Synthesis and Spectroscopic Study of Naphtholic and Phenolic Azo Dyes

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Authors’ contributions
This work was carried out in collaboration between the authors. OOA designed the scheme, the protocol for synthetic pathway and wrote the first draft. OEA carried out the synthesis. AOA did the collation of the data and editing of the write-up. AEO & WUA managed the analysis of the study and spectroscopic evaluation. All authors read and approved the final manuscript.

ABSTRACT
Azo dyes are known to represent a class of medicinally important compounds which are extensively used as antibacterial agents. Hence, a series of naphtholic azo dyes 1-9 were synthesized via diazotisation of substituted aniline derivatives followed by azo coupling with 2-naphthol. In similar manner, diazotisation followed by azo coupling with phenol afforded phenolic azo dyes 10-17 in excellent yields. The chemical structures of all synthesized compounds were confirmed using analytical data and spectroscopic technique which include Uv-visible, IR, Mass spectra, ¹H- and ¹³C-NMR.

Keywords: Azo dye; colour pigment; diazotization; spectral study, naphthol.
1. INTRODUCTION

Human’s love of colour could be dated back to antiquity, yet it is not actually until the modern era that the full range of the rainbow has been accessible to the majority of people in their clothes and other textiles (Gung and Taylor, 2004). Colorants (dyes and pigments) are important industrial chemicals. Following the technological nomenclature, pigments are colorants that are insoluble in the application medium whereas dyes are applied in soluble form (Bolt and Golka, 1993; Myslak and Bolt, 1988). Over 10,000 different dyes or pigments are currently used worldwide in various industries like dyeing, printing, textile, non-textile (Corbett, 2000) and pharmaceutical industries (Park et al., 2007; Revenkar and Lele, 2007). Dyes are versatile chemicals which are also consumed by a number of other chemical industries such as paper, food and cosmetics industries (Khalid et al., 2008). Of all classes of dyestuffs, azo dyes have attained the widest range of usage because variations in chemical structure are readily synthesized and methods of application are generally not complex (Chudgar and Oakes, 2003). There are azo dyes for dyeing all natural substrates such as cotton, paper, silk, leather, and wool. They are considered as xenobiotic compounds that are very recalcitrant to biodegradation processes (Elisangela et al., 2009).

Among various dyes commercially in use, azo dyes find the largest applications (Carliell et al., 1995). This is because 60-70% of all dyes stuff in use and production fall in this group. An azo dye can simply be defined as any of a class of artificial dyes that contains the azo group (-N=N-). According to a statistical data survey, one million tons of azo dyes are produced annually worldwide (Stolz 2001; Pandey et al., 2007). In fact, on the basis of chemical composition, there are various classes of azo dyes of which reactive dyes are the most important of them (Ahmad and Hameed, 2010). Most of the reactive dyes (80-95%) have azo group as chromogen (Zollinger, 2003). Most important characteristic of reactive dyes is their ability to form covalent bond with fabric on which they are applied (Namboodri et al., 1994). Many azo pigments are non-toxic, although some, such as dinitroaniline orange, ortho-nitroaniline orange, or pigment orange 1, 2, and 5 have been found to be mutagenic. Likewise, several case studies have linked azo pigments with basal cell carcinoma (Engel et al., 2008). In the past, studies in exposed workers have demonstrated that the azoreduction of benzidine-based dyes occurs in man (Golka et al., 2004). Based on diverse
application of azo dyes, it is conceivable to development synthesis of such scaffolds in expeditious way in order to unfold many more potentials of such compounds.

2. MATERIALS AND METHODS

2.1 General Conditions

All chemical compounds were obtained from Sigma-Aldrich Chemical, but were made available by the Department of Chemistry, Covenant University. Solvents used were of analytical grade and, when necessary, were purified and dried by standard methods. Melting points were determined in open capillary tubes on a Stuart melting point apparatus and were uncorrected. The IR spectra were run in the single beam Nicolet IR 100 (Fourier-Transform); while UV of all the samples were run in methanol using UV-Genesys spectrophotometer. Their mass spectral data were obtained from waters GCT premier spectrometer. The $^1$H-NMR and $^{13}$C-NMR spectra were recorded in DMSO-d$_6$ using NMR Bruker DPX 400 spectrophotometer operating at 400 MHz and 100 MHz respectively. TMS was used as internal standard with the deuterium signal of the solvent as the lock and chemical shifts δ recorded in ppm. The elemental analysis (C, H, N) of the compounds were performed using Flash EA 1112 elemental analyzer while the pH was monitored using Portable pH Meter Model PHB4. Compounds were routinely checked by TLC on silica gel G plates using three different eluting solvents depending on the polarity disparity. The solvent systems are petroleum ether: chloroform (9:1, v/v), petroleum ether: chloroform (6:4, v/v) and chloroform: methanol (9:1, v/v) Also, the developed plates were visualized using UV lamp for the presence of spots and $R_f$ values were duly calculated.

