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FACILE SYNTHESIS OF FULLY CONJUGATED AMINOPYRAZINE BASED DIAZOBENZENES AND DIAZOAMINOBENZENES WITH ARYLDIAZONIUM SALTS

Idris Karakaya*

Department of Chemistry, College of Basic Sciences, Gebze Technical University, 41400 Gebze, Turkey; Email: karakaya@gtu.edu.tr

Abstract – Herein, we report the diazotization of aminopyrazine achieved in good to excellent yields using electronically disparate aryldiazonium salts at room temperature. These novel and fully conjugated diazobenzenes and diazoaminobenzenes were characterized utilizing NMR, HRMS, single crystal X-ray diffraction, and UV–Vis techniques. Depending on the position of the functional groups substituted on the aryldiazonium salts and their ability to forge hydrogen bonds, these reactions can diverge into two possible pathways to give diazobenzenes or diazoaminobenzenes selectively. Based on the results of UV-Vis spectroscopic analysis, it was determined that the maximum absorbance band of the compounds was between 333 nm and 363 nm due to their interacting π-π* transitions. These results are further supported by DFT calculations, showing these molecules exhibit high absorbance.

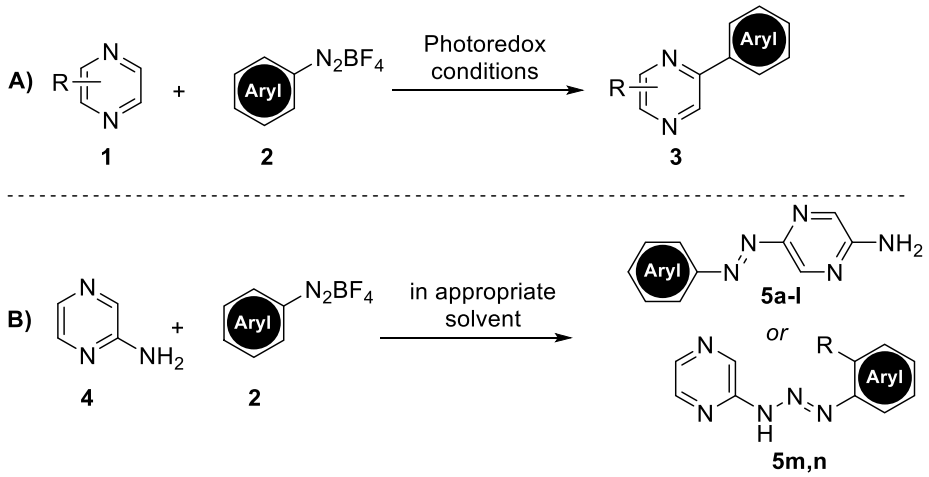
INTRODUCTION

The synthesis and chemistry of azobenzenes have been extensively studied due to their varied structural features and numerous applications. They are used in a variety of chemical industries including as dyes and pigments,[1] food additives,[2] cosmetics, protein probes,[3] protective eye glasses, filters[4], and polymers.[5] Since naturally obtained dyes do not always adequately bracket the full scope of wavelengths, it is unsurprising that some will be produced synthetically to fill these gaps. In particular, due to the low cost and relative ease of preparation, azo dyes are among the most popular synthetic dyes exhibiting the full range of colors. Moreover, photo-rearrangement of the azobenzenes mediated by irradiation with a particular wavelength can be used to switched reversibly to either the *cis* or *trans* isomer. Owing to these unique photochromic properties, azobenzenes recently have been utilized for applications as chemosensors,[6] liquid crystals,[7]

nonlinear optics,[8] and nanotubes.[9] In addition, other applications of azo compounds include electronics,[10] drug delivery, and photopharmacology.[11] Azo compounds can also be used as diagnostic probes for visualizing amyloid plaques in the brains of Alzheimer's patients.[12] Azo compounds show numerous biological, antimicrobial and antibacterial activities which make them attractive compounds medically.[13] Recently, another positive feature of azo compounds has been their use as inhibitor against HIV proliferation.[14] Given these innumerable applications, methods that allow access to these structures in unique and differential ways are consequently valuable to the scientific community at large.

