2-Alkyl-1,2,3,4-benzotetrazinium Salts: Synthesis and NMR Studies of the Novel 2-Alkyl-1,2,3,4-tetrazinium/*ortho*-(Alkylazo)diazonium Equilibrium

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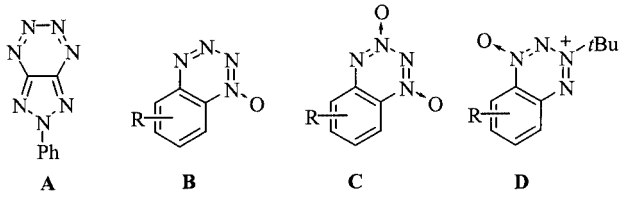
The diazotization of anilines bearing the *ortho*-alkylazo group resulted in benzenediazonium salts **3**, which exist in equilibrium with the 2-alkyl-1,2,3,4-benzotetrazinium salt cyclic isomers **4**. The structures of **3** and **4** were confirmed by ^{1}H, ^{13}C, and ^{15}N NMR studies. The relative proportions of the cyclic and open-chain forms were determined by a ^{1}H NMR study. The **3** ⇄ **4** equilibrium is fast on the NMR timescale, and only one set of signals is observed in the ^{1}H and ^{13}C NMR spectra. The equilibrium strongly depends on the substituents on the aromatic ring, while being practically unaffected by the substituents (methyl or *tert*-butyl) on the azo group. Some of the investigated salts exist only in the cyclic form (**4f**, **4g**), others only in the open-chain form (**3k**).

Introduction

Fully unsaturated 1,2,3,4-tetrazines are among the basic six-membered azaaromatics,[1] but are nevertheless poorly investigated.[2] Only annulated representatives of this class are available: triazolo-annulated 1,2,3,4-tetrazine[3] **A**, benzo-annulated 1,2,3,4-tetrazine 1-*N*-oxides[4] **B**, benzo- (**C**), and furazano-annulated 1,2,3,4-tetrazine 1,3-di-*N*-oxides,[5] and 2-alkyl-1,2,3,4-benzotetrazinium 4-*N*-oxide salts **D**.[4]



A **B** **C** **D**

E cyclic form ⇌ **E′** open-chain form

Here a new type of 1,2,3,4-tetrazine derivative, the 2-alkyl-1,2,3,4-benzotetrazinium salts **E**, has been investigated. A priori, these cycles could exist in equilibrium with the open-chain diazonium salts **E′**.[6]

Results and Discussion

Synthesis

Diazonium tetrafluoroborates **3a**−**j** and **3k** were synthesized by diazotization of azoanilines **2a**−**j** and aminoazopyridine **2k**, respectively, with nitrosonium tetrafluoroborate (Scheme 1 and Scheme 2). The starting azoanilines **2a**−**i** were obtained by reduction of the appropriate (alkyl-*NNO*-azoxy)anilines **1a**−**i** with $LiAlH_4$ (Scheme 1). The preparation of these latter azoxyanilines has been described recently,[7] except for that of **1g**. This was obtained by chlorination of **1a** with a HCl/H_2O_2 mixture. Azoaniline **2j**[8,8a] and aminoazopyridine **2k**[9] were obtained by literature procedures.

In salts **3**, intramolecular interaction between the diazonium group and the *ortho*-azo group could result in the formation of 1,2,3,4-tetrazinium cyclic species to afford salts **4**. This reaction could be reversible, with the equilibrium depending on the substituents R on the azo group and X on the aromatic ring.

NMR Study

The diazonium tetrafluoroborate **3j**, with the phenyl group as an azo-substituent, was described previously by A. Katritzky.[8] This salt was assigned the structure of an open-chain tautomer on the basis of its IR spectrum (KBr,

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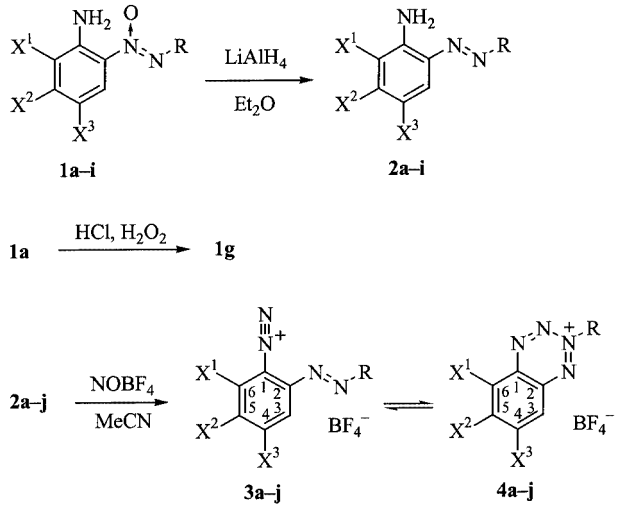
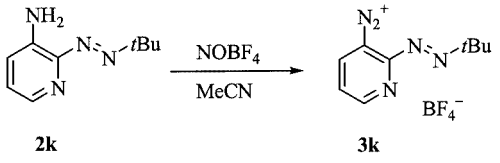


	a	b	c	d	e	f	g	h	i	j
R	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	Me	Me	Ph
X^1	H	H	H	H	H	Br	Cl	H	Br	H
X^2	H	H	Br	H	Me	H	H	H	H	H
X^3	H	Br	H	Me	H	Br	Cl	H	Br	H

Scheme 1



Scheme 2

$\tilde{\nu}$ = 2300 cm^{-1}, N_2^+). We additionally confirmed this structure from its IR spectrum in solution[10] (acetone, $\tilde{\nu}$ = 2290 cm^{-1}, N_2^+) and its ^{14}N NMR spectrum. The latter exhibits a signal typical of a diazonium group at δ = −153 ppm (−*N*≡N^+).[11] Salt **3j** was also studied by ^1H and ^{13}C NMR, full assignment of signals being carried out by HSQC-qs and HMBC-qs experiments. The signals practically did not change their positions when the sample was cooled from 293 to 273 K, indicating that no cyclic structure was formed.