2.2. General Procedure for the Synthesis of Naphtholic Azo Dyes

Concentrated hydrochloric acid (2.5 mL) was added to a solution of corresponding substituted aniline (10.7 mmol) in water (5 mL) in a beaker, swirled thoroughly and the solution was kept in an ice bath prior to use. In another beaker, NaNO$_2$ (1.0 g, 11.8 mmol) was dissolved in water (5 mL) and keep in an ice bath; add this solution drop-wisely to the aniline solution with continuous stirring for about 5 minutes within a carefully controlled temperature range (0-5 °C) to generate diazonium salt. The azo coupling was then achieved by adding a solution of 2-naphthol (1.0 g, 6.9 mmol) in 10% NaOH (10 mL) to the diazonium solution slowly at 0-5 °C with continuous
stirring for 5 minutes. The resulting solution formed a coloured precipitate which was filtered by
suction to give a coloured crystalline solid 1-9.

2.2.1. 1-(Phenyldiazenyl)naphthalene-2-ol, 1.
Azo coupling afforded a red crystal, 1 (1.7 g, 98.84%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 484 (4.38), 424
(4.20), 226 (4.73). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3402 (OH), 2720 C-H aromatic), 1618 (C=C aromatic),
750 (Ar-H). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.56-8.54 (d, $J = 8$ Hz, 1H, Ar-H), 8.24-8.22 (d,
$J = 8$ Hz, 1H, Ar-H), 8.07-8.05 (d, $J = 8$ Hz, 1H, Ar-H), 7.88-7.82 (t, $J = 9.8$ Hz, 1H, Ar-H),
7.74-7.70 (t, $J = 8$ Hz, 2H, Ar-H), 7.65-7.63 (d, $J = 8$ Hz, 2H, Ar-H), 7.51-7.47 (t, $J = 7.6$ Hz,
1H, Ar-H), 7.30-7.27 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.79-6.77 (d, $J = 8$ Hz, 1H, Ar-H). $^{13}$C-NMR
(100 MHz, DMSO-d$_6$) $\delta$: 130.7, 130.4, 130.4, 128.4, 128.4, 128.4, 128.1, 127.5, 126.6, 125.7, 124.3,
123.8, 121.2, 121.2, 119.9, 119.9, 117.4 ppm.

2.2.2. 1-((3-nitrophenyl)diazenyl)naphthalene-2-ol, 2.
Azo coupling afforded a red crystal, 2 (2.0 g, 98.52%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 472 (3.85), 301
(3.68), 223 (4.30). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3320 (OH), 2723 (C-H aromatic), 1614 (C=C aromatic),
1532 (NO$_2$), 724 (Ar-H). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.53 (s, 1H, Ar-H), 8.54-8.52 (d, $J =
8$ Hz, 1H, Ar-H), 8.22-8.20 (d, $J = 8$ Hz, 1H, Ar-H), 8.06-8.04 (d, $J = 8$ Hz, 2H, Ar-H), 7.88-7.84
(t, $J = 9.8$ Hz, 1H, Ar-H), 7.74-7.70 (t, $J = 8$ Hz, 2H, Ar-H), 7.65-7.63 (d, $J = 8$ Hz, 1H, Ar-H),
7.51-7.47 (t, $J = 7.6$ Hz, 1H, Ar-H), 7.30-7.27 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.79-6.77 (d, $J = 8$ Hz, 1H, Ar-H).
$^{13}$C-NMR (100 MHz, DMSO-d$_6$) $\delta$: 134.5, 130.7, 130.4, 130.4, 128.4, 128.4, 128.1, 127.5, 126.6, 125.7, 124.3, 123.7, 121.1, 121.1, 119.9, 119.9 ppm. MS-EI: m/z (rel. %): 295.10
(M + 2, 3%), 294.09 (20%), 293.07 (99%), 292.07 (24%), 171.05 (37%), 143 (100%), 115.04
(84%), 114.04 (10%), 76.02 (4%).

2.2.3. 1-((4-Bromophenyl)diazenyl)naphthalene-2-ol, 3.
Azo coupling afforded a red crystal, 3 (2.3 g, 99.56%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 476 (3.95), 428
(3.88), 224 (4.63). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3405 (OH), 2723 (C-H aromatic), 1619 (C=C aromatic),
512 (C-Br), 723 (Ar-H). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.56-8.54 (d, $J = 8$ Hz, 1H, Ar-H),
8.10 (d, $J = 1.7$ Hz, 1H, Ar-H), 7.97-7.95 (d, $J = 9.4$ Hz, 1H, Ar-H), 7.80-7.78 (d, $J = 8$ Hz, 2H,
2.2.4. 1-((4-Chlorophenyl)diazenyl)naphthalen-2-ol, 4.
Azo coupling afforded a red crystal, 4 (1.5 g, 76.53%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 478 (3.92), 370 (3.78), 316 (3.63), 226 (4.35). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3320 (OH), 2723 (C-H aromatic), 1621 (C=C aromatic), 826 (C-Cl), 723 (Ar-H). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.56-8.54 (d, $J = 8$ Hz, 1H, Ar-H), 8.10-8.07 (d, $J = 12$ Hz, 1H, Ar-H), 7.97-7.95 (d, $J = 9.5$ Hz, 1H, Ar-H), 7.81-7.79 (d, $J = 8$ Hz, 2H, Ar-H), 7.63-7.61 (d, $J = 8$ Hz, 1H, Ar-H), 7.54-7.51 (m, 2H, Ar-H), 6.99-6.96 (d, $J = 9.6$ Hz, 1H, Ar-H), 2.39 (s, 3H, Ar-H). $^{13}$C-NMR (100 MHz, DMSO-d$_6$) $\delta$: 149.0, 148.6, 148.6, 138.4, 134.5, 132.1, 132.1, 130.7, 130.4, 128.5, 128.5, 127.5, 127.5, 126.6, 125.7 ppm.