Functionalized heterocyclic structures are found in nature and in the structure of many biological compounds such as nucleic acids, antibiotics, amino acids.[15] The pyrazine ring is a part of the structures of polycyclic molecules such as quinoxaline, phenazine, pteridine, and flavin, which are of great importance in synthetic organic chemistry. Owing to the vacant p molecular orbitals, pyrazine exhibits distinctive physicochemical properties and provides the ability to be utilized as a bridging ligand. This unique structural motif allows these structures to be used to study molecular and intermolecular electron transfer in organic reactions.[16] Pyrazine derivatives also have a wide range of biological activities and have been shown to exhibit good target efficiency at low concentrations. This has naturally attracted high interest in pharmaceutical medicinal chemistry[17] where pyrazine containing pharmaceuticals are widely employed as diuretics, anti-inflammatory agents, antibacterial, antifungal, antituberculosis, antitumor and anticancer.[18] In addition, due to their structural features, these molecules also have strong scents with low detection limits for the human nose, allowing synthetic pyrazine-based structures to be widely employed as fragrances and flavorings in the cosmetic and processed food industries.[19]

Aryldiazonium salts have been widely used as reagents in aromatic substitution reactions and/or as a source of aryl radicals in synthetic sequences. As such, many diazonium salts are commercially available and can be synthesized with high yields from cheap and easily accessible aniline derivatives.[20]
It is known that unsubstituted pyrazine or pyrazines substituted with electron withdrawing groups (**1**) will give C-H arylation products when combined with weakly electrophilic diazonium salts under photoredox reaction conditions.[21] On the other hand, pyrazine, bearing electron donating groups such as -OH or -NH_2, provides the formation of aminodiazo compounds in polar solvents. In this study, we successfully synthesized a series of novel fully conjugated pyrazine-based diazobenzenes and diazoaminobenzenes between the reaction of 2-aminopyrazine and aryldiazonium salts (Scheme 1).

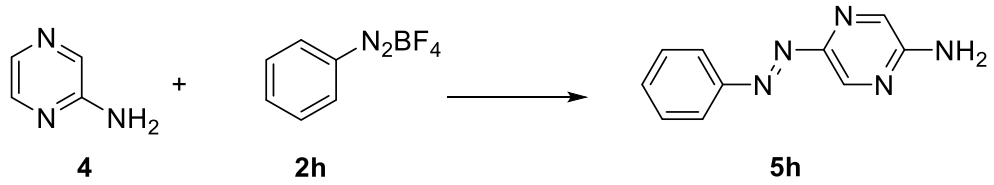


Scheme 1. (Amino)pyrazine reactions with aryldiazonium salts

RESULTS AND DISCUSSION

As depicted in Table 1, a series of solvents were employed to investigate the influence of solvent upon the reaction using phenyldiazonium salt **2h** as a model substrate. Here, it was observed that the reaction conversion was directly related to the solubility of the aryldiazonium salts. Although the reaction resulted in good yields in polar solvents such as DMSO, MeCN and DMF, no conversion was observed in presence of the less solubilizing EtOAc, CH_2Cl_2, THF and dioxane. While no conversion was detected in the water media, diazo product could be attained with low conversions in the presence of acetone and MeOH.

Table 1. Comparison of solvents



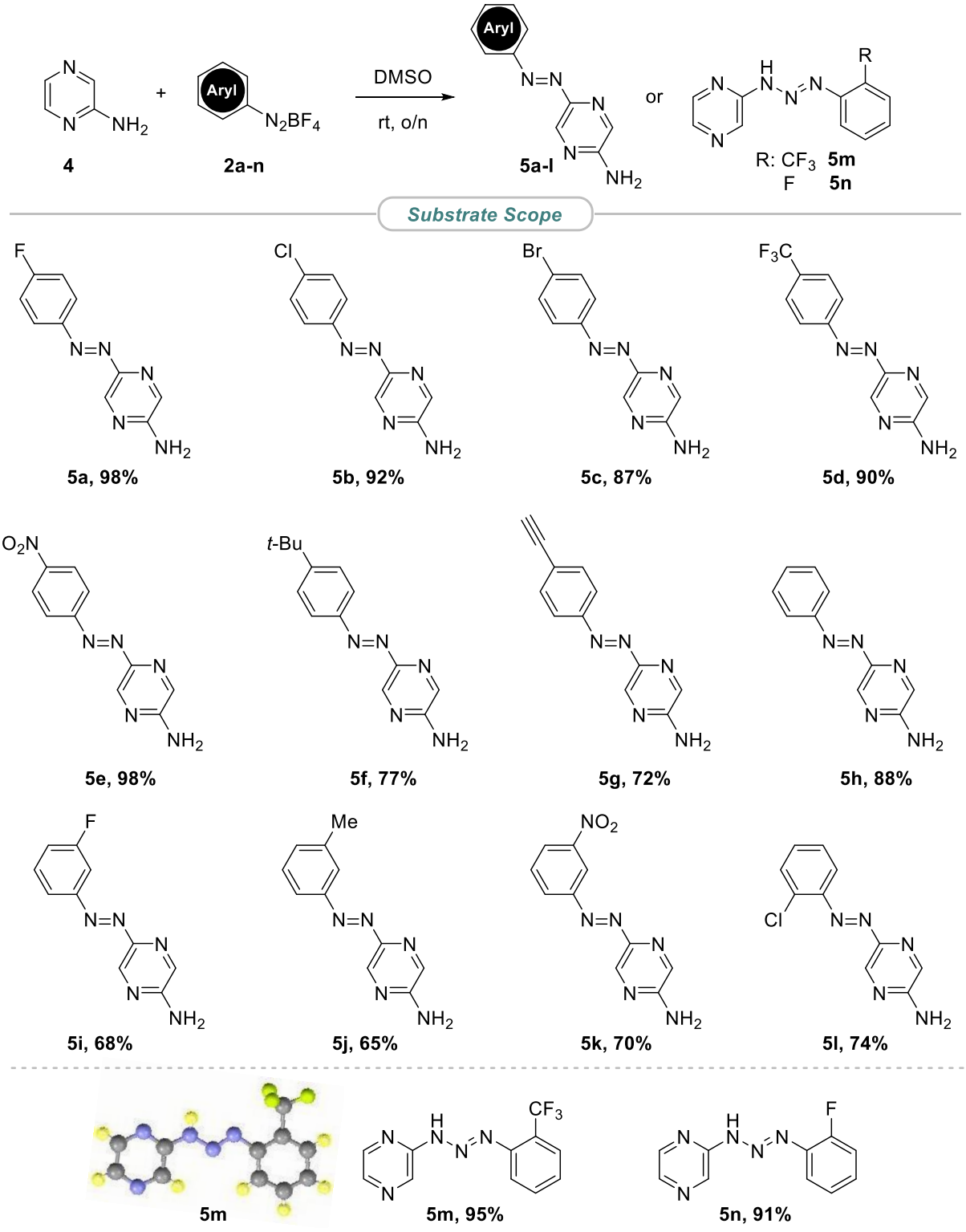
entry	solvent	yield [%][a]
1	DMSO	88
2	H_2O	n.r.
3	MeCN	64
4	CH_2Cl_2	n.r.
5	MeOH	25
6	EtOAc	n.r.
7	DMF	67
8	THF	n.r.
9	acetone	15