Similarly, the pyridinediazonium salt **3k**, with the *tert*-butyl group as an azo-substituent, exists only in the open-chain form. Its structure was confirmed by its IR spectra in the solid state (KBr, $\tilde{\nu}$ = 2250 cm^{-1}, N_2^+) and in solution (acetone, $\tilde{\nu}$ = 2240 cm^{-1}, N_2^+), by its ^{14}N NMR spectrum (δ = −195 ppm, −*N*≡N^+), and by its ^{15}N NMR/INEPT spectrum at 250 K. This last spectrum shows a signal typical of an azo group at δ = 208.6 ppm (−N=*N*−*t*Bu).[12] Variations in temperature from 330 to 210 K essentially did not change the signal of the *tert*-butyl group in the ^1H NMR (δ_H = 1.43) and ^{13}C NMR spectra (δ_C = 27.2, CH_3; 72.6, *C*Me_3) of **3k**.

In contrast, the equilibrium in salt **3f/4f** (R = *t*Bu, X^1 = X^3 = Br) is entirely shifted in favor of the cyclic form **4f**. The distinctive features of this form include a lack of peaks typical of a diazonium ion in the IR and the ^{14}N NMR spectra and the downfield shift of signals of the *tert*-butyl group in the ^1H and ^{13}C NMR spectra [δ_H = 2.16; δ_C = 29.4 (CH_3), 82.9 (*C*Me_3)]. This shift is indicative of the *tert*-butyl group being directly attached to the positively charged N atom; similar chemical shifts were observed for the *tert*-butyl group of the related tetrazinium *N*-oxide salts **D** [R = 6,8-Br_2, δ_H = 2.08 ppm; δ_C = 28.0 (CH_3), 85.8 (*C*Me_3) ppm].[4] On cooling of the sample of **4f** from 297 to 263 K the ^1H and ^{13}C NMR signals were not shifted. In the ^{15}N NMR/INEPT spectra of **4f** at 273 K, the nitrogen attached to the *tert*-butyl group was observed at δ_N = −134.1 ppm. Taking into account that the signal of this nitrogen in the open-chain salt **3k** is seen at δ_N = 208.6 ppm, we can state that the ^{15}N NMR unambiguously confirms the cyclic structure of salt **4f**.

If salts **3a−g/4a−g** existed solely in their open-chain forms, the chemical shifts of their *tert*-butyl groups would not exceed the shift in salt **4k** (δ = 1.43 ppm). For **3a−g**, we take this signal as δ = 1.41±0.02 ppm, allowing for the fact that the influence of electron-withdrawing substituents on the benzene ring of **3a−g** is not as strong as that of the nitrogen atom in the pyridine ring of **4k**. This assumption seems justified since the influence of the substituents on the benzene ring on the chemical shift of the *tert*-butyl group is fairly weak, with electron-withdrawing substituents shifting the signal slightly downfield. For example, in the series of *ortho*-[(*tert*-butyl)azo]anilines **2a−2g** the signals range from δ = 1.31 ppm in **2e** (X^2 = Me) to δ = 1.35 ppm in **2g** (X^1 = X^3 = Cl) and are equal to δ = 1.36 ppm in the aminopyridine **2k**. Similarly, were salts **3a−g/4a−g** to exist in their cyclic forms, the chemical shifts of their *tert*-butyl groups would be the same as in salt **4f** (δ = 2.16 ppm). The observed signals of salts **3a−g/4a−g** are located between these two extremes, indicating equilibria between cyclic and open-chain forms. Each salt investigated exhibits only one set of signals in its ^1H and ^{13}C NMR spectra both at room temperature and at low temperatures, indicating that the equilibrium is fast on the NMR timescale.

The percentage of the cyclic form p_c was determined by Equation (1). We assume that the error is no more than 5% of the measurement. The **3/4** ratios determined at 297 K are listed in Table 1.

$$p_c = \frac{\delta_H(obsd.) - \delta_H(acyclic)}{\delta_H(cyclic) - \delta_H(acyclic)} \times 100 = \frac{\delta_H(obsd.) - 1.41}{0.75} \times 100 \quad (1)$$

Equation (1): The percentage of the cyclic form **3** in the equilibrium **3** ⇄ **4**:

δ_H(obsd.) − the observed ^1H NMR signals of the *tert*-butyl group

δ_H(acyclic) = 1.41 − signal of the *tert*-butyl group of the open-chain salt

δ_H(cyclic) = 2.16 − signal of the *tert*-butyl group of the cyclic salt

Table 1. The ^{1}H NMR chemical shifts of the *tert*-butyl or methyl groups of salts **3/4** and the ratio of tautomers **3** ⇄ **4** at 297 K with the substituent X

Compound	R	X	δ_H [ppm]	**3/4** ratio [%]
3a/4a[a]	*t*Bu	−	1.93	30:70
3b/4b[a]	*t*Bu	4-Br	1.74	55:45
3c/4c[a]	*t*Bu	5-Br	2.07	15:85
3d/4d[a]	*t*Bu	4-Me	1.87	40:60
3e/4e[a]	*t*Bu	5-Me	2.06	15:85
3f/4f[a]	*t*Bu	4,6-Br_2	2.16	0:100
3g/4g[a]	*t*Bu	4,6-Cl_2	2.15	0:100
3h/4h[b]	Me	−	4.94	30:70
3i/4i[b] [c]	Me	4,6-Br_2	5.25	5:95

[a] In [D_6]acetone solution. [b] In CD_3CN solution. [c] At 273 K δ_H = 5.30 ppm, 100% of **4i**.