2.2.5. 1-((2-Bromo-4-methylphenyl)diazenyl)naphthalen-2-ol, 5.
Azo coupling afforded a deep red crystal, 5 (2.2 g, 96.49%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 484 (4.33), 310 (3.94), 262 (4.21), 223 (4.97). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3440 (OH), 2723 (C-H aromatic), 1600 (C=C aromatic), 723 (Ar-H), 513 (C-Br). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.54-8.52 (d, $J = 8$ Hz, 1H, Ar-H), 8.09 (s, 1H, Ar-H), 7.98-7.95 (d, $J = 9.6$ Hz, 1H, Ar-H), 7.78-7.76 (d, $J = 8$ Hz, 2H, Ar-H), 7.63-7.61 (d, $J = 8$ Hz, 1H, Ar-H), 7.54-7.51 (m, 2H, Ar-H), 6.99-6.96 (d, $J = 9.6$ Hz, 1H, Ar-H), 2.39 (s, 3H, Ar-H). $^{13}$C-NMR (100 MHz, DMSO-d$_6$) $\delta$: 167.2, 167.2, 145.4, 139.6, 137.4, 132.6, 132.3, 132.3, 128.8, 125.5, 124.8, 123.5, 122.2, 121.1, 118.2, 118.2, 22.4 ppm.

2.2.6. 1-((3-bromo-4-methylphenyl)diazenyl)naphthalen-2-ol, 6.
Azo coupling afforded a red crystal, 6 (2.0 g, 87.72%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 478 (4.14), 310 (3.74), 223 (4.63). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3410 (OH), 2723 (C-H aromatic), 1617 (C=C aromatic), 723 (Ar-H), 513 (C-Br). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.56-8.54 (d, $J = 8$ Hz, 1H, Ar-H), 8.10 (s, 1H, Ar-H), 7.96-7.94 (d, $J = 9.3$ Hz, 1H, Ar-H), 7.80-7.78 (d, $J = 8$ Hz, 2H, Ar-H), 7.62-7.60 (d, $J = 8$ Hz, 1H, Ar-H), 7.51-7.44 (m, 2H, Ar-H), 6.96-6.94 (d, $J = 9.3$ Hz, 1H, Ar-H), 2.39 (s, 3H, Ar-H). $^{13}$C-NMR (100 MHz, DMSO-d$_6$) $\delta$: 166.9, 166.9, 139.7, 137.2, 132.1, 132.1,
129.9, 129.1, 127.9, 125.6, 125.0, 123.4 122.2, 121.2, 118.6, 118.6, 22.4 ppm. MS-EI: m/z (rel. %): 342.02 (M + 2, 65%), 340.02 (M+, 70%), 261.10 (3%), 171.05 (21%), 143.04 (100%), 115.05 (55%), 89.03 (10%), 77.03 (Ph+, 5%).

2.2.7. 1-((4-Bromo-2-methylphenyl)diazenyl)naphthalen-2-ol, 7.
Azo coupling afforded a red crystal, 7 (2.2 g, 99.12%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 488 (4.37), 314 (4.14), 260 (4.35), 224 (5.04). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3448 (OH), 2723 (C-H aromatic), 1627 (C=C aromatic), 512 (C-Br), 723 (Ar-H). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.06-8.04 (d, J = 8 Hz, 2H, Ar-H), 8.02-8.00 (d, J = 7.5 Hz, 1H, Ar-H), 7.80-7.77 (d, J = 9.5 Hz, 2H, Ar-H), 7.58 (s, 1H, Ar-H), 7.55-7.53 (t, J = 8 Hz, 1H, Ar-H), 7.46-7.44 (t, J = 8 Hz, 1H, Ar-H), 7.19-7.17 (d, J = 7.5 Hz, 1H, Ar-H), 2.35 (s, 3H, CH$_3$-Ar). $^{13}$C-NMR (100 MHz, DMSO-d$_6$) $\delta$: 156.2, 151.0, 134.1, 134.1, 129.5, 129.3, 128.9, 128.0, 127.7, 126.8, 126.0, 125.5, 125.1, 123.7, 17.9 ppm.

2.2.8. 1-((4-aminophenyl)diazenyl)naphthalen-2-ol, 8.
Azo coupling afforded a black crystal, 8 (1.8 g, 97.83%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 496 (3.36), 316 (3.15), 271 (3.92), 223 (5.05). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3402 (OH), 3110 (NH$_2$), 2723 (C-H aromatic), 1628 (C=C aromatic), 723 (Ar-H). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.07-8.05 (d, J = 8 Hz, 2H, Ar-H), 7.99-7.97 (d, J = 7.8 Hz, 1H, Ar-H), 7.56-7.54 (t, J = 8 Hz, 1H, Ar-H), 7.47-7.45 (t, J = 8 Hz, 1H, Ar-H), 7.18-7.16 (d, J = 7.8 Hz, 1H, Ar-H), 6.87-6.89 (d, J = 8.5 Hz, 2H, Ar-H), 6.39 (s, 2H, NH$_2$-Ar).