10	dioxane	n.r.

The reaction was performed with **4** (0.3 mmol), **2h** (1.2 equiv.) in 2.0 mL of solvent, rt, 3 h. [a]Isolated yields, n.r.: no reaction.

With DMSO determined as a clear front-runner in yield, the final reaction condition for diazotization of aminopyrazine was selected as 2 mL volume of DMSO as solvent, 0.3 mmol 2-aminopyrazine, 1.2 equivalents aryldiazonium salt at ambient temperature over a 3 h reaction time. Under the established conditions, we examined the scope of the reaction of 2-aminopyrazine with aryldiazonium salts incorporating various electron donating and withdrawing groups (Scheme 2). Particularly, aryldiazonium salts with electron withdrawing groups in the *para* position gave excellent yields ranging between 90% to 98% of related diazobenzene product **5a-e** due to both increasing the electrophilicity and having less steric hindrance. In addition, in the presence of electron donating *tert*-butyl and alkyne functional groups in the *para* position of aryldiazonium salt, the reaction resulted in good yields of 77% and 72% for **5f** and **5g** respectively. Alternatively, due to their lower electrophilicity and greater steric hindrance, moderate yields ranging between 65% to 70% (**5i-k**) were achieved using the *meta*-substituted aryldiazonium salts.

While the reaction resulted in the expected product **5l** with moderate yield in the presence of 2-chlorophenyldiazonium salt, surprisingly, the structurally similar 2-F and 2-CF_3 substituted substrates gave the unexpected diazoamino form (**5m**,**n**) with excellent yields. As illustrated in the plausible mechanism (Scheme 3), while the nucleophilic amino group of the pyrazine attacks the electrophilic nitrogen center, the *ortho*-substituted either -F or -CF_3 fluorine atoms in the aryldiazonium salt and the hydrogen atoms of the amine come close enough to form hydrogen bonding. From here, this interaction becomes a driving force for the formation of the diazoamino form. To confirm this unexpected structure, compound **5m** was examined by single X-ray crystallography and the structure was confirmed to be the trans form with the -NH and -CF_3 groups oriented in the same direction (Figure 1). Full details regarding the crystal structure can be found given in supporting information.