Similarly, the percentage of the cyclic form can be calculated from the ^{13}C NMR signals of the *tert*-butyl group. In a qualitative sense the results of these calculations are in agreement with the results obtained from the ^{1}H NMR spectra. However, the ratio values are a bit different.

In order to ascertain the dependence of the ring-chain equilibrium on the azo substituent, salts **3h/4h** and **3i/4i**, bearing *N*-methyl groups, were investigated. Similarly to **3f/4f**, salt **3i/4i** ($X^1 = X^3$ = Br) exists only in the cyclic form at 273 K. This statement is supported by the downfield shift of the ^{1}H NMR signals of the methyl group (δ_H = 5.30 ppm) and by the good agreement of the ^{13}C NMR signals[13] of the benzene ring with the appropriate signals for **4f**. On further cooling of the CD_3CN solution[14] of **3i/4i** to 253 K, the ^{1}H and ^{13}C chemical shifts remained constant.

The **3h/4h** ratio in MeCN, which proved to be very close to the **3a/4a** ratio (Table 1), was determined as described above by use of Equation (1), where δ_H(obsd.) represents the observed signals of the methyl group; δ_H(acyclic) = 4.0 ppm is the signal of the methyl group of the open-chain salt, and δ_H(cyclic) = 5.30 ppm is the signal of the methyl group of the cyclic salt. The signal of the open-chain salt δ_H(acyclic) was taken as that of the aniline **2h** (δ = 3.93 ppm), with a correction to allow for the electron-withdrawing properties of the diazonium group. This is a rough value, but it is nevertheless safe to state that the ring-chain equilibrium is virtually unaffected by the replacement of the *tert*-butyl group with the methyl group.

Table 2. The ^{1}H NMR chemical shifts[a] of the *tert*-butyl group of salt **3a/4a** and the percentage of the cyclic tautomer **4a** in the **3** ⇄ **4** equilibrium in dependence of the temperature

Entry[a]	*T* [K]	δ_H [ppm]	**4a** [%]
1	320	1.78	49
2	297	1.93	69
3	260	2.05	85
4	250	2.08	89
5	240	2.10	92
6	220	2.11	93

[a] In [D_6]acetone solution.

Temperature Study

On cooling of the samples, the ^{1}H and ^{13}C NMR signals of the *tert*-butyl group of **3a**−**e**/**4a**−**e** and the methyl group of **3h** and **3i/4h** and **4i** were shifted downfield, indicating an increase in the amount of the cyclic form. For **3a/4a** these changes in the ^{1}H NMR spectra are presented in Table 2.

The changes in the 6-H signals of **3a**−**e** and **3h/4a**−**e** and **4h** are only moderate, due to close agreement of these signals in the cyclic and in the open-chain forms. It is difficult to follow the course of the temperature changes of the other protons, as they manifest as wide multiplets (see Supporting Information for variable-temperature ^{1}H NMR spectra of **3a/4a**). At the same time, though, we can conveniently monitor the changes in the ^{13}C NMR signals. The temperature dependence of these signals for **3a/4a** is shown in Table 3 (Exp. Sect.) and in the Figures S1 and S2 in the Supporting Information (see footnote on the first page of the article). The C-1 and C-2 signals were observed only when the sample was cooled to 250−220 K. The signal of the C-4 atom is practically temperature-independent (δ = 143.5−144.3 ppm). The strongest changes occur for the C-5 signal, which is in the position *para* to the azo group (from δ = 141.7 ppm at 320 K to δ = 149.4 ppm at 220 K). Similar temperature dependence was observed for the carbon signals of the benzene rings in **3d/4d** and **3h/4h**.

HSQC-qs, HMBC-qs, SPT, and DEPT experiments allowed assignment of the C-signals in **3d/4d**. The signals of **3a/4a** were unambiguously assigned by analogy with **3d/4d**, with reference to the substituent chemical shifts of the methyl group (s_{ipso} = 9.1, s_{ortho} = 0.7, s_{meta} = −0.1, s_{para} = −3.0).[15]

As mentioned above, the signals of the nitrogen atoms attached to the *tert*-butyl group were observed in the ^{15}N NMR/INEPT spectra of the open-chain salt **3k/4k** (δ_N = 208.6 ppm at 250 K) and the cyclic salt **3f/4f** (δ_N = −134.1 ppm at 273 K). The nitrogen signal of **3a/4a** was observed at δ_N = −57.0 ppm at 220 K, indicating the predominance of the cyclic form. However, the signals of **3k** and **4f** cannot be taken as representative of the signals of the open-chain and cyclic forms of **3a/4a** [Equation (1)], due to their strong dependence on the substituents on the benzene ring. ^{15}N NMR spectroscopy cannot therefore be applied for the study of this equilibrium.