2.2.9. 1-((3-Aminophenyl)diazenyl)naphthalen-2-ol, 9.
Azo coupling afforded a grey crystal, 9 (1.5 g, 81.97%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 329 (4.29), 272 (4.86), 227 (5.35). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3447 (OH), 3180 (NH$_2$), 2723 (C-H aromatic), 1630 (C=C aromatic), 723 (Ar-H). $^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.19-8.17 (d, J = 8 Hz, 1H, Ar-H), 8.12-8.10 (d, J = 7.8 Hz, 1H, Ar-H), 8.04-8.02 (d, J = 8.7 Hz, 1H, Ar-H), 7.78-7.76 (d, J = 9.5 Hz, 1H, Ar-H), 7.56-7.54 (t, J = 8 Hz, 1H, Ar-H), 7.47-7.45 (t, J = 7.8 Hz, 1H, Ar-H), 7.41-7.38 (d, J = 12 Hz, 1H, Ar-H), 7.21-7.19 (d, J = 8.7 Hz, 1H, Ar-H), 7.04-7.02 (t, J = 9.5 Hz, 1H, Ar-H), 6.86-6.83 (d, J = 12 Hz, 1H, Ar-H), 6.52 (s, 2H, NH$_2$-Ar), 6.03 (s, 1H, NH).
2.3. General Procedure for the Synthesis of Phenolic Azo Dyes

To a mixture of substituted aniline (10.7 mmol) and water (5 mL) was added conc. hydrochloric acid (2.5 mL) prior to use. NaNO$_2$ (1.0 g, 11.8 mmol) was dissolved in water (5 mL) and kept in an ice bath; this solution was added drop-wise to the aniline solution at 0-5 °C with continuous stirring for about 5 minutes. In the coupling reaction, a solution of phenol (1 mL) in 10% NaOH (10 mL) was added slowly to the diazonium solution obtained above, with continuous stirring for 5 minutes (0-5 °C). The resulting solution formed a black precipitate which was filtered by suction to give a coloured crystalline solid.

2.3.1. 4-(Phenyldiazenyl)phenol, 10.

Azo coupling afforded a black crystal, 10 (2.5 g, 87.1%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 344 (4.81), 230 (4.56). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3160 (OH), 2723 (C-H aromatic), 1589 (C=C aromatic), 723 (Ar-H).

$^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.26-8.23 (d, $J = 10.5$ Hz, 2H, Ar-H), 7.84-7.82 (d, $J = 8$ Hz, 2H, Ar-H), 7.65-7.68 (t, $J = 10.5$ Hz, 2H, Ar-H), 7.28-7.26 (t, $J = 10.5$ Hz, 1H, Ar-H), 7.01-7.03 (d, $J = 8$ Hz, 2H, Ar-H), 5.35 (s-br, IH, OH).

$^{13}$C-NMR (100 MHz, DMSO-d$_6$) $\delta$: 160.2, 152.6, 145.3, 130.8, 129.1, 129.1, 124.5, 124.5, 123.0, 123.0, 116.4, 116.4 ppm.

2.3.2. 4-((3-Nitrophenyl)diazenyl)phenol, 11.

Azo coupling afforded a red crystal, 11 (3.5 g, 99.43%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 356 (4.27), 245 (4.24), 206 (4.34). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3423 (OH), 2723 (C-H aromatic), 1637 (C=C aromatic), 1590 (NO$_2$), 723 (Ar-H).

$^1$H-NMR (400 MHz, DMSO-d$_6$) $\delta$: 8.68 (s, 1H, Ar-H), 8.39-8.38 (d, $J = 4.9$ Hz, 1H, Ar-H), 8.20-8.19 (d, $J = 5.5$ Hz, 1H, Ar-H), 7.94-7.91 (m, 1H, Ar-H), 7.85-7.83 (d, $J = 8$ Hz, 2H, Ar-H), 7.01-6.99 (d, $J = 8$ Hz, 2H, Ar-H), 5.34 (s-br, IH, OH).

$^{13}$C-NMR (100 MHz, DMSO-d$_6$) $\delta$: 152.0, 151.6, 150.7, 129.4, 129.4, 129.0, 129.1, 129.1, 129.0, 125.0, 125.0, 123.7, 122.9 ppm.

2.3.3. 4-((4-Bromophenyl)diazenyl)phenol, 12.

Azo coupling afforded a brown crystal, 12 (2.7 g, 67.33%). $\lambda_{\text{max}}$ in nm (log $\varepsilon_{\text{max}}$): 352 (4.04), 238 (3.28). IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 3398 (OH), 2723 (C-H aromatic), 1617 (C=C aromatic), 723 (Ar-H),
\[ ^1 \text{H-NMR (400 MHz, DMSO-d}_6 \text{)} \delta: \ 7.81-7.79 (d, J = 8 \text{ Hz}, 1 \text{H, Ar-H}), 7.75-7.73 (m, 2 \text{H, Ar-H}), 7.67-7.65 (m, 2 \text{H, Ar-H}), 7.58-7.56 (m, 1 \text{H, Ar-H}), 7.40-7.38 (m, 1 \text{H, Ar-H}), 6.96-6.94 (m, 1 \text{H, Ar-H}). \]

\[ ^{13} \text{C-NMR (100 MHz, DMSO-d}_6 \text{)} \delta: \ 152.4, 152.0, 132.3, 132.1, 132.1, 131.9, 126.1, 125.0, 123.9, 123.7, 123.1, 116.1 \text{ ppm. MS-EI: m/z (rel. %): 276.99 (M + 1, 37%), 275.99 (M}, 37\%), 172.96 (90\%), 170.97 (100\%), 121.04 (59\%), 93.03 (89\%), 65.03 (40\%), 43.98 (24\%). \]

2.3.4. 4-((4-Chlorophenyl)diazenyl)phenol, 13.

