First Evidence for Wheland Intermediates in Azo-Coupling Reactions − Reactions between 1,3,5-Tris(dialkylamino)benzene and Arenediazonium Salts

Carla Boga,[a] Erminia Del Vecchio,[a] and Luciano Forlani*[a]

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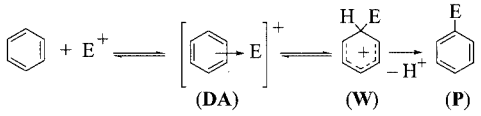
We have investigated reactions between 1,3,5-tris(1-piperidyl)benzene and 1,3,5-tris(4-morpholinyl)benzene and 4-substituted arenediazonium tetrafluoroborate salts, mainly by NMR spectroscopic measurements. The main products are σ complexes (Wheland-like intermediates) which are formed in almost quantitative yields and are moderately stable compounds. From these covalent complexes, products of the azo-coupling reaction may be obtained as salts or as free bases.

Introduction

The general pathway of the electrophilic aromatic substitution reaction[1,2] (Scheme 1) involves a first fast equilibrium between the electron-rich aromatic substrate and the electron-deficient reagent. The formation of the donor−acceptor complex[3,4] (or π complex, **DA**) is followed by another equilibrium (or an irreversible step) producing the σ complex (the Wheland intermediate, **W**).[5] From **W** the substitution products **P** are obtained by proton loss in a step which is usually considered, for the azo-coupling reaction, to be irreversible[1,4] and a fast step. Generally, the rate-limiting step of the overall reaction is considered to be the formation of the σ adduct **W**.[4] In Scheme 1, the transformation **DA** → **W** is the rate-limiting step. The formation of a donor−acceptor complex is corroborated by numerous spectroscopic transient observations or by isolation.[3]

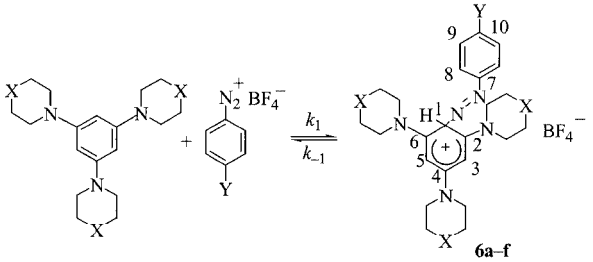


Scheme 1

It is of interest to note that in SN_{Ar} reactions, the presence of donor−acceptor complexes[6] was proposed to enhance the reactivity of the substrate in solvents of low polarity. In fact, both terms "substrate" and "reagent" are conventional in character.[7] In practice, the same behaviour observed in so-called nucleophilic substitution reactions may also be observed in electrophilic substitution reactions. The observation of Wheland complexes is a rare experimental feature,[8] because Wheland intermediates are considered to exist only in very low concentrations as the steady-state theory requires.

Isolation or spectroscopic observation of σ complexes is possible when strong electron-donating groups are bonded to the benzene ring.[9] In particular, σ complexes in azo-coupling reactions[10] have not been directly observed so far, although in the literature[11] complexes arising from azo coupling between *p*-benzoquinone diazide and 2,6-dialkylphenols were not isolated, but only hypothesized on the basis of kinetic data.

Now we report the direct observation (in ^1H NMR spectroscopy) of Wheland complexes in the reactions of 1,3,5-tris(1-piperidyl)benzene and 1,3,5-tris(4-morpholinyl)benzene and arenediazonium tetrafluoroborate salts, and their transformation into the corresponding azo dyes, as reported in Scheme 2.



	6a	6b	6c	6d	6e	6f
X	CH_2	CH_2	CH_2	O	O	O
Y	OCH_3	NO_2	Br	OCH_3	NO_2	Br

Scheme 2

Results and Discussion

When compound **1** (or **2**) was dissolved in CD_3CN and mixed, directly in the NMR spectroscopy tube, with a

[a] Dipartimento di Chimica Organica "A. Mangini"
Viale Risorgimento 4, 40136 Bologna, Italia
Fax: (internat.) + 39-051-2093654
E-mail: forlani@ms.fci.unibo.it

Table 1. ^{1}H NMR selected spectroscopic data in $CDCl_3$ (unless otherwise indicated), at 20 °C of compounds of Schemes 2 and 3