Scheme 2. Aryldiazonium salt scope

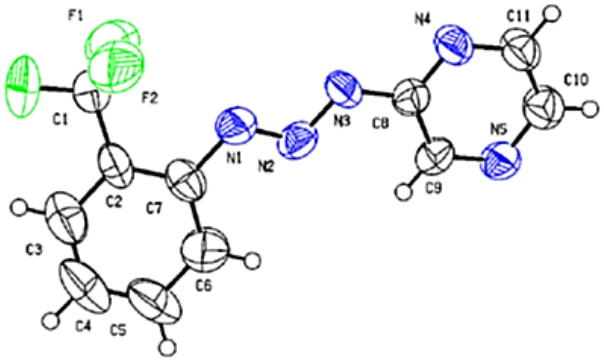


Figure 1. The X-ray crystal structure of the compound **5m**

To better understand these materials as possible dyes, UV-Vis spectrums of the compounds were recorded in ethanol and were plotted in Figure 2. Their absorption maximum point and molar absorption coefficients are also included. The absorption maxima values of the compounds range between 333 nm and 363 nm due to key π-π^* transition.[22] In order to examine the substitution effect, the observed absorbance bands and the calculated molar absorption coefficient (ε) were compared to those of **5h** compound where there was no substitution on the phenyl group of **5h**. The absorption bands are generally red-shifted in the order of **5e**, **5k**, **5n**, **5g**, **5j**, **5d**, **5c**, **5m**, **5b**, **5f**, **5i** and **5a**. Generally, as the electron donor strength increases, the absorption band maximums shifts to longer wavelengths;[23] however, here the opposite effect was observed matching the previous literature with these compounds.[24] **5i** had the biggest molar absorption coefficient, and **5k** had the lowest molar absorption coefficient among the compounds examined. It can be concluded that the compounds have more absorbance ability in the strong donor systems.

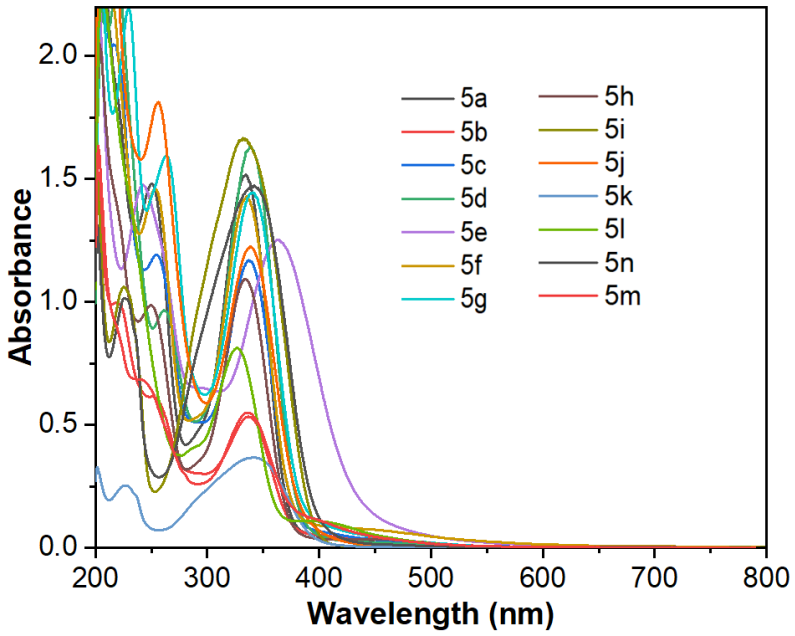


Figure 2. UV-Vis spectrum of the compounds (20 μM) in EtOH

Table 2. Maximum absorption point and molar absorption coefficient of the compounds

	Absorption Maxima (nm)	**Molar Absorption Coefficient (ε) ($cm^{-1}M^{-1}$)**
5a	334	$7{,}60*10^4$
5b	336	$2{,}60*10^4$
5c	337	$5{,}80*10^4$
5d	338	$8{,}10*10^4$
5e	363	$6{,}25*10^4$
5f	335	$7{,}12*10^4$
5g	340	$7{,}25*10^4$
5h	334	$5{,}47*10^4$
5i	334	$8{,}32*10^4$
5j	339	$6{,}10*10^4$
5k	341	$1{,}61*10^4$
5l	326	$4{,}03*10^4$
5m	336	$2{,}72*10^4$
5n	341	$7{,}35*10^4$

To better understand the interesting UV-Vis properties, calculations were performed to compare how the substituent groups affect the ΔE values (using the Wave function's Spartan 14 software with Density Functional B3LYP model and 6-31 G* basis set).[25] Here, the band gap of the compounds was also compared with that of **5h**. Figure 3 showed that the bandgaps of the compounds follow the order as **5k**<**5e**<**5b**<**5c**<**5g**<**5i**<**5j**<**5l**<**5a**<**5d**<**5h**<**5n**<**5m**. These results mostly supported the results obtained in the UV-Vis spectra analysis and suggest calculation as a viable alternative to collecting the raw data in this system. Of the compounds examined, only **5n** and **5m** showed a blue shift compared to that of **5h**. The authors postulate that this is likely attributed to broken conjugation between the arenes expected in both **5n** and **5m**.