Azo coupling afforded a black crystal, 13 (1.2 g, 37.04%). \( \lambda_{\text{max}} \) in nm (log \( \varepsilon_{\text{max}} \)): 346 (4.69), 238 (4.20). IR (KBr, cm\(^{-1}\)) \( \nu_{\text{max}} \): 3394 (OH), 2723 (C-H aromatic), 1576 (C=C aromatic), 829 (C-Cl), 723 (Ar-H). \[ ^1 \text{H-NMR (400 MHz, DMSO-d}_6 \text{)} \delta: \ 8.03-8.02 (d, J = 4 \text{ Hz, 1H, Ar-H}), 7.84-7.79 (m, 2 \text{H, Ar-H}), 7.74-7.72 (d, J = 8 \text{ Hz, 1H, Ar-H}), 7.63-7.61 (d, J = 8 \text{ Hz, 1H, Ar-H}), 7.56-7.51 (m, 2 \text{H, Ar-H}), 6.97-6.95 (d, J = 8 \text{ Hz, 1H, Ar-H}). \]

\[ ^{13} \text{C-NMR (100 MHz, DMSO-d}_6 \text{)} \delta: \ 152.6, 152.0, 132.3, 132.1, 132.1, 131.9, 126.0, 125.0, 123.9, 123.7, 123.1, 116.2 \text{ ppm. MS-EI: m/z (rel. %): 234.04 (M + 2, 11\%), 232.04 (M}, 70\%), 218.99 (29\%), 130.99 (5\%), 121.04 (41\%), 93.03 (100\%), 68.99 (22\%), 67.99 (20\%), 43.98 (12\%). \]

2.3.5. 4-((2-Bromo-4-methylphenyl)diazenyl)phenol, 14.

Azo coupling afforded a yellow crystal, 14 (2.3 g, 56.93%). \( \lambda_{\text{max}} \) in nm (log \( \varepsilon_{\text{max}} \)): 361 (4.79), 247 (4.46), 205 (4.44). IR (KBr, cm\(^{-1}\)) \( \nu_{\text{max}} \): 3325 (OH), 2723 (C-H aromatic), 1589 (C=C aromatic), 518 (C-Br). \[ ^1 \text{H-NMR (400 MHz, DMSO-d}_6 \text{)} \delta: \ 7.83-7.81 (d, J = 8 \text{ Hz, 2H, Ar-H}), 7.66 (s, 1 \text{H, Ar-H}), 7.55-7.53 (d, J = 8 \text{ Hz, 1H, Ar-H}), 7.29-7.27 (d, J = 8 \text{ Hz, 1H, Ar-H}), 7.00-6.97 (dd, J1 = 4 \text{ Hz, J2 = 12 \text{ Hz, 2H, Ar-H}}), 2.37 (s, 3 \text{H, Ar-H}). \]

\[ ^{13} \text{C-NMR (100 MHz, DMSO-d}_6 \text{)} \delta: \ 146.8, 145.2, 142.2, 133.5, 129.2, 125.2, 125.2, 124.1, 117.1, 116.3, 116.3, 114.1, 20.5 (\text{CH}_3) \text{ ppm. MS-EI: m/z (rel. %): 292.00 (M + 2, 82\%), 290.00 (M}, 91\%), 170.96 (24\%), 168.96 (30\%), 121.03 (97\%), 93.02 (100\%), 90.04 (15\%), 89.03 (12\%), 65.03 (22\%), 63.02 (3\%). \]

2.3.6. 4-((2-Bromo-4-methylphenyl)diazenyl)phenol, 15.
Azo coupling afforded an orange crystal, 15 \((1.7 \text{ g, 42.1 \%})\). \(\lambda_{\text{max}}\) in nm (log \(\varepsilon_{\text{max}}\)): 355 (5.30), 241 (5.02), 205 (5.06). IR (KBr, cm\(^{-1}\)) \(\nu_{\text{max}}\): 3290 (OH), 2724 (C-H aromatic), 1589 (C=C aromatic), 723 (Ar-H), 582 (C-Br). \(^1\)H-NMR (400 MHz, DMSO-d\(_6\)) \(\delta\): 7.83-7.81 (d, \(J = 8\) Hz, 2H, Ar-H), 7.72 (s, 1H, Ar-H), 7.54-7.52 (d, \(J = 8\) Hz, 1H, Ar-H), 7.29-7.27 (d, \(J = 8\) Hz, 1H, Ar-H), 7.00-6.97 (dd, \(J_1 = 4\) Hz, \(J_2 = 12\) Hz, 2H, Ar-H), 2.37 (s, 3H, Ar-H). \(^{13}\)C-NMR (100 MHz, DMSO-d\(_6\)) \(\delta\): 146.8, 145.2, 142.2, 133.5, 129.2, 125.2, 125.2, 124.1, 117.1, 117.1, 116.3, 114.1, 20.1 (CH\(_3\)) ppm.