	δ1-H	δ3,5-H[a]	δ8,9-H[a]	J_{8-9} [Hz]	δH_{OCH3}	δH_{NH}	Others[b]
1	6.11						1.52−1.73 (m, 18 H), 3.01−3.11 (m, 12 H)
2	6.07						3.11−3.16 (NCH_2, 12 H), 3.82−3.87 (OCH_2, 12 H)
6a[c]	6.42	5.50	7.10, 7.70	8.8	3.92		1.54−1.81 (m, 18 H), 3.52−3.82 (m, 12 H)
6b[c]	6.71	5.50	7.89, 8.42	8.7			1.54−1.82 (m, 18 H), 3.43−3.85 (m, 12 H)
6c[c]	6.55	5.50	7.62, 7.79	8.9			1.47−1.81 (m, 18 H), 3.41−3.91 (m, 12 H)
6d[c]	6.48	5.50	7.11, 7.73	9.2	3.91		3.45−3.80 (m, 24 H)
6e[c]	6.72	5.53	7.89, 8.42	9.1			3.61−3.76 (m, 24 H)
6f[c]	6.60	5.51	7.64, 7.79	9.0			3.43−3.95 (m, 24 H)
7a		5.81, 6.13	6.94, 7.25	9.0	3.81	12.51	1.42−1.99 (m, 18 H), 2.85−2.93 (m, 2 H), 3.31−3.35 (m, 2 H), 3.55−3.63 (m, 4 H), 3.66−3.73 (m, 4 H)
7b		5.71, 6.09	7.37, 8.19	9.8		11.89	1.65−1.89 (m, 18 H), 2.89−2.99 (m, 2 H), 3.41−3.52 (m, 2 H), 3.59−3.66 (m, 4 H), 3.73−3.81 (m, 4 H)
7c		5.71, 6.02	7.10, 7.39	8.7		11.99	1.58−1.89 (m, 18 H), 2.75−2.86 (m, 2 H), 3.25−3.34 (m, 2 H), 3.52−3.57 (m, 4 H), 3.62−3.68 (m, 4 H)
7d		5.91, 6.17	6.95, 7.26	8.6	3.77	12.47	3.06−3.09 (m, 2 H), 3.22−3.26 (m, 2 H), 3.69−4.06 (m, 20 H)
7e[d]		5.89, 6.09	7.56, 8.31	9.2		11.85	3.04−3.15 (m, 2 H), 3.31−3.39 (m, 2 H), 3.77−4.03 (m, 20 H)
7f[d]		5.89, 6.09	7.37, 7.61	8.8		11.95	3.07−3.11 (m, 2 H), 3.29−3.33 (m, 2 H), 3.75−4.04 (m, 20 H)
8a		6.27	6.98, 7.88	8.9	3.87		1.53−1.78 (m, 18 H), 2.98−3.12 (m, 8 H), 3.21−3.28 (m, 4 H)
8b		5.97	7.82, 8.25	9.2			1.56−1.82 (m, 18 H), 3.11−3.18 (m, 8 H), 3.37−3.44 (m, 4 H)
8c		6.15	7.53, 7.73	9.0			1.58−1.72 (m, 18 H), 3.02−3.06 (m, 8 H), 3.29−3.32 (m, 4 H)
8d		6.27	6.99, 7.83	9.0	3.88		3.05−3.08 (m, 8 H), 3.24−3.27 (m, 4 H), 3.81−3.83 (m, 8 H), 3.86−3.89 (m, 4 H)
8e		6.06	7.82, 8.29	9.0			3.09−3.15 (m, 8 H), 3.29−3.34 (m, 4 H), 3.78−3.87 (m, 12 H)
8f		6.18	7.57, 7.67	9.0			3.09−3.12 (m, 8 H), 3.29−3.32 (m, 4 H), 3.82−3.89 (m, 12 H)

[a] Doublets, interchangeable assignment. [b] Piperidine or morpholine moiety. [c] In CD_3CN at $T = -30$ °C. [d] In CD_3CN.