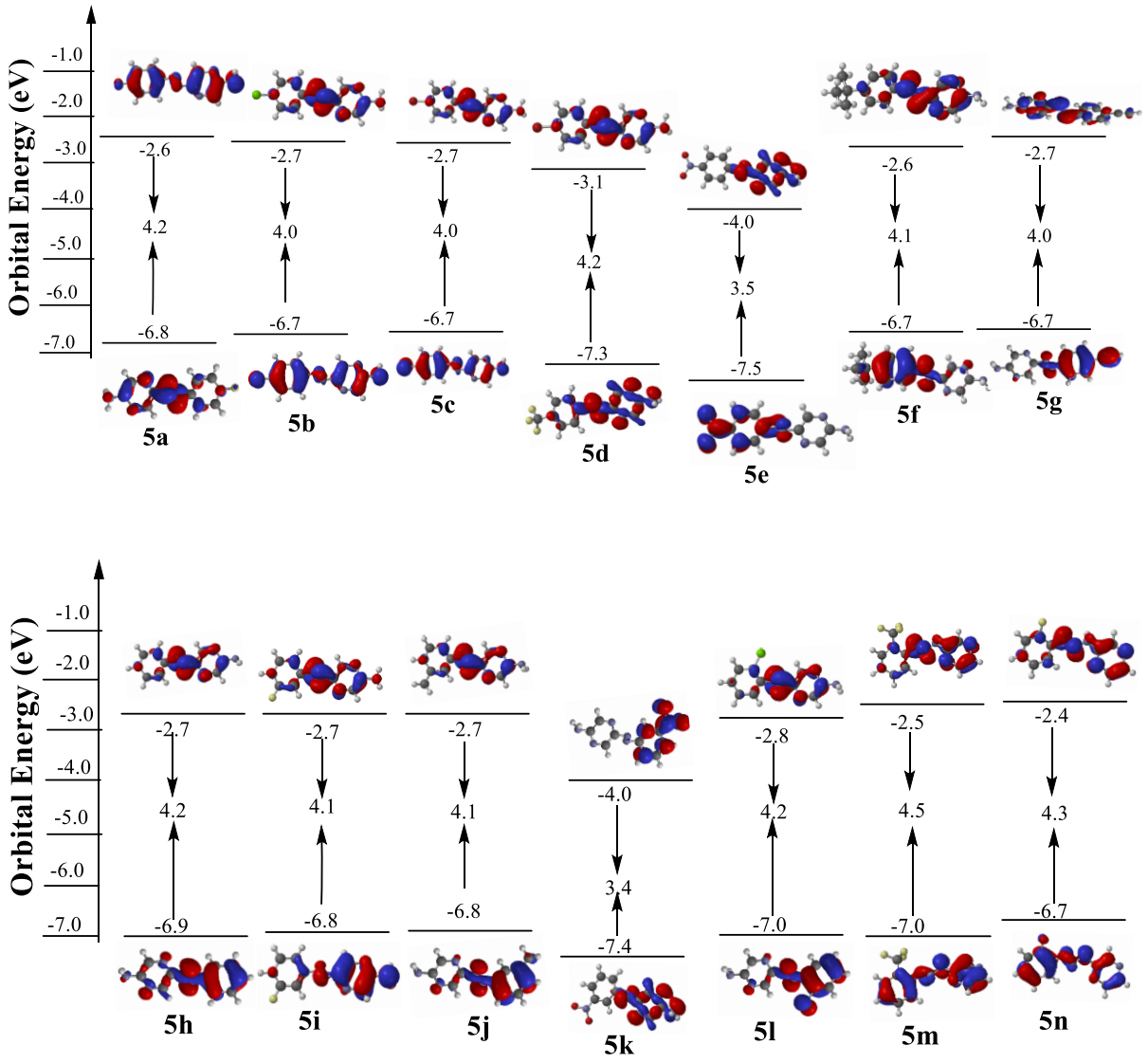
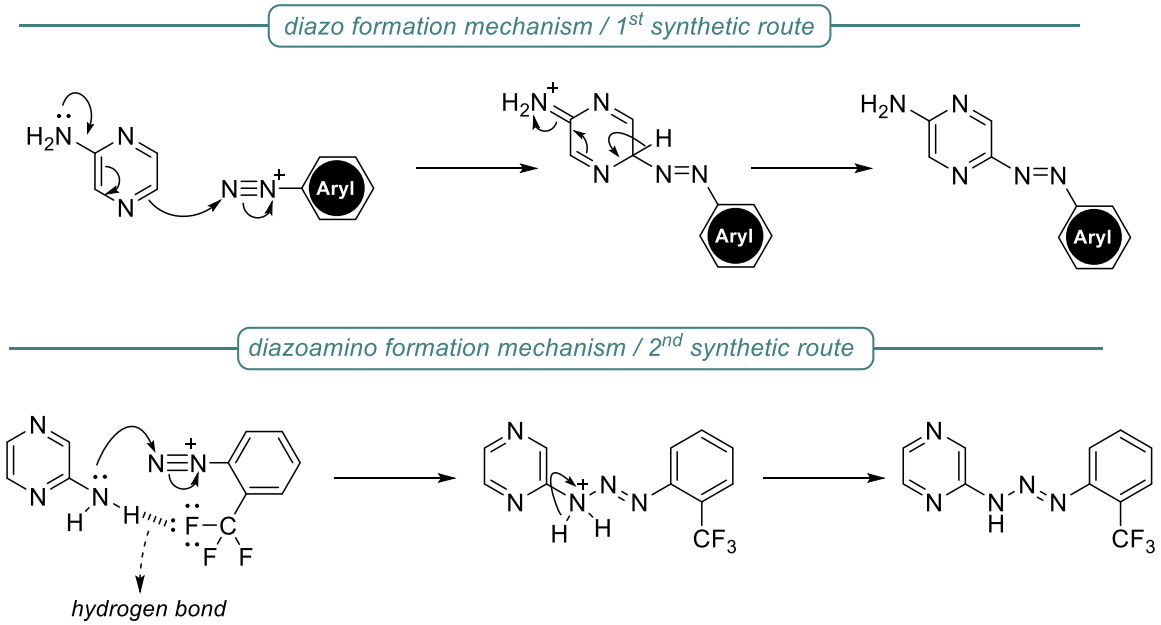