2.3.7. 4-((4-Bromo-2-methylphenyl)diazenyl)phenol, 16.

Azo coupling afforded a brown crystal, 16 \((g, 44.55\%)\). \(\lambda_{\text{max}}\) in nm (log \(\varepsilon_{\text{max}}\)): 361 (5.14), 241 (4.91), 205 (4.96). IR (KBr, cm\(^{-1}\)) \(\nu_{\text{max}}\): 3337 (OH), 2724 (C-H aromatic), 1586 (C=C aromatic), 723 (Ar-H). \(^1\)H-NMR (400 MHz, DMSO-d\(_6\)) \(\delta\): 7.95-7.93 (d, \(J = 8\) Hz, 2H, Ar-H), 7.87-7.84 (d, \(J = 12\) Hz, 2H, Ar-H), 7.67 (s, 1H, Ar-H), 7.16-7.14 (d, \(J = 8\) Hz, 2H, Ar-H), 5.35 (s-br, 1H, OH), 2.38 (s, 3H, CH\(_3\)-Ar). \(^{13}\)C-NMR (100 MHz, DMSO-d\(_6\)) \(\delta\): 158.7, 151.2, 143.5, 134.2, 133.5, 128.9, 125.3, 125.2, 124.4, 124.4, 116.7, 116.7, 21.3 ppm.

2.3.8. 4-((4-Aminophenyl)diazenyl)phenol, 17.

Azo coupling afforded a black crystal, 17 \((0.7 \text{ g, 30.84\%})\). \(\lambda_{\text{max}}\) in nm (log \(\varepsilon_{\text{max}}\)): 595 (2.60), 568 (2.60), 394 (3.83), 205 (4.00). IR (KBr, cm\(^{-1}\)) \(\nu_{\text{max}}\): 3261 (OH), 3100 (NH\(_2\)), 2723 (C-H aromatic), 1589 (C=C aromatic), 723 (Ar-H). \(^1\)H-NMR (400 MHz, DMSO-d\(_6\)) \(\delta\): 8.78-8.75 (d, \(J = 12\) Hz, 2H, Ar-H), 7.86-7.84 (d, \(J = 8\) Hz, 2H, Ar-H), 7.22-7.20 (d, \(J = 8\) Hz, 2H, Ar-H), 6.75 (s, 2H, NH\(_2\)), 5.35 (s-br, 1H, OH). \(^{13}\)C-NMR (100 MHz, DMSO-d\(_6\)) \(\delta\): 159.3, 150.7, 148.2, 148.2, 125.1, 125.1, 124.4, 124.4, 116.5, 116.5, 113.9, 113.9 ppm.

3. RESULTS AND DISCUSSION

3.1 Synthetic Pathway to the Azo Dyes

First and foremost, it is important to note that the azo dyes synthesized were of two forms based on the nature of the starting material common to each group. The first set of these series have
naphtholic group common to them; hence, they are referred to as the naphtholic azo dyes 1-9 while the second set are called the phenolic azo dyes 10-17 because they have phenolic group in common. However, the two sets were prepared using the same procedure as reported by Wang et al., (2003) but in modified version. In a nutshell, to understand the detail of the observed reaction, it is essential to explain the formation of compound 1 as a representative of the naphtholic azo dyes. The naphtholic azo dye 1 was prepared in excellent yield by coupling of 2-naphthol with aniline. The same procedure was repeated with substituted aniline derivative to afford other eight naphtholic azo dyes 2 – 9. Generally speaking, the naphtholic azo dyes, 1-9 were prepared in good to excellent yield (76.53 - 99.56%) by the diazo coupling of the aniline and substituted anilines with 2-naphthol at 0-5 °C as shown in Scheme 1.

The formation of 1, involved two steps reaction as shown in Scheme 2a while the detail mechanism was as presented in Scheme 2b. The first step involved the diazotization of aniline to form a reactive intermediate, benzene diazonium chloride while the second step involved the formation of carbanion of 2-naphthol by a nucleophilic attack initiated by the chloride ion. The nucleophilic 2-naphthol generated, then attacks the diazonium nitrogen to form the naphtholic azo dye 1 (Scheme 2b). This mechanism was also adopted for the coupling of substituted aniline ii to ix to afford the corresponding naphtholic azo dyes 2 to 9 respectively. In a similar manner, to understand the detail of the observed reaction above, it is also essential to explain the formation of compound 10 as a representative of the phenolic azo dyes. The formation of 10 involved two steps reactions. The first step involved the diazotization of aniline to form a reactive intermediate, benzene diazonium chloride while the second step involved the formation of carbanion of phenol by a nucleophilic attack initiated by the chloride ion. The nucleophilic phenol generated, then attacks the diazonium nitrogen to form the phenolic azo dye 10. This mechanism was also adopted for the coupling of substituted aniline xi to xvii to afford phenolic azo dyes 11 to 17 respectively as shown in Scheme 3.
Reaction Condition and Reagents used: NaNO₂/Conc. HCl at 0-5°C. (i) aniline (ii) 3-nitroaniline (iii) 4-bromoaniline (iv) 4-chloroaniline (v) 2-bromo-4-methylaniline (vi) 3-bromo-4-methylaniline (vii) 4-bromo-2-methylaniline (viii) 3-nitrophenylenediamine (ix) m-phenylenediamine