CD_3CN solution containing an equimolar amount (with respect to **1**) of arenediazonium tetrafluoroborate **3** (or **4**, or **5**), a spectrum consistent with the structure of the σ complexes **6a**−**f** was recorded (see Scheme 2). ^{1}H NMR spectroscopic data of these σ complexes are presented in Table 1. The major peculiarity of ^{1}H NMR spectra regarding the tris(amino)benzene moiety of the Wheland intermediates is the presence of two slightly broad singlets in the region at δ = 6.5 and 5.5 ppm, which integrate as 1 and 2 protons, respectively. These signals are related to CH of C-1 (sp^3) and to CH of C-3 and -5, respectively, of complexes **6a**−**f**.

In the case of reaction between **1** and **3**, when the reaction is carried out in an acetone/CH_2Cl_2 mixture (8:2) at −90 °C, compound **6a** was separated as a semi-solid by precipitation with *n*-hexane. Compound **6a** was quickly collected and dissolved in CD_3CN to record its ^{13}C NMR spectrum, which is reported in Table 2. In particular, this spectrum shows a signal at δ = 68 ppm, which may be assigned (with the support of DEPT experiments) to C-1 of **6a**. Attempts to obtain ^{13}C NMR spectroscopic data of other complexes **6b**−**f** failed.

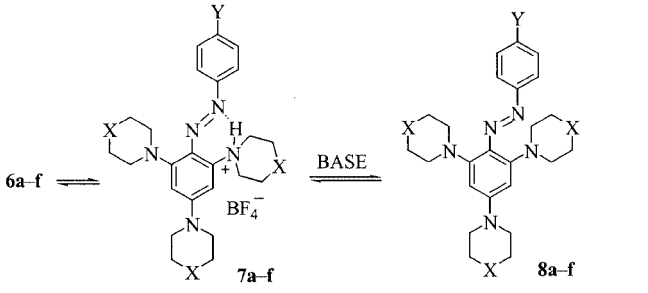
Compounds **6a**−**f** are unstable and they spontaneously produce, in high yields, salts **7a**−**f**, as reported in Scheme 3. Spectroscopic data of compounds **7a**−**f** are also presented in Table 1 and 2. The attribution of an acidic proton (δ ≈ 12 ppm) bonded to the nitrogen atom of the heterocycle bonded in position 2 with respect to the aza group is obtained from ^{1}H NMR spectroscopic data. In particular, the different values of chemical shifts observed for protons and carbon atoms bonded in positions 3 and 5 of compounds **7a**−**f** (see Tables 1 and 2) clearly indicate that in these salts the proton cannot be bonded to the nitrogen atoms of the azo group or to the heterocyclic nitrogen atom bonded in position 4 because, in such cases, 3-H and 5-H and their related carbon atoms should be equivalent. In principle, other positions for the proton in compounds **7a**−**f** are also possible, but the present spectroscopic data agree with structures **7a**−**f** depicted in Scheme 3 even if, by comparing spectroscopic data of compounds **7a**−**f** with those of the corresponding neutral forms **8a**−**f**, it is evident that the protonation of one amino substituent (producing an electron-accepting ammonium group) leads to an unexpected shielding of 3-H compared to that of compounds **8a**−**f**. Probably, such protons of compounds **7a**−**f** are relatively free to shift to other positions,[12] for instance to the aza nitrogen atoms. Acidic proton mobility, which represents an interesting behaviour, is also suggested by the moderate broadness of the 3-H and 5-H signals. The only reasonable explanation of this shielding feature, in our opinion, is the possibility that the positive charge is far from aromatic ring carbon atoms.

In agreement with ^{1}H NMR spectroscopic data, UV/Vis spectroscopic inspection of the reaction mixtures of **1** (or **2**) and **3**, **4** and **5** (in equimolar amount, in the range from 2×10^{-5} to 1×10^{-4} mol·dm^{-3}) shows the immediate appearance of a maximum of absorbance which is related to the Wheland complexes [**6a**: $\lambda_{max.}$ = 430 nm (log ε = 4.05); **6b**: $\lambda_{max.}$ = 425 nm (log ε = 4.30); **6c**: $\lambda_{max.}$ = 431 nm (log ε = 4.10); **6d**: $\lambda_{max.}$ = 415 nm (log ε = 4.48)]. This maximum spontaneously and slowly evolves to an absorbance maximum value of the related substitution products **7a**−**d**