Figure 3. Molecular structure; HOMO and LUMO electron density and orbital energy level at S_0 state calculated by the DFT B3LYP/6-31G* for all compounds

To better understand the chemistry of formation, plausible mechanisms for these transformations are outlined in Scheme 3. In the first synthetic route, amine activates the 5 position of pyrazine and attack the terminal nitrogen of the -N=N^+ group to produce the diazo compounds as expected while following the electrophilic aromatic substitution mechanism. On the other hand, in the second synthetic route; where ortho substituted –F or –CF_3 aryldiazonium salts are employed, nucleophilic attack of the amine's nitrogen on the diazonium cation's terminal nitrogen takes place to yield diazoamino form. The driving force differentiating this transformation from the first synthetic pathway is anticipated to be hydrogen bond formed as the aniline and fluorine atom come into close proximity during the attack on the diazo salt.



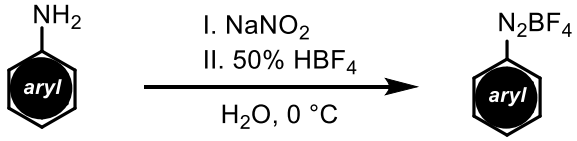
Scheme 3. Plausible mechanism

CONCLUSION

In conclusion, we have disclosed the synthesis of fully conjugated diazobenzenes and diazoaminobenzenes with aminopyrazine and a variety of aryldiazonium salts. The compounds were obtained in yields from good to excellent ranging between 65% to 98%. Unlike the other substrates, as a result of being able to form hydrogen bond between fluorine atom and amine's proton, diazonium salts containing *ortho*-substituted –F or –CF_3 gave diazoaminobenzenes by nucleophilic substitution reaction between amine of pyrazine and terminal nitrogen of the -N=N^+ group. The maximum absorbance band of the compounds were in the range of 333 nm and 363 due to π-π* transition. It may be deduced that the molecules have higher absorbance ability in the strong donor systems, which was also supported by the DFT calculation. In particular, the conjugation of the structure can be further increased from the free amine group of the pyrazine, and it also provides opportunities for different transformations such as amidation, Schiff base formation, amino coupling etc.

EXPERIMENTAL

General procedure for the preparation of aryl diazonium tetrafluoroborates



To a solution of 5.00 mmol aniline derivatives in 4 mL of distilled water was added 1.70 mL of 50% HBF_4 aq. The resultant mixture was cooled to 0 °C using ice bath and then sodium nitrite (346 mg, 5.0 mmol) was added dropwise. After stirring for 30 min, the precipitate was collected by filtration and washed

profusely with H_2O and Et_2O. Obtained crystals dried under vacuum and yielded the desired product.

General procedure of diazo(amino)benzene synthesis

2-Aminopyrazine (0.3 mmol, 1.0 equiv.) and aryldiazonium salt (0.36 mmol, 1.2 equiv.) were dissolved in 2.0 mL DMSO and stirred 3 h at rt. Extracted with EtOAc, dried over Na_2SO_4 and evaporated in vacuo. The crude was purified by silica gel column chromatography, eluting with EtOAc in hexanes to yield desired product.