Scheme 1. Synthesis of naphtholic azo dyes 1 – 9

(a) Equation of reaction

(b) Mechanism involved

Scheme 2. Equation and mechanism for the formation of naphtholic azo dye, 1
3.2. Physico-Chemical Parameter Analysis

The physico-chemical parameters in terms of the report of the molecular formula, molecular weight, percentage yields, melting points, R_f values as well as the elemental analysis results are as shown in Table 1. The molecular weights of the compounds range from the highest 341 which was obtained for compounds 5, 6, 7 to the lowest 198 which could be found in compound 10. The entire compounds were synthesized in good (56.93%) to excellent yield (99.56%) except for compounds 13, 15, 16, 17 where-in arbitrarily low yields of 37.04%, 42.10%, 44.60% and 30.84% were observed respectively. The melting points of the entire compounds ranged between 134-136 °C for compound 2 and 269-271 °C, for compound 17. The low melting point observed in 2 might be as a result of inductive effect generated by the -NO_2 at the meta position of the
ring, while the high melting point experienced in 17 might be as a result of phenolic –OH which had intra-molecular hydrogen bond tendency. The TLC spotting was done in order to monitor the progress of the reaction and to confirm the purity level of the products obtained. The R_f values of all the compounds ranged from 0.18 to 0.94 using petroleum ether/chloroform solvent system. Although, the solvent systems are the same for all the compounds except 8 and 17 (Chloroform/methanol → 9:1), the eluting ratio varies depending on the polarity disparity of the synthesized compounds. The calculated values for the C, H, N elemental analysis was also reported in Table 1 to be in agreement with the found values within the limit of ±0.20. The colours of the synthesized compounds ranges from red to black except for compounds 9, 14 and 15 in which the colours are grey, yellow and orange respectively (Experimental).

3.3. Spectral Studies
The structures of newly synthesized compounds were elucidated by IR, UV, NMR, mass spectral studies, and elemental analysis. Generally speaking, from the spectroscopic study, the ultraviolet absorption and infrared data of all compounds were listed in the experimental section. The electronic transition of uv-visible spectra in methanol gave rise to wavelength (λ_max) ranging from 205 nm to 595 nm. The first wavelength (λ_max) for all the compounds were found between 205 - 227 nm as a result of π→π* transition of the compounds indicating the presence of C=C peculiar to benzene nucleus. This is in agreement with earlier report by Mielgo et al., as per benzenoid uv-visible absorption (Mielgo et al., 2001). The uv-visible absorption spectrum of 1-(phenyldiazenyl) naphthalene-2-ol, 1, as a representative of naphtholic azo dye, showed a peak at λ_max = 226 nm (log ε_max = 4.73) and two other bathochromic shift at λ_max = 424 nm (log ε_max = 4.20) and λ_max = 484 nm (log ε_max = 4.38). All the wavelength (λ_max) above benzenoid region (i.e. between 424 nm to 484 nm) was as a result of π→n transition and extended conjugation contributed by the C=C and the conjugative linkage performed by the N=N group. An incomparably strong bathochromic shift occurred in compound 17 that resulted in wavelength at far visible region of light at λ_max of 595 nm (log ε_max = 2.60) was due to the presence of an auxochrome (-NH_2) in the skeletal framework of compound 17 which improved the colour deepening attribute by delocalization of the lone pair of electron present on the nitrogen atom.
Furthermore, the IR spectra of all the compounds were run in nujol using single beam FT-IR. The infrared spectra of the compounds 1-17 showed absorption bands due to the stretching vibrations of OH of phenol and 2-naphthol, C-H aromatic, C=C of aromatic and Ar-H bending vibration at 3160- 3448 cm\(^{-1}\), 2720 - 2724 cm\(^{-1}\), 1589 - 1637 cm\(^{-1}\) and 723 - 750 cm\(^{-1}\) respectively. Specifically speaking, using IR spectrum of 7 as representative example of the azo dyes, the highest but broad band observed at 3402 cm\(^{-1}\) was as a result of OH functionality of phenol while CH of aromatic appeared at 2720 cm\(^{-1}\). The absorption bands at 1618 cm\(^{-1}\) and 750 cm\(^{-1}\) depicted the present of C=C and Ar-H respectively. The \(^1\)H- and \(^13\)C-NMR analysis of 1 was run at 400 MHz and 100 MHz respectively using deuterated DMSO. The \(^1\)H-NMR spectrum of compound 1 showed signals down field in the aromatic region of the TMS scale which was between \(\delta\) 8.56-8.54 and 6.79-6.77 ppm as one proton doublet each with coupling constant of 8 Hz. Other prominent signals include one proton doublet each at \(\delta\) 8.24-8.22 and 8.07-8.05; two proton doublets at 7.65-7.63; two proton triplet at \(\delta\) 7.74-7.70 and one proton triplet each at \(\delta\) 7.88-7.82, 7.51-7.47 and 7.30-7.27 respectively. The \(^13\)C-NMR spectrum of 1 showed it to have sixteen aromatic carbon atoms ranging from 130.7 ppm to 117.4 ppm.