Table 2. ^{13}C NMR spectroscopic data in $CDCl_3$

	δC-1	δC-2	δC-3,5[a]	δC-8,9[a]	δC_{OCH3}	δC-α,α′,α′′[a] [b]	δC-β,β′,β′′ [a][b]	δC-γ,γ′,γ′′ [a][b]	δC[c]
1	153.78	99.02				51.38	26.0	24.35	
2	153.17	97.23				49.91	66.93		
6a	68.32		85.06	114.56, 124.49	55.51	48.88, 49.43	25.78, 26.21	23.75, 23.84	135.70, 157.43, 158.31, 163.15
7a[d]			92.37, 98.46	115.23, 116.99	55.65	49.63, 51.94, 52.52	25.86, 26.21, 26.27	23.20, 23.91, 24.11	124.24, 135.56, 151.58, 157.66, 158.17, 160.01
7b			90.98, 98.62	114.62, 125.78		50.35, 51.29, 51.88	25.60, 26.21, 26.46	23.41, 23.85, 24.01	129.46, 143.02, 147.31, 151.33, 159.18, 159.45
7c			91.49, 98.32	116.72, 132.65		49.91, 51.57, 52.19	25.72, 26.25, 26.32	23.30, 23.86, 24.02	117.19, 125.96, 140.89, 151.64, 158.59, 159.85
7d			92.56, 98.32	115.27, 117.27	55.63	48.18, 50.82, 51.43	66.32, 66.46, 66.79		123.31, 134.83, 151.81, 157.97, 158.92, 159.87
7e[e]			91.15, 97.77	115.34, 125.65		48.70, 50.38, 50.96	65.69, 66.13, 66.41		128.04, 143.60, 147.05, 151.16, 159.77, 159.86
7f[e]			91.55, 97.55	117.57, 132.54		48.37, 50.53, 51.16	65.76, 66.11, 66.45		116.94, 125.18, 141.15, 151.39, 159.56, 159.98
8a[d]			99.97	113.85, 123.24	55.41	50.05, 54.36	25.74, 26.37	24.45, 24.56	124.00, 131.50, 149.50, 153.14, 160.22
8b			95.12	121.42, 124.70		48.70, 53.86	25.60, 26.17	24.45, 24.48	128.31, 145.10, 152.91, 155.30, 159.58
8c			97.89	123.25, 131.69		49.28, 54.31	25.59, 26.21	24.38, 24.46	121.22, 129.24, 150.92, 153.71, 153.94
8d			99.43	114.47, 123.47	55.52	48.69, 53.35	66.74, 67.16		131.63, 148.14, 148.44, 152.51, 160.86
8e			95.82	121.75, 124.82		47.49, 53.12	66.51, 67.02		128.63, 146.22, 151.43, 154.99, 158.44
8f			97.89	123.25, 132.09		48.09, 53.40	66.63, 67.10		122.57, 129.77, 149.66, 153.16, 153.58

[a] Interchangeable assignment. [b] δC-α,α′,α′′, δC-β,β′,β′′, and δC-γ,γ′,γ′′ (the last is absent in the case of compounds bearing morpholine rings) values are referred to the relative position of the carbon atom with respect to the heterocyclic nitrogen atom of nonequivalent piperidine or morpholine rings. [c] Signals corresponding to quaternary carbon atoms. [d] $T = 40$ °C [e] In CD_3CN.



	7a	7b	7c	7d	7e	7f	8a	8b	8c	8d	8e	8f
X	CH_2	CH_2	CH_2	O	O	O	CH_2	CH_2	CH_2	O	O	O
Y	OCH_3	NO_2	Br	OCH_3	NO_2	Br	OCH_3	NO_2	Br	OCH_3	NO_2	Br

Scheme 3

[**7a**: $\lambda_{max.} = 478$ nm (log ε = 4.49); **7b**: $\lambda_{max.} = 445$ nm (log ε = 4.65); **7c**: $\lambda_{max.} = 448$ nm (log ε = 4.31); **7d**: $\lambda_{max.} = 487$ nm (log ε = 4.35)].

Also in the case of the experimental conditions used for UV/Vis spectrophotometric measurements, the formation of complexes **6a**−**f** is a fast process, while the formations of the substitution compounds from the Wheland intermediate occur in a slow step.