The ring/chain equilibrium strongly depends on the substituents on the benzene ring. For salts **3a/4a** and **3h/4h**, bearing no substituents, the **3/4** ratio is ca. 30:70. A bromine or methyl group in the position *para* to the diazonium group increases the percentage of the open-chain form. Contrarily, the presence of these groups in the *meta*-position increase the percentage of the cyclic form (salts **3c/4c** and **3e/4e**). The presence of two chlorine or bromine atoms in *ortho*/*para*-positions makes the salt exist only in the cyclic form (**3f/4f**, **3g/4g**, and **3i/4i**). On a general assumption, substituents that increase the nucleophilicity of the azo group and the electrophilicity of the diazonium group should be

favorable to the cyclic form. The influence of substituents favorable to the open-chain form is the opposite. This reasoning adequately explains both the effect of the methyl group (salts **3d** and **3e**/**4d** and **4e**) and the effect of the replacement of the CH fragment of the benzene ring by the nitrogen atom (salt **3k**). At the same time, the influence of the bromine atoms in salts **3b** and **3c**/**4b** and **4c** is not conventional. In fact, they affect the molecule as electron-releasing substituents. As for the dibromo-substituted salts **4f** and **4i**, the bulky substituents *ortho* to the diazonium group probably favor the formation of the cycle.

In summary, diazonium salts bearing *ortho*-alkylazo groups have been synthesized. A novel ring-chain equilibrium between these salts and 2-alkyl-1,2,3,4-benzotetrazinium salts was observed. This equilibrium is fast on the NMR timescale, only one set of signals being observed even at low temperatures. A ^{1}H NMR study of the equilibrium allowed the relative quantities of the acyclic and cyclic forms to be determined.

Experimental Section

General Remarks: NMR spectra were recorded with an AM 300 Bruker spectrometer (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 21.69 MHz for ^{14}N, and 30.42 MHz for ^{15}N) at 297 K unless otherwise stated; chemical shifts are δ units downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N). Negative values of δ_N correspond to upfield shifts. Assignment of the ^{13}C NMR signals was performed by several techniques,[17] or in some cases by calculation (additive schemes). The samples used for NMR study were 0.05−0.15 M solutions of salts **3**/**4**. The **3** ⇄ **4** equilibrium is virtually independent of concentration in this range. Mass spectroscopic data were obtained at 70 eV by electron impact. Melting points were determined with a Kofler apparatus and are uncorrected.

2-(*tert*-Butyl-*NNO*-azoxy)-4,6-dichloroaniline (1g): Aqueous H_2O_2 (30%, 1.6 mL) was added dropwise at 50−60 °C to a stirred solution of aniline **1a** (1.2 g, 7 mmol) in conc. HCl (10 mL). After the addition was complete, the mixture was stirred for an additional 5 min at this temperature and the solution was then cooled, poured into H_2O (50 mL), neutralized with aqueous Na_2CO_3, and extracted with Et_2O. The extract was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was purified by chromatography (silica gel, CH_2Cl_2) to yield 1.12 g (61%) of **1g**, m.p. 33−34 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.47 (s, 9 H, *t*Bu), 6.56 (s, 2 H, NH_2), 7.45 (d, *J* = 2.2 Hz, 1 H, 5-H), 7.91 (d, *J* = 2.2 Hz, 1 H, 3-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 26.1 (CH_3), 60.2 (*C*Me$_3$), 119.6 (C-4), 122.1 (C-6), 124.1 (C-3), 131.9 (C-5), 134.4 (C-2), 139.2 (C-1) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −51 [$\Delta\nu_{1/2}$ = 70 Hz, N(O)=N], −320 ($\Delta\nu_{1/2}$ = 430 Hz, NH_2). IR (KBr): $\tilde{\nu}$ = 1480 cm^{-1} [N(O)=N], 3340, 3460 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 261, 263, 265 (4:2:1) [M$^+$]. $C_{10}H_{13}Cl_2N_3O$ (262.14): calcd. C 45.82, H 5.00, Cl 27.05, N 16.03; found C 45.76, H 5.02, Cl 27.17, N 16.19.

General Procedure for the Reduction of Anilines 1a−i: A solution of aniline **1** (2.9 mmol) in dry Et_2O (10 mL) was added dropwise at −15 °C over a period of 10 min to a stirred suspension of $LiAlH_4$ (220 mg, 5.8 mmol) in dry Et_2O. The solution was stirred for an additional 1 h at room temperature and was then quenched with cold water and extracted with Et_2O. The extract was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was purified by chromatography (silica gel, $CHCl_3$ or C_6H_6).

2-(*tert*-Butylazo)aniline (2a): Brownish oil (500 mg, 93%), identical with an authentic sample.[16] ^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 9 H, *t*Bu), 5.30 (br. s, 2 H, NH_2), 6.68 (t, 1 H, 6-H), 6.74 (t, 1 H, 4-H), 7.12 (t, 1 H, 5-H), 7.62 (t, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.3 (CH_3), 67.0 (*C*Me$_3$), 116.8 (C-6), 117.1 (C-4), 125.9 (C-3), 131.0 (C-5), 136.1 (C-2), 142.3 (C-1) ppm.

4-Bromo-2-(*tert*-butylazo)aniline (2b): Yellow solid (700 mg, 94%), m.p. 54−56 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.32 (s, 9 H, *t*Bu), 6.83 (d, *J* = 8.9 Hz, 1 H, 6-H), 7.24 (dd, *J* = 8.9, 2.5 Hz, 1 H, 5-H), 7.61 (d, *J* = 2.5 Hz, 1 H, 3-H) ppm. ^{13}C NMR[17a] ([D$_6$]acetone): δ = 27.6 (CH_3), 67.9 (*C*Me$_3$), 107.8 (C-4), 119.4 (C-3), 126.8 (C-6), 134.4 (C-5), 137.0 (C-2), 144.4 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 1460 cm^{-1}, 3290, 3440 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 255, 257 (1:1) [M$^+$]. $C_{10}H_{14}BrN_3$ (256.14): calcd. C 46.89, H 5.51, Br 31.20, N 16.41; found C 46.84, H 5.53, Br 31.42, N 16.21.