In addition, the result of the mass spectral data of some selected compounds which include compounds 2, 6, 12, 13 and 14 was as reported in the experimental section. The molecular ion peaks obtained from all the spectra were consistent with the molecular mass of the proposed structures while some other daughters and base peaks were observed based on some fragmentation patterns. The mass spectral data of 6, for instance, showed molecular ion peak at m/z 340.02 (70%) which was in concordance with the molecular mass (340.02) of the compound (C\(_{17}\)H\(_{13}\)BrN\(_2\)O) while base peak was observed at m/z 143.04 (100%). A highly intense peak with m/z 342.02 was as a result of (M + 2) pattern. Other prominent peaks appeared at m/z 261.10, 171.05, 115.05 and 89.03 with relative intensities of 3% 21%, 55% and 10% respectively due to some fragmentation processes as shown in the Table 4.4. Specifically, the fragmentation that led to phenylium cation (Ph\(^+\)) was responsible for m/z of 77.03; although, with low relative intense (5%).
Table 1. Physico-Chemical Properties of Compounds Synthesized.

<table>
<thead>
<tr>
<th>No</th>
<th>Molecular Formula</th>
<th>Mol. Wt.</th>
<th>Yield (%)</th>
<th>Melting Pt. (°C)</th>
<th>Melting Rf</th>
<th>Elem. Anal: %Calcd. (%Found)</th>
<th>C</th>
<th>H</th>
<th>N</th>
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<tbody>
<tr>
<td>1</td>
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<td>248</td>
<td>98.84</td>
<td>138-140</td>
<td>0.27a</td>
<td>77.40(77.36)</td>
<td>4.87(4.89)</td>
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<td>2</td>
<td>C16H11N3O3</td>
<td>293</td>
<td>98.52</td>
<td>134-136</td>
<td>0.89b</td>
<td>65.53(65.47)</td>
<td>3.78(3.89)</td>
<td>14.33(14.27)</td>
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<td>3</td>
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<td>327</td>
<td>99.56</td>
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<td>58.74(58.59)</td>
<td>3.39(3.46)</td>
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<td>282</td>
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<td>67.97(68.07)</td>
<td>3.92(4.04)</td>
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<td>5</td>
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<td>341</td>
<td>96.49</td>
<td>231-233</td>
<td>0.21a</td>
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<td>3.84(3.67)</td>
<td>8.21(8.13)</td>
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</tr>
<tr>
<td>6</td>
<td>C17H13BrN2O</td>
<td>341</td>
<td>87.72</td>
<td>217-219</td>
<td>0.24a</td>
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<td>3.84(3.97)</td>
<td>8.21(8.30)</td>
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<tr>
<td>7</td>
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<td>99.12</td>
<td>219-221</td>
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<td>3.84(3.69)</td>
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<tr>
<td>8</td>
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<td>263</td>
<td>97.83</td>
<td>248-250</td>
<td>0.94c</td>
<td>72.99(73.12)</td>
<td>4.98(5.11)</td>
<td>15.96(16.09)</td>
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<td>52.01(51.96)</td>
<td>3.27(3.41)</td>
<td>10.11(10.21)</td>
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<tr>
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<td>37.04</td>
<td>188-190</td>
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<td>61.95(62.02)</td>
<td>3.90(4.08)</td>
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<td>56.93</td>
<td>252-254</td>
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<td>53.63(53.51)</td>
<td>3.81(3.69)</td>
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<tr>
<td>15</td>
<td>C13H11BrN2O</td>
<td>291</td>
<td>42.10</td>
<td>248-250</td>
<td>0.60a</td>
<td>53.63(53.77)</td>
<td>3.81(3.89)</td>
<td>9.62(9.51)</td>
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<tr>
<td>16</td>
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<td>223-225</td>
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<td>53.63(53.52)</td>
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<td>269-271</td>
<td>0.94c</td>
<td>67.59(67.68)</td>
<td>5.20(5.11)</td>
<td>19.71(19.89)</td>
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</table>

aSolvent System: Pet ether: CHCl₃ (9:1, v/v); Pet ether: CHCl₃ (6:4, v/v); CHCl₃: CH₃OH (9:1, v/v).
4. CONCLUSION
In summary, the synthesis of series of naphtholic azo dyes 1 – 9 and phenolic azo dyes 10 – 17 was successfully achieved using various substituted aniline derivatives as the coupling agents. The functionalized azo dyes might have good biological properties based on historical report of usage of dye as antibacterial agents. Thus, the azo dyes herein synthesized are good candidates for further study in terms of the investigation of their biological activities. This might create a new vista of opportunity in new drug discovery and medicinal research.

ACKNOWLEDGEMENTS
OOA gratefully acknowledged Professor Feipeng Wu and his research group (New Functional Polymeric Material Group) in Technical Institute of Physics and Chemistry (CAS), Beijing for the assistance in running $^1$H-, $^{13}$C-NMR and mass spectra of the compounds.

COMPETING INTERESTS
Authors have declared that no competing interests exist.

REFERENCES


