Synthesis of brominated 2-(*tert*-butyl-*NNO*-azoxy)anilines

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2-(*tert*-Butyl-*NNO*-azoxy)aniline was prepared by selective reduction of 2-(*tert*-butyl-*NNO*-azoxy)nitrobenzene. Its bromination yielded the corresponding *para*-bromo- and *ortho,para*-dibromoanilines (**3a,b**). *meta*-Bromoanilines (**6a,b**) were synthesized by selective replacement of the *ortho*-bromine atoms in *ortho,para*-bromo(*tert*-butylazoxy)benzenes (**5a,b**) by ammonia in toluene under pressure.

Key words: aromatic amino, azoxy, nitro, and nitroso compounds; selective reduction of a nitro group; bromination; selective nucleophilic substitution.

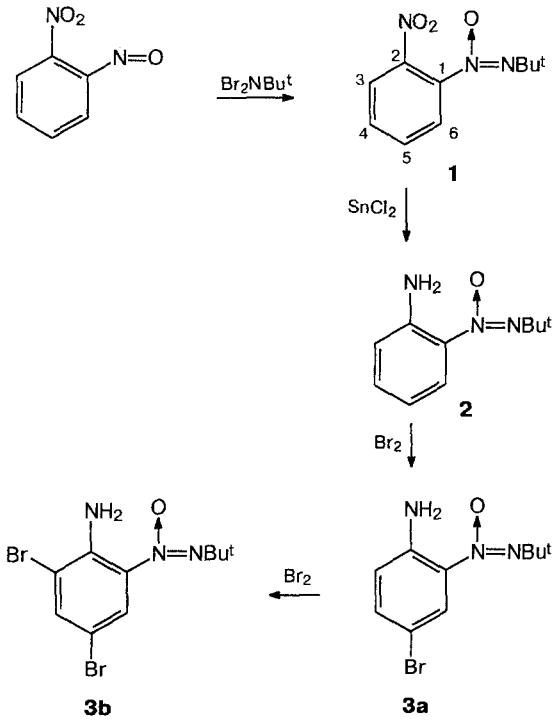
In the framework of the general program of a study of 1,2,3,4-tetrazines[1] we planned to prepare benzo-1,2,3,4-tetrazine 1,3-dioxides containing bromine atoms in various positions of the benzene ring. In the present work we suggest two approaches to the synthesis of the necessary starting compounds, *viz.*, brominated 2-(*tert*-butyl-*NNO*-azoxy)anilines.

The optimal pathway for the synthesis of *para*-bromo- and *ortho,para*-dibromoanilines (Scheme 1) is bromination of 2-(*tert*-butyl-*NNO*-azoxy)aniline (**2**), which, in turn, can be prepared[2] by the reaction of *N*-trimethylsilyl-*ortho*-nitroaniline with $Bu^tNHMgBr$. However, in the present work we found another method: reduction of 2-(*tert*-butyl-*NNO*-azoxy)nitrobenzene (**1**) with tin dichloride. The nitro group is selectively reduced in this reaction, while the azoxy group remains unchanged. Compound **1** can be readily obtained according to the Kovacic[3] method, consisting of the reaction of *ortho*-nitronitrosobenzene with *N,N*-dibromo-*tert*-butylamine.

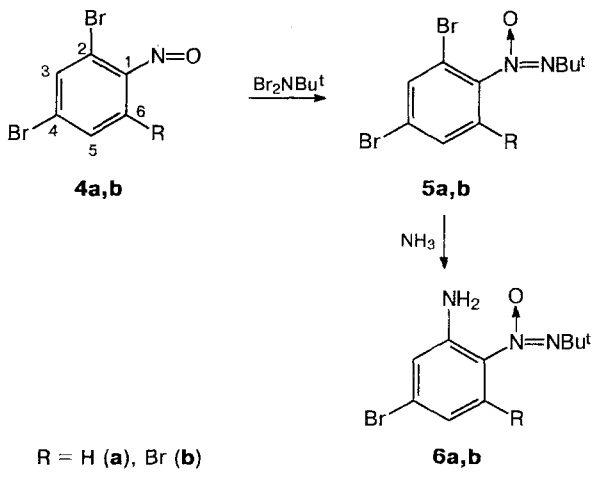
Treatment of compound **2** with bromine in acetic acid in the presence of sodium acetate results in *para*-bromoaniline **3a** and dibromoaniline **3b**.

To prepare *meta*-substituted anilines **6a,b** we used nucleophilic substitution of ammonia for bromine in bromo(*tert*-butylazoxy)benzenes **5a,b**, which are readily prepared from nitroso compounds **4a,b** according to Kovacic (Scheme 2).

Scheme 1



Scheme 2



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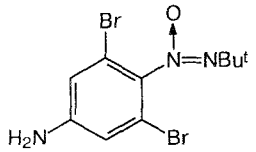
According to the literature data,[4] the reaction of 2,4-dichloronitrobenzene with an ethanolic solution of ammonia at 160 °C involves replacement of the Cl atom in the *ortho*-position with respect to the nitro group. However, the reaction of 2,4,6-tribromo(*tert*-butyl-*NNO*-azoxy)benzene (**5b**) with ammonia under similar conditions occurs at a lower rate and its direction unexpectedly changes. The reaction yields the *para*-substituted product, 3,5-dibromo-4-(*tert*-butyl-*NNO*-azoxy)-aniline (**7**). However, we managed to select conditions under which the substitution occurs at an acceptable rate and involves almost exclusively the *ortho*-position. The reaction of a solution of compound **5** in toluene with ammonia was carried out in an autoclave at 180 °C for 8 h. A pressure of 200 atm in the reaction was ensured by a great excess of ammonia (decreasing the pressure diminishes the rate of the reaction). The change in the reaction pathway is probably due to the use of nonpolar toluene; this is in line with the regularities of the reaction between halonitrobenzenes and aliphatic amines,[5] where the proportion of the *ortho*-substitution product increases as the polarity of the solvent decreases.