5-Bromo-2-(*tert*-butylazo)aniline (2c): Yellow solid (600 mg, 80%), m.p. 52−54 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.32 (s, 9 H, *t*Bu), 6.43 (br. s, 2 H, NH_2), 6.78 (dd, *J* = 8.1, 2.2 Hz, 1 H, 4-H), 7.06 (d, *J* = 2.2 Hz, 1 H, 6-H), 7.45 (d, *J* = 8.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR[17a] ([D$_6$]acetone): δ = 27.6 (CH_3), 67.6 (*C*Me$_3$), 119.4 (C-3), 119.7 (C-6), 128.4 (C-4), 131.9 (C-5), 135.2 (C-2), 145.6 (C-1). IR (KBr): $\tilde{\nu}$ = 1460 cm^{-1}, 3290, 3450 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 255, 257 (1:1) [M$^+$]. $C_{10}H_{14}BrN_3$ (256.14): calcd. C 46.89, H 5.51, Br 31.20, N 16.41; found C 46.92, H 5.52, Br 31.29, N 16.27.

2-(*tert*-Butylazo)-4-methylaniline (2d): Orange solid (400 mg, 72%), m.p. 41−43 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.32 (s, 9 H, *t*Bu), 2.23 (s, 3 H, CH_3), 5.95 (br. s, 2 H, NH_2), 6.73 (d, *J* = 8.3 Hz, 1 H, 6-H), 7.36 (d, *J* = 1.8 Hz, 1 H, 3-H), 7.96 (dd, *J* = 8.3, 1.8 Hz, 1 H, 5-H) ppm. ^{13}C NMR[17a][17b] ([D$_6$]acetone): δ = 20.4 (CH_3), 27.8 [C(*CH$_3$*)], 67.2 (*C*Me$_3$), 117.7 (C-3), 125.6 (C-4), 126.2 (C-6), 132.9 (C-5), 136.3 (C-2), 142.3 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 1460 cm^{-1}, 3300, 3450 (NH_2). MS (70 eV): *m*/*z* = 191 [M$^+$]. $C_{11}H_{17}N_3$ (191.27): calcd. C 69.07, H 8.96, N 21.97; found C 68.94, H 8.92, N 22.19.

2-(*tert*-Butylazo)-5-methylaniline (2e): Yellow oil (420 mg, 76%). ^{1}H NMR ([D$_6$]acetone): δ = 1.31 (s, 9 H, *t*Bu), 2.23 (s, 3 H, CH_3), 6.21 (br. s, 2 H, NH_2), 6.49 (dd, *J* = 8.1, 2.2 Hz, 1 H, 4-H), 6.62 (d, *J* = 2.2 Hz, 1 H, 6-H), 7.45 (d, *J* = 8.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR[17a] ([D$_6$]acetone): δ = 21.5 (CH_3), 27.7 [C(*CH$_3$*)], 66.8 (*C*Me$_3$), 117.6 (C-3), 117.9 (C-6), 126.2 (C-5), 127.5 (C-4), 134.7 (C-2), 144.1 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 1480 cm^{-1}, 3300, 3460 (NH_2). MS (70 eV): *m*/*z* = 191 [M$^+$]. $C_{11}H_{17}N_3$ (191.27): calcd. C 69.07, H 8.96, N 21.97; found C 68.99, H 8.97, N 22.04.

2,4-Dibromo-6-(*tert*-butylazo)aniline (2f): Orange solid (780 mg, 80%), m.p. 39−40 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.33 (s, 9 H, *t*Bu), 5.92 (br. s, 2 H, NH_2), 7.54 (d, *J* = 2.3 Hz, 1 H, 3-H), 7.71 (d, *J* = 2.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR[17c][17d] ([D$_6$]acetone): δ = 27.2 (CH_3), 68.0 (*C*Me$_3$), 108.0 (C-2), 110.5 (C-4), 126.9 (C-5), 135.6 (C-3), 136.5 (C-6), 139.8 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 1440 cm^{-1}, 3300, 3440 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 333, 335, 337 (1:2: 1) [M$^+$]. $C_{10}H_{13}Br_2N_3$ (335.04): calcd. C 35.85, H 3.91, Br 47.70, N 12.54; found C 35.89, H 3.90, Br 47.82, N 12.39.

2-(*tert*-Butylazo)-4,6-dichloroaniline (2g): Yellow solid (640 mg, 90%), m.p. 24−26 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.35 (s, 9 H,

*t*Bu), 6.28 (br. s, 2 H, NH_2), 7.40 (d, J = 2.2 Hz, 1 H, 5-H), 7.46 (d, J = 2.2 Hz, 1 H, 3-H) ppm. ^{13}C NMR[17a] ([D$_6$]acetone): δ = 27.4 (CH_3), 68.1 (CMe$_3$), 118.6 (C-6), 121.2 (C-4), 122.8 (C-3), 129.4 (C-5), 134.1 (C-1), 135.7 (C-6) ppm. IR (KBr): $\tilde{\nu}$ = 1440 cm^{-1}; 3310, 3440 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 245, 247, 249 (4:2: 1) [M$^+$]. $C_{10}H_{13}Cl_2N_3$ (246.14): calcd. C 48.80, H 5.32, Cl 28.81, N 17.07; found C 48.86, H 5.34, Cl 28.79, N 17.01.

