideneamino)(aryl phenyl) methyl)-6-bromo-3-(4-nitrophenyl) diazenyl) naphthalene-2-ol (2a-2j).

Table 1. Biological activities of azo-azoimine dyes (2a-2j).

Bacterial strain	Zone of inhibition in mm along without well diameter (5mm) for compounds										
	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**	**2j**	**Standard Nystatin**
E. coil (mixed)	9.3	17.8	15.8	19.7	24	22.1	15	12	16	7.1	17
B. subtilis	12	11.4	13	8.9	12	12.5	12	7	0	0	6
Pseudomonas sp.	0	0	9	13.7	6.2	0	5.8	8	8.2	13	12
S. aureus	13	8.1	9	0	0	0	11.7	8	0	20	9
P. vulageris	21	23.6	26.1	27.4	8.6	27.3	30.8	0	11	0	17
Salmonella sp.	21.6	24.8	16	17.8	13.7	31.3	17.2	11	19.4	18.2	19.1
E. coil(+ve strain)	0	0	7	9	0	0	0	0	13	9.2	11
Rhodococci	0	5.2	0	12	12.8	0	7.5	8	13	17	6
B. stearothermopelus	0	9.1	12	9	6.3	0	7.7	0	9	16	7.2

Antimicrobial Activity of azo-azoimine dyes.

Antibacterial activities of all the compounds were studied against nine different bacterial strains (*E. coil (mixed), B. subtilis, Pseudomonas sp., S.aureus, P.vulageris, Salmonella sp. , E. coil(+ve strai,), Rhodococci, B. stearothermopelus,)* by measuring the zone of inhibition on agar plates. It can be observed from these results that compounds (**2a-2j**) have shown positive bacterial activity against different bacterial species, which are also known as human pathogenic bacteria. The compounds possess moderate to good activity against all stains in comparison with standard drug (**Table 1**).

It can be observed from these results that compounds (**2a-2j**) have shown positive bacterial activity against different bacterial species, which are also known as human pathogenic bacteria. It was also observed that within the synthesized compound extracts, highest zone of inhibition recorded in 6-bromo-1-((4-hydroxybenzylideneamino)(4-hydroxyphenyl)methyl)-3-((4-nitrophenyl)diazenyl)naphth -alen-2-ol (**2f**) extract against the *Salmonella sp.* i.e. 31.3 mm, which is more than standard i.e. 19.1mm zone of inhibition.

Conclusion

A series of novel azo-azoimine dyes based on the Schiff bases via Betti's condensation reaction were succesfully synthesized and charecterized using IR and ^{1}H-NMR spectroscopy and elemental analysis. Our study clearly demonstrate that novel azo-azoimine dyes had significant antimicrobial activity against different bacterial species. As a consequence, we can conclude that newly synthesized azo-azoimine dyes can be used for the development of new antibacterial drugs to cure many disorders caused by the different bacterial species.

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