(*E*)-5-((4-Fluorophenyl)diazenyl)pyrazin-2-amine (5a): Obtained as a brown solid (64 mg, 98%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (d, *J* = 2.4 Hz, 1H), 8.00 (d, *J* = 2.2 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.5 Hz, 2H), 4.77 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.57, 164.11, 162.13, 152.28, 141.07, 139.93, 134.67, 133.26 (d, *J* = 3.5 Hz), 130.11 (d, *J* = 8.4 Hz), 116.14 (d, *J* = 21.9 Hz); FT-IR (cm^{-1}) 3565, 3490, 3097, 1594, 1511, 1483, 1414, 1401, 1334, 1321, 1251, 1179, 820, 752; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9FN_5$, 218.0842; found 218.0820.

(*E*)-5-((4-Chlorophenyl)diazenyl)pyrazin-2-amine (5b): Obtained as a dark brown solid (65 mg, 92%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.04 (s, 1H), 7.99 (s, 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 2H), 4.82 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.27, 141.22, 139.60, 135.63, 135.11, 134.64, 129.51, 129.27; FT-IR (cm^{-1}) 3226, 3205, 3070, 3057, 1729, 1663, 1589, 1545, 1424, 1359, 1344, 1149, 1130, 1008, 929, 754; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9ClN_5$, 234.0546; found 234.0541.

(*E*)-5-((4-Bromophenyl)diazenyl)pyrazin-2-amine (5c): Obtained as a brown solid (70 mg, 87%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 (d, *J* = 2.3 Hz, 1H), 8.02 (d, *J* = 2.1 Hz, 1H), 7.69–7.62 (m, 4H), 4.76 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.18, 141.34, 139.61, 136.11, 134.79, 132.27, 129.78, 123.38; FT-IR (cm^{-1}) 3425, 3010, 2987, 1648, 1535, 1450, 1321, 1284, 1100, 1087, 982, 752; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9BrN_5$, 278.0041; found 278.0098.

(*E*)-5-((4-(Trifluoromethyl)phenyl)diazenyl)pyrazin-2-amine (5d): Obtained as a maroon solid (72 mg, 90%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (d, *J* = 2.4 Hz, 1H), 8.05 (d, *J* = 2.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 4.81 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.26, 141.80, 140.79, 139.08, 134.88, 131.05 (q, *J* = 32.8 Hz), 128.59, 126.03 (q, *J* = 3.7 Hz), 60.40; FT-IR (cm^{-1}) 3349, 2918, 2850, 1735, 1618, 1466, 1433, 1352, 1269, 1168, 1128, 1069, 1013, 747; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{11}H_9F_3N_5$: 268.0810, found 268.0789.

(*E*)-5-((4-Nitrophenyl)diazenyl)pyrazin-2-amine (5e): Obtained as a maroon solid (72 mg, 98%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.38 (d, *J* = 8.1 Hz, 2H), 8.11 (d, *J* = 14.7 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 4.83 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.21, 147.95, 143.61, 142.39, 137.90, 135.19, 129.18, 124.28; FT-IR (cm^{-1}) 3504, 3296, 3145, 2914, 1630, 1596, 1511, 1436, 1344, 1273, 1206, 1107, 853, 750, 699; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9N_6O_2$, 245.0787; found 245.0754.

(*E*)-5-((4-(*tert*-Butyl)phenyl)diazenyl)pyrazin-2-amine (5f): Obtained as a dark brown solid (59 mg, 77%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 4.81 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.38, 152.30, 141.08, 140.63, 134.55, 134.30, 127.75, 126.03, 34.79, 31.26; FT-IR (cm^{-1}) 3450, 2919, 2851, 1735, 1626, 1454, 1323 1265, 1156, 1102, 867, 747; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}N_5$, 256.1562; found 256.1534.

(*E*)-5-((4-Ethynylphenyl)diazenyl)pyrazin-2-amine (5g): Obtained as a pale brown solid (48 mg, 72%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07 (d, *J* = 2.4 Hz, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 4.79 (s, 2H), 3.19 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.24, 141.34, 139.82, 137.56, 134.77, 132.78, 128.08, 122.90, 83.10, 78.53; FT-IR (cm^{-1}) 3296, 3193, 30558, 2919, 2912, 1736, 1611, 1579, 1518, 1386, 1165, 1111, 1083, 962, 756; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{10}N_5$, 224.0936; found 224.0913.

(*E*)-5-(Phenyldiazenyl)pyrazin-2-amine (5h): Obtained as a brown solid (53 mg, 88%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 (d, *J* = 2.7 Hz, 1H), 8.00 (d, *J* = 2.7 Hz, 1H), 7.81–7.68 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.48-745 (m, 1H), 4.80 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.34, 140.97, 140.92, 137.21, 134.59, 129.12, 129.10, 128.09; FT-IR (cm^{-1}) 3353, 2919, 2850, 1735, 1612, 1528 1466, 1429, 1262, 1201, 1179, 1020, 971, 754; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_{10}N_5$, 200.0936; found 200.0957.