From salts **7a**−**f**, compounds **8a**−**f** may be obtained by addition of different bases (NaOH, Et_3N, DABCO) but the better yields (about quantitative) were obtained by percolation of **7a**−**f** on a basic Al_2O_3 column (see Exp. Sect.). Some spectroscopic properties of compounds **8a**−**f** are also reported in Tables 1 and 2.

Usually,[12,13] in polymethyl- and polymethoxy-substituted benzenes, when a carbon atom changes its hybridization from sp^2 to sp^3 (because of its protonation) the signal of the bonded hydrogen atoms are shifted toward higher field, but at lower field than those of the aliphatic CH_2 group.

Complexes **6a**−**f** show the signal related to 1-H, bonded to the sp^3 carbon atom, shifted toward lower field than that of the starting materials, by about 0.5 ppm. Probably, the presence of the positive charge and of the heteroatoms balances the chemical shift difference due to the hybridization change. When electrophiles other than protons are used in forming σ complexes, such as halogens,[14] acyl or sulfonyl chlorides,[15] the sp^3 C−H proton chemical shift may be near to that of the starting material, or slightly shifted toward lower field.

As expected by considering the loss of aromaticity in the **W** intermediates (with respect to the starting amines), the 3-H and 5-H signals of compounds **6a**−**f** move up-field in

forming intermediate **W**, in spite of the introduction of the positive charge, which, probably, is localized on the nitrogen atoms, and thus away from the ring. This behaviour agrees with that observed for other electrophilic reagents which produce the same effect in forming **W** complexes.[14,15]

It is noteworthy that the complexes are present in detectable amounts as only one isomer. For instance, no evidence for an attack on nitrogen atoms was found.

Electrophilic aromatic substitution reactions (as well as electrophilic addition to the double bond of alkenes) proceed with common initial steps, involving the formation of a donor−acceptor complex, followed by the formation of the covalent complex (σ complex), as reported in Scheme 1. Under our experimental conditions, we were not able to collect evidence for the presence of **DA** complexes because the formation of **W** complexes is very fast. Finally, the present system is a strongly activated system: in fact, the presence of strong electron-donating groups stabilizes the positively charged complex. Proton loss becomes the rate-determining step in obtaining the products of the diazo-coupling reaction.

Experimental Section

General Remarks: The ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini 300 spectrometer at 300 and 75.46 MHz, respectively. The ^1H NMR spectra were recorded in $CDCl_3$ or CD_3CN. Chemical shifts were measured in δ (ppm) with reference to the solvent (δ = 7.27 and 77.0 ppm for $CDCl_3$ and δ = 2.0 and 0.3 ppm for CD_3CN for ^1H and ^{13}C NMR, respectively). *J* values are given in Hz. Signal multiplicities were established by DEPT experiments. Chromatographic purifications were carried out on columns of aluminum oxide, activated, basic, Brockmann I, standard grade ca. 150 mesh (Aldrich) at medium pressure. UV/Vis spectrophotometric data were recorded with a Perkin−Elmer (model Lambda 12) spectrophotometer. EI-MS and high-resolution results were obtained with a Kratos MS80 mass spectrometer equipped with a home-built data system. ESI-MS spectra were recorded with a WATERS 2Q 4000 instrument. Melting points were measured with a Büchi 535 apparatus and are uncorrected.

Materials: 1,3,5-Tris(dialkylamino)benzenes **1** and **2** were prepared from 1,3,5-trichlorobenzene (Sigma−Aldrich) with a modification of the literature[16] method. Compound **1** was purified on an Al_2O_3 chromatographic column (eluent: light petroleum/diethyl ether, 80:20) and crystallized from $CHCl_3$; m.p. 178−181 °C [ref.[16] oil; ref.[17] 183−184 °C (from acetone)]. ES+: *m*/*z* = 328. Compound **2** was obtained by extracting the reaction mixture with water and dichloromethane; m.p. 306−310 °C (from chloroform) (ref.[17] 308−312 °C). ES+: *m*/*z* = 334. The arenediazonium tetrafluoroborate salts were commercial materials (Sigma−Aldrich).