2-(Methylazo)aniline (2h): Brownish oil (360 mg, 91%). ^{1}H NMR ([D$_6$]acetone): δ = 3.93 (s, 3 H, CH_3), 6.20 (br. s, 2 H, NH_2), 6.64 (t, J = 8.2 Hz, 1 H, 6-H), 6.81 (d, J = 8.1 Hz, 1 H, 4-H), 7.12 (t, J = 8.2 Hz, 1 H, 5-H), 7.51 (d, J = 8.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR[17e] ([D$_6$]acetone): δ = 56.8 (CH_3), 116.5 (C-6), 117.6 (C-4), 127.1 (C-3), 132.1 (C-5) ppm. ^{14}N NMR ([D$_6$]acetone): δ = 128 ($\Delta\nu_{1/2}$ = 650 Hz, N=N); −330 ($\Delta\nu_{1/2}$ = 670 Hz, NH_2) ppm. IR (KBr): $\tilde{\nu}$ = 1450 cm^{-1}, 3280, 3430 (NH_2). MS (70 eV): *m*/*z* = 135 [M$^+$]. $C_7H_9N_3$ (135.17): calcd. C 61.20, H 6.71, N 32.09; found C 61.16, H 6.70, N 32.14.

2,4-Dibromo-6-(methylazo)aniline (2i): Orange solid (160 mg, 19%), m.p. 67−69 °C. ^{1}H NMR ([D$_6$]acetone): δ = 4.02 (s, 3 H, CH_3), 6.30 (br. s, 2 H, NH_2), 7.51 (d, J = 2.1 Hz, 1 H, 3-H), 7.63 (d, J = 2.1 Hz, 1 H, 5-H) ppm. ^{1}H NMR (CD_3CN): δ = 4.00 (s, 3 H, CH_3), 6.03 (br. s, 2 H, NH_2), 7.59 (d, J = 2.0 Hz, 1 H, 3-H), 7.65 (d, J = 2.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR[17a] ([D$_6$]acetone): δ = 57.3 (CH_3), 107.6 (C-2), 111.0 (C-4), 126.2 (C-5), 136.7 (C-3), 137.6 (C-6), 142.0 (C-1) ppm. ^{13}C NMR[17e] (CD_3CN): δ = 57.5 (CH_3), 126.5 (C-5), 136.8 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 1460 cm^{-1}, 3300, 3460 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 291, 293, 295 (1:2: 1) [M$^+$]. $C_7H_7Br_2N_3$ (292.96): calcd. C 28.70, H 2.41, Br 54.55, N 14.34; found C 28.65, H 2.40, Br 54.43, N 14.52.

Reduction of 1i with Red-Al: A solution of aniline **1i** (370 mg, 1.2 mmol) in dry Et_2O (10 mL) was added dropwise at −15 °C over a period of 10 min to a stirred 33% solution of Na-bis(2-methoxyethoxy)aluminium hydride (Red-Al) in toluene. The solution was then stirred for an additional 1 h at room temperature, quenched with cold water, and extracted with Et_2O. The extract was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was purified by chromatography (silica gel, $CHCl_3$) to yield 200 mg (57%) of **2i**, identical with the sample obtained above.

General Procedure for the Diazotization of Anilines 2a−k: A solution of aniline **2** (1 mmol) in dry MeCN (5 mL) was added dropwise at −15 °C over a period of 10 min to a stirred suspension of $NOBF_4$ (129 mg, 1.1 mmol) in dry MeCN (5 mL). After 20 min stirring at this temperature, the solution was concentrated by ca. 90% in vacuo at a temperature of 0 °C. Cooled Et_2O was added to the resultant suspension. The precipitate was filtered off, washed with cooled Et_2O and then with pentane, and dried in vacuo.

Table 3. Variable-temperature ^{13}C NMR[17a,17e] (δ, ppm) of **3a** in [D$_6$]acetone solution

T [K]	CH_3	CMe$_3$	C-3	C-4	C-5	C-6
320	28.1	76.5	128.2	143.8	141.3	132.3
297	28.4	78.0	128.5	143.8	141.9	131.8
273	28.9	79.3	129.9	143.9	144.1	131.1
260	29.0	80.7	130.3	144.0	145.6	130.4
250	29.3	81.2	131.0	144.1	146.9	130.1
240	29.4	81.4	131.4	144.1	147.2	130.0
220	29.5	81.6	131.9	144.3	147.6	129.9

2-(*tert*-Butylazo)benzenediazonium Tetrafluoroborate (3a): Brownish solid (260 mg, 93%), m.p. 75−77 °C (decomp). ^{1}H NMR at 297 K ([D$_6$]acetone): δ = 1.93 (s, 9 H, *t*Bu), 8.73 (m, 3 H, 3-H, 4-H, 5-H), 8.96 (d, J = 7.8 Hz, 1 H, 6-H). The 6-H signals shifted downfield from δ = 8.94 ppm at 320 K to δ = 9.03 ppm at 260 K. Further cooling to 220 K results in an upfield shift to δ = 8.95 ppm. For details see Table 3 and the Supporting Information. ^{15}N NMR/INEPT at 220 K ([D$_6$]acetone): δ = −57.0 (N-*t*Bu). $C_{10}H_{13}BF_4N_4$ (276.04): calcd. C 43.51, H 4.75, N 20.30; found C 43.54, H 4.72, N 20.41.