(*E*)-5-((3-Fluorophenyl)diazenyl)pyrazin-2-amine (5i): Obtained as a pale brown solid (44 mg, 68%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07 (d, *J* = 2.6 Hz, 1H), 8.02 (d, *J* = 2.6 Hz, 1H), 7.56-7.54 (m, 1H), 7.53–7.45 (m, 2H), 7.19-7.15 (m, 1H), 4.84 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.13, 162.16, 152.18, 141.42, 139.37, 134.66, 130.74 (d, *J* = 8.5 Hz), 123.65 (d, *J* = 2.8 Hz), 116.15 (d, *J* = 21.2 Hz), 115.38 (d, *J* = 22.2 Hz); FT-IR (cm^{-1}) 3485, 3275, 2952, 2824, 1730, 1629, 1554, 1443, 1404, 1373, 1231, 1179, 1033, 731; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9FN_5$, 218.0842; found 218.0819.

(*E*)-5-(*m*-Tolyldiazenyl)pyrazin-2-amine (5j): Obtained as a cream color solid (42 mg, 65%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (d, *J* = 2.6 Hz, 1H), 7.98 (d, *J* = 2.6 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.27 (s, 1H), 4.84 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.36, 141.18, 140.75, 139.02, 137.09, 134.44, 129.91, 128.91, 128.88, 124.88, 29.76; FT-IR (cm^{-1}) 3482, 3308, 2919, 2850, 1614, 1526, 1462, 1430, 1349, 1201, 1102, 978, 735; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{12}N_5$, 214.1093; found 214.1076.

(*E*)-5-((3-Nitrophenyl)diazenyl)pyrazin-2-amine (5k): Obtained as a light brown solid (51 mg, 70%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.66 (t, *J* = 1.8 Hz, 1H), 8.30 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 8.19–8.02 (m, 3H), 7.71 (t, *J* = 8.0 Hz, 1H), 4.86 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.21, 148.71, 142.18, 139.01, 137.83, 135.06, 134.12, 130.12, 123.77, 123.25; FT-IR (cm^{-1}) 3317, 2921, 2852, 1732, 1606, 1529, 1435, 1273, 1182, 990, 834, 781, 707; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9N_6O_2$, 245.0787; found

245.0781.

(*E*)-5-((2-Chlorophenyl)diazenyl)pyrazin-2-amine (5l): Obtained as a brown solid (52 mg, 74%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (dd, *J* = 8.1, 2.3 Hz, 2H), 7.58–7.52 (m, 1H), 7.47–7.41 (m, 3H), 4.57 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.54, 142.02, 139.46, 135.55, 134.02, 133.10, 131.13, 130.55, 130.24, 127.65; FT-IR (cm^{-1}) 3308, 3243, 3035, 2977, 1653, 1534, 1459, 1361, 1264, 1183, 1063, 942, 757; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9ClN_5$, 234.0546; found 234.0534.

(*E*)-2-(3-(2-(Trifluoromethyl)phenyl)triaz-2-en-1-yl)pyrazine (5m): Obtained as a light brown solid (76 mg, 95%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.19 (s, 1H), 9.05 (s, 1H), 8.50 (s, 1H), 8.39 (d, *J* = 2.2 Hz, 1H), 7.78 (dd, *J* = 7.9, 2.4 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.65, 146.64, 141.61, 139.22, 132.76 (d, *J* = 10.0 Hz), 127.87, 126.63 (d, *J* = 5.4 Hz), 125.02, 122.85, 118.58, 116.71; FT-IR (cm^{-1}) 3345, 3069, 2952, 2854, 1709, 1561, 1450, 1424, 1314, 1268, 1120, 1054, 1034, 757; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{11}H_9F_3N_5$, 268.0810; found 268.0806.

(*E*)-2-(3-(2-Fluorophenyl)triaz-2-en-1-yl)pyrazine (**5n):** Obtained as a light brown solid (59 mg, 91%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.75 (s, 1H), 8.98 (s, 1H), 8.36 (d, *J* = 9.3 Hz, 2H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.35–7.31 (m, 1H), 7.22 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.81, 142.05, 139.28, 132.96, 129.42 (d, *J* = 8.3 Hz), 124.89, 124.57 (d, *J* = 3.7 Hz), 119.37, 116.91, 116.75; FT-IR (cm^{-1}) 3334, 2917, 2850, 1730, 1571, 1488, 1467, 1418, 1381, 1267, 1194, 1179, 747; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9FN_5$, 218.0842; found 218.0832.

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