Reaction between Arenediazonium Tetrafluoroborates 3, 4, 5 and 1,3,5-Tris(dialkylamino)benzenes 1, 2. General Procedure for the Synthesis of Compounds 7a−f: 1,3,5-Tris(dialkylamino)benzene (0.092 mmol) was dissolved in CH_3CN (2 mL) and cooled to −30 °C; then the arenediazonium salt (0.092 mmol) was added. Immediately after mixing, a yellow colour developed and the solution was stirred for 20 min; in this interval the colour turned to red. TLC analysis (eluent: light petroleum/diethyl ether, 50:50) showed the disappearance of the starting 1,3,5-tris(dialkylamino)benzene. After removal of the solvent in vacuo, the crude product was dissolved in CH_2Cl_2 (2 mL) and the compounds **7a−f** were precipitated by adding Et_2O. The products **7a−f** were isolated as dark-red solids in 80−90% yield and crystallized from CH_2Cl_2 and *n*-hexane. ^1H and ^{13}C NMR spectra of compounds **7a−f** are reported in Tables 1 and 2; other chemico-physical data are reported as follows.

1-[2-(4-Methoxyphenylazo)-3,5-dipiperidin-1-ylphenyl]piperidinium Tetrafluoroborate (7a): 45.5 mg, 90% yield, m.p. 199−201 °C. $C_{28}H_{40}BF_4N_5O$ (549.46): calcd. C 61.21, H 7.34, N 12.75; found C 61.19, H 7.36, N 12.73. ES+: *m*/*z* = 462. ES−: *m*/*z* = 87.

1-[2-(4-Nitrophenylazo)-3,5-dipiperidin-1-ylphenyl]piperidinium Tetrafluoroborate (7b): 41.5 mg, 80% yield, m.p. 169−171 °C. $C_{27}H_{37}BF_4N_6O_2$ (564.43): calcd. C 57.46, H 6.61, N 14.89; found C 57.43, H 6.64, N 14.91. ES+: *m*/*z* = 477. ES−: *m*/*z* = 87.

1-[2-(4-Bromophenylazo)-3,5-dipiperidin-1-ylphenyl]piperidinium Tetrafluoroborate (7c): 46.8 mg, 85% yield, m.p. 146−148 °C. $C_{27}H_{37}BBrF_4N_5$ (598.33): calcd. C 54.20, H 6.23, N 11.70; found C 54.18, H 6.26, N 11.68. ES+: *m*/*z* = 512. ES−: *m*/*z* = 87.

4-[2-(4-Methoxyphenylazo)-3,5-dimorpholin-4-ylphenyl]morpholin-4-ium Tetrafluoroborate (7d): 45.0 mg, 88% yield, m.p. 116−118 °C. $C_{25}H_{34}BF_4N_5O_4$ (555.38): calcd. C 54.07, H 6.17, N 12.61; found C 54.05, H 6.20, N 12.62. ES+: *m*/*z* = 468. ES−: *m*/*z* = 87.

4-[3,5-Dimorpholin-4-yl-2-(4-nitrophenylazo)phenyl]morpholin-4-ium Tetrafluoroborate (7e): 42.0 mg, 80% yield, m.p. 157−159 °C, ES+: *m*/*z* = 483, $C_{24}H_{31}BF_4N_6O_5$ (570.35): calcd. C 50.54, H 5.48, N 14.73; found C 50.53, H 5.50, N 14.76. ES−: *m*/*z* = 87.

4-[2-(4-Bromophenylazo)-3,5-dimorpholin-4-ylphenyl]morpholin-4-ium Tetrafluoroborate (7f): 46.7 mg, 84% yield, m.p. 156−158 °C. $C_{24}H_{31}BBrF_4N_5O_3$ (604.25): calcd. C 47.71, H 5.17, N 11.59; found C 47.69, H 5.20, N 11.56. ES+: *m*/*z* = 518. ES−: *m*/*z* = 87.

Preparation of Compounds 8a−f: The products **8a−f** were isolated in quantitative yield by column chromatography (basic aluminum oxide) of compounds **7a−f** (eluent: light petroleum/diethyl ether, 80:20) and crystallized from CH_2Cl_2 and *n*-hexane. ^1H and ^{13}C NMR spectra of compounds **8a−f** are reported in Tables 1 and 2; other chemico-physical data are reported as follows.