4-Bromo-2-(*tert*-butylazo)benzenediazonium Tetrafluoroborate (3b): Yellow solid (280 mg, 80%), m.p. 115−118 °C (decomp). ^{1}H NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 1.74 (1.87) (s, 9 H, *t*Bu), 8.68 (8.68) (dd, J = 8.8, 1.5 Hz, 1 H, 5-H), 8.71 (8.76) (d, J = 1.5 Hz, 1 H, 3-H), 8.96 (8.76) (d, J = 8.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 28.0 (28.4) (CH_3), 77.1 (CMe$_3$), 129.4 (CH), 134.0 (CH), 139.0 (C-4), 142.2 (CH) ppm. $C_{10}H_{12}BBrF_4N_4$ (354.94): calcd. C 33.84, H 3.41, N 15.79; found C 33.80, H 3.40, N 15.83.

5-Bromo-2-(*tert*-butylazo)benzenediazonium Tetrafluoroborate (3c): Yellow solid (290 mg, 83%), m.p. 56−60 °C (decomp). ^{1}H NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 2.07 (2.10) (s, 9 H, *t*Bu), 8.87 (8.96) (d, J = 8.6 Hz, 1 H, 3-H), 8.90 (9.07) (dd, J = 8.6, 1.5 Hz, 1 H, 4-H), 9.36 (9.43) (d, J = 1.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR at 273 K (at 297 K in parentheses) ([D$_6$]acetone): δ = 29.4 (29.2) (CH_3), 81.4 (CMe$_3$), 132.3 (CH), 132.5 (CH), 147.3 (CH) ppm. $C_{10}H_{12}BBrF_4N_4$ (354.94): calcd. C 33.84, H 3.41, N 15.79; found C 33.79, H 3.41, N 15.88.

2-(*tert*-Butylazo)-4-methylbenzenediazonium Tetrafluoroborate (3d): Brownish solid (170 mg, 60%), m.p. 113−116 °C (decomp). ^{1}H NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 1.87 (1.98) (s, 9 H, *t*Bu), 2.89 (2.93) (s, 3 H, CH_3), 8.45 (br. s, 1 H, 3-H), 8.51 (br. d, 1 H, 5-H), 8.87 (8.92) (d, J = 8.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR[17a][17b][17f] at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 23.2 (23.3) (CH_3), 28.5 (29.0) [C(CH_3)$_3$], 77.9 (79.5) (CMe$_3$), 127.4 (128.3) (C-3), 131.9 (130.5) (C-6), 142.6 (146.2) (C-5), 157.8 (157.9) (C-4) ppm. $C_{11}H_{15}BF_4N_4$ (290.07): calcd. C 45.55, H 5.21, N 19.32; found C 45.49, H 5.23, N 19.39.

2-(*tert*-Butylazo)-5-methylbenzenediazonium Tetrafluoroborate (3e): Brownish solid (190 mg, 67%), m.p. 121−123 °C (decomp). ^{1}H NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 2.06 (2.10) (s, 9 H, *t*Bu), 2.99 (3.02) (s, 3 H, CH_3), 8.78 (8.83) (m, 3 H, 3-H, 4-H, 6-H) ppm. ^{13}C NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 23.8 (24.0) (CH_3), 29.3 (29.4) [C(CH_3)$_3$], 80.1 (80.2) (CMe$_3$), 128.9 (CH), 130.1 (CH), 145.9 (CH) ppm. $C_{11}H_{15}BF_4N_4$ (290.07): calcd. C 45.55, H 5.21, N 19.32; found C 45.58, H 5.21, N 19.40.

2,4-Dibromo-2-(*tert*-butylazo)benzenediazonium Tetrafluoroborate (3f): Yellow solid (360 mg, 80%), m.p. 43−44 °C (decomp). ^{1}H NMR at 297 K ([D$_6$]acetone): δ = 2.16 (s, 9 H, *t*Bu), 9.44 (d, J = 2.1 Hz, 1 H, 3-H), 9.56 (d, J = 2.1 Hz, 1 H, 5-H). The signals remain unchanged on cooling of the sample to 263 K. ^{13}C NMR[17a][17d] at 297 K ([D$_6$]acetone): δ = 29.4 (CH_3), 82.9 (CMe$_3$), 126.4 (C-2), 132.8 (C-3), 135.0 (C-6), 139.6 (C-4), 141.1 (C-1), 152.0 (C-5). The signals remain unchanged on cooling of the sample to 263 K. ^{15}N NMR/INEPT at 273 K ([D$_6$]acetone): δ = −134.1 (N-*t*Bu) ppm. $C_{10}H_{11}BBr_2F_4N_4$ (433.83): calcd. C 27.69, H 2.56, N 12.91; found C 27.63, H 2.55, N 12.85.

2-(*tert*-Butylazo)-4,6-dichlorobenzenediazonium Tetrafluoroborate (3g): Yellow solid (270 mg, 78%), m.p. 51−54 °C (decomp). ^{1}H

NMR at 297 K ([D$_6$]acetone): δ = 2.14 (s, 9 H, *t*Bu), 9.16 (d, *J* = 1.5 Hz, 1 H, 5-H), 9.19 (d, *J* = 1.5 Hz, 1 H, 3-H). The signals remain unchanged on cooling of the sample to 273 K. ^{13}C NMR at 297 K ([D$_6$]acetone): δ = 29.4 (CH_3), 82.4 (CMe_3), 128.9 (C-5), 145.7 (C-3) ppm. $C_{10}H_{11}BCl_2F_4N_4$ (344.93): calcd. C 34.82, H 3.21, N 16.24; found C 34.78, H 3.20, N 16.29.