1-(4-Methoxyphenyl)-2-(2,4,6-tripiperidin-1-ylphenyl)diazene (8a): M.p. 155−157 °C. $C_{28}H_{39}N_5O$ (461.65): calcd. C 72.85, H 8.52, N 15.17; found C 72.80, H 8.54, N 15.20. ES+: *m*/*z* = 462. MS: *m*/*z* (%) = 461 (1) [M^+], 340 (13), 339 (52), 338 (100), 326 (6), 135 (2), 123 (42), 121 (3). HRMS: *m*/*z* = 461.3142, calcd. for $C_{28}H_{39}N_5O$ 461.3155.

1-(4-Nitrophenyl)-2-(2,4,6-tripiperidin-1-ylphenyl)diazene (8b): M.p. 204−206 °C. $C_{27}H_{36}N_6O_2$ (476.62): calcd. C 68.04, H 7.61, N 17.63; found C 68.00, H 7.63, N 17.68. ES+: *m*/*z* = 477. MS: *m*/*z* = 340 (4) [$M^+ - NC_6H_4NO_2$], 339 (26), 338 (100), 337 (14), 326 (6), 138 (77). HRMS: [M^+] not available.

1-(4-Bromophenyl)-2-(2,4,6-tripiperidin-1-ylphenyl)diazene (8c): M.p. 174−177 °C. $C_{27}H_{36}BrN_5$ (510.52): calcd. C 63.52, H 7.11, N 13.72; found C 63.48, H 7.14, N 13.70. ES+: *m*/*z* = 512. MS: *m*/*z* = 511 (0.9) [M^+ + 2], 509 (0.9) [M^+], 340 (24), 339 (70), 338 (29), 336 (4), 185 (2), 183 (1), 173 (13), 171 (13).

1-(4-Methoxyphenyl)-2-(2,4,6-trimorpholin-4-ylphenyl)diazene (8d): M.p. 193−195 °C. $C_{25}H_{33}N_5O_4$ (467.57): calcd. C 64.22, H 7.11, N 14.98; found C 64.19, H 7.13, N 14.95. ES+: *m*/*z* = 468. MS:

m/*z* = 467 (3) [M^+], 348 (12) 346 (16), 345 (53), 135 (3), 123 (17). HRMS: *m*/*z* = 467.2527, calcd. for $C_{25}H_{33}N_5O_4$ 467.2533.

1-(4-Nitrophenyl)-2-(2,4,6-trimorpholin-4-ylphenyl)diazene (8e): M.p. 233−235 °C. $C_{24}H_{30}N_6O_5$ (482.54): calcd. C 59.74, H 6.27, N 17.42; found C 59.69, H 6.29, N 17.44. ES+: *m*/*z* = 483. MS: *m*/*z* = 482 (0.8) [M^+], 348 (10), 346 (15), 345 (50), 150 (2), 138 (20).

1-(4-Bromophenyl)-2-(2,4,6-trimorpholin-4-ylphenyl)diazene (8f): M.p. 194−196 °C. $C_{24}H_{30}BrN_5O_3$ (516.44): calcd. C 55.82, H 5.86, N 13.56; found C 55.78, H 5.87, N 13.59. ES+: *m*/*z* = 518. MS: *m*/*z* = 517 (0.7) [$M^+ + 2$], 515 (0.7) [M^+], 348 (12), 346 (16), 345 (45).

Study of the Formation of σ Complexes 6a−f by ^{1}H NMR Spectroscopy: Arenediazonium tetrafluoroborate (0.025 mmol) was dissolved in CD_3CN (0.5 mL) and cooled to −30 °C. This solution was added to a solution of 1,3,5-tris(dialkylamino)benzene (0.025 mmol) in CD_3CN (0.5 mL), directly prepared in a ^{1}H NMR spectroscopy tube at −30 °C. The ^{1}H NMR spectrum was recorded at −30 °C at various time intervals but generally as rapidly as possible at the start of the reaction and then at progressively longer intervals as the reaction proceeded. The system was monitored until no further change could be detected in the recorded spectrum. Table 1 shows the signals of intermediates that were assigned to compounds **6a−f**. The signals of compounds **6a−f** were present in the spectrum immediately after the addition of diazonium salt and gradually decayed with time as new signals of compounds **7a−f** appeared.

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