2-(Methylazo)benzenediazonium Tetrafluoroborate (3h): Brownish solid (140 mg, 58%), m.p. 83−84 °C (decomp). ^{1}H NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 5.20 (5.43) (s, 3 H, CH_3), 8.88 (m, 3 H, 3-H, 4-H, 5-H), 9.11 (d, *J* = 7.8 Hz, 1 H, 6-H) ppm. ^{1}H NMR at 297 K (at 273 K in parentheses) (CD_3CN): δ = 4.94 (5.17) (s, 3 H, CH_3), 8.76 (8.79) (m, 2 H), 8.97 (8.90) (m, 2 H) ppm. ^{13}C NMR at 297 K (at 273 K in parentheses) ([D$_6$]acetone): δ = 54.3 (55.9) (CH_3), 130.4 (131.7) (C-3), 130.6 (129.9) (C-6), 144.9 (144.8) (C-4) ppm. $C_7H_7BF_4N_4$ (233.96): calcd. C 35.94, H 3.02, N 23.95; found C 35.87, H 3.02, N 24.01.

2,4-Dibromo-2-(methylazo)benzenediazonium Tetrafluoroborate (3i): Yellow solid (330 mg, 85%), m.p. 110−112 °C (decomp). ^{1}H NMR at 297 K (at 273 K in parentheses) (CD_3CN): δ = 5.25 (5.30) (s, 3 H, CH_3), 9.01 (9.05) (d, *J* = 1.5 Hz, 1 H, 3-H), 9.25 (9.29) (d, *J* = 1.5 Hz, 1 H, 5-H) ppm. ^{1}H NMR at 263 K (CD_3CN): δ = 5.30 (s, 3 H, CH_3), 9.10 (d, *J* = 1.9 Hz, 1 H, 3-H), 9.33 (d, *J* = 1.9 Hz, 1 H, 5-H) ppm. The signals remain unchanged on cooling of the sample to 253 K. ^{13}C NMR at 297 K (at 263 K in parentheses) (CD_3CN): δ = 56.1 (56.0) (CH_3), 127.0 (126.8) (C-2), 132.4 (132.5) (C-3), 140.8 (141.0) (C-4), 152.8 (153.3) (C-5) ppm. $C_7H_5BBr_2F_4N_4$ (391.75): calcd. C 21.46, H 1.29, N 14.30; found C 21.43, H 1.29, N 14.34.

2-(Phenylazo)benzenediazonium Tetrafluoroborate (3j): Brownish solid (240 mg, 61%), m.p. 143−144 °C (decomp) [ref.[8] m.p. 144 °C (decomp)]. ^{1}H NMR at 297 K ([D$_6$]acetone): δ = 7.73 (t, *J* = 7.7 Hz, 2 H, H_m), 7.75 (t, *J* = 7.6 Hz, 1 H, H_p), 8.18 (d, *J* = 8.1 Hz, 2 H, H_o), 8.21 (t, *J* = 7.8 Hz, 1 H, 5-H), 8.46 (d, *J* = 7.7 Hz, 1 H, 3-H), 8.54 (t, *J* = 7.4 Hz, 1 H, 4-H), 9.10 (d, *J* = 8.1 Hz, 1 H, 6-H) ppm. The signals remain unchanged on cooling of the sample to 273 K. ^{13}C NMR[17f] at 297 K ([D$_6$]acetone): δ = 114.2 (C-1), 123.0 (C-3), 125.3 (C_o), 130.8 (C_m), 134.4 (C-5), 135.4 (C-6), 135.9 (C_p), 143.6 (C-4), 151.2 (C-2), 152.7 (C_i) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −153 ($\Delta\nu_{1/2}$ = 170 Hz, N_2^+) ppm. IR (acetone): $\tilde{\nu}$ = 2290 cm^{-1} (N_2^+).

2-(*tert*-Butylazo)-3-pyridinediazonium Tetrafluoroborate (3k): Brownish solid (220 mg, 80%), m.p. 132−136 °C (decomp). ^{1}H NMR at 297 K ([D$_6$]acetone): δ = 1.43 (s, 9 H, *t*Bu), 8.34 (t, *J* = 6.7 Hz, 1 H, 5-H), 9.03 (m, 1 H, 6-H), 9.48 (d, *J* = 8.2 Hz, 1 H, 4-H) ppm. Variations in temperature from 330 K to 210 K virtually did not change the signals. ^{13}C NMR at 297 K ([D$_6$]acetone): δ = 27.2 (CH_3), 72.6 (CMe_3), 121.6, 129.7, 142.4, 151.2 ppm. Variations in temperature from 330 K to 210 K virtually did not change the signals. ^{14}N NMR ([D$_6$]acetone): δ = −195 ($\Delta\nu_{1/2}$ = 110 Hz, N_2^+) ppm. ^{15}N NMR/INEPT at 250 K ([D$_6$]acetone): δ = 208.6 (N-*t*Bu) ppm. IR (acetone): $\tilde{\nu}$ = 2250 cm^{-1} (N_2^+) ppm. IR (KBr): $\tilde{\nu}$ = 2240 cm^{-1} (N_2^+). $C_9H_{12}BF_4N_5$ (277.03): calcd. C 39.02, H 4.37, N 25.28; found C 38.96, H 4.38, N 25.32.

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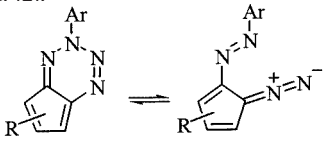

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