7

The structures of the new compounds were determined by NMR spectroscopy and mass spectrometry. For the nitroso derivative **4a**, the temperature dependence of the NMR spectra was studied, and a dynamic equilibrium between the monomer and the *cis*- and *trans*-dimers (**4a′** and **4a″**) was found. At 30 °C, only monomer **4a** is observed in the ^1H and ^{13}C NMR spectra. Its distinctive features are abnormally high-field signals for H(6) and C(6), a low-field signal for C(1), and a signal (δ 516) typical of the N atom of the nitroso group in the ^{15}N NMR spectrum. At −40 °C, the proportion of dimers **4a′** and **4a″** (in a ratio of 3 : 1) is as high as 60 %. A signal corresponding to the dimers (δ −77.66) appears in the ^{15}N NMR spectrum.

The parameters of the ^{13}C NMR spectra of 2-(*tert*-butyl-*NNO*-azoxy)anilines are listed in Table 1. All of the signals were unambiguously assigned using the techniques of recording the spectra without proton decoupling, with selective decoupling of separate protons, various versions of H—H and H—C correlations, and the selective polarization transfer from protons (SPT). The $J_{^1H,^{13}C}$ spin-spin coupling constants were also taken into account. In some cases, the $^3J_{^1H,^{13}C}$ and $^2J_{^1H,^{13}C}$ constants from the protons of the NH_2 groups were observed. An increased intensity of the C(Br) signals due to the decrease in the relaxation time is typical of bromo derivatives. In the case of dibromo derivatives **3b** and **6b**, the signals for the two C(Br) atoms differ in multiplicity in the spectra recorded without proton decoupling.

As can be seen from the data of Table 1, the additive scheme provides a satisfactory approximation for the chemical shifts observed and, therefore, it can be used for determining the positions of substituents in the ring for this type of compound. In the case of tetrasubsituted benzenes, deviations of up to 5 ppm from the calculated values are observed in the positions of some signals, which is due to "pushing away" of the substituents and variation of their contributions with respect to those used in the calculations. The contributions of the Br and NH_2 groups were taken from the literature,[6] while those for the —N(O)=N—Bu^t fragment were derived from the ^{13}C NMR spectrum of PhN(O)=N—Bu^t and are equal to +20.2, −6.4, −0.2, and +2.4 ppm for *ipso*-, *ortho*-, *meta*-, and *para*-positions, respectively.

The data of the ^1H, ^{14}N, and ^{15}N NMR spectroscopy of 2-(*tert*-butyl-*NNO*-azoxy)anilines are summarized in Table 2. The ^1H NMR signals of the NH_2 groups are broadened due to exchange processes. The signal for the protons of the Bu^t group occurs in the region typical of the —N(O)=N—Bu^t moiety. The ^{14}N NMR spectra contain a relatively narrow signal for the N(O) atom

Table 1. ^{13}C NMR spectra of 2-(*tert*-butyl-*NNO*-azoxy)anilines

Compound	δ [calculated chemical shifts]							
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C	CH_3
2	141.71 [144.1]	133.5 br [131.1]	124.58 [126.7]	117.99 [119.0]	131.53 [130.7]	116.57 [115.6]	59.08	26.08
3a	142.71 [140.6]	133.71 br [138.8]	127.48 [127.0]	106.57 [113.7]	134.88 [134.1]	120.50 [118.4]	59.61	26.24
3b	138.8 [144.0]	133.8 br [141.1]	126.9 [126.1]	111.6 [116.0]	136.8 [137.5]	106.5 [113.1]	59.56	25.86
6a	142.72 [143.2]	br [135.0]	126.21 [125.3]	119.70 [122.3]	125.61 [126.7]	120.13 [119.4]	59.33	26.08
6b	144.12 [146.1]	136.20 br [139.0]	116.97 [120.6]	123.18 [125.8]	123.70 [129.4]	119.37 [117.5]	60.65	25.62

Note. The solvent used for **2**, **3a**, and **6a** was $CDCl_3$, that for **3b** and **6b** was acetone-d_6.

Таблица 2. ^{1}H NMR, ^{14}N NMR, and ^{15}N NMR spectra of 2-(*tert*-butyl-*NNO*-azoxy)anilines

Compound	δ ^{1}H (*J*/Hz)						δ ^{14}N ($\Delta\nu_{0.5}$/Hz)		δ ^{15}N ($^1J_{N,H}$/Hz),
	H(3)	H(4)	H(5)	H(6)	NH_2	CH_3	N→O	NH_2	NH_2
2	7.96 q (8.2, 1.4)	6.61—6.69 m	7.09—7.15 m	6.61—6.69 m (7.5, 1.4)	5.60 br	1.47 s	−47.8 (100)	−323±3 (800)	*a*
3a	8.10 d (2.4)	—	7.27 q (8.8)	6.86 d	6.45 br	1.45 s	−49.3 (150)	—	−317.95 (89)
3b	7.58 d (2.1)	—	8.12 d	—	6.25 br	1.46 s	−51.8 (130)	−314±10 (>1000)	*b*
6a	7.87 d (8.9)	6.80 dd (8.9, 2.0)	—	6.90 d	5.76 br	1.46 s	−49.6*c* (120)	−320±3 (700)	−318.50 (86.4)
6b	—	7.07 d or 7.14 d (2.0)	—	7.14 d or 7.07 d	5.20 br	1.47 s	−54.6 (100)	−333±10 (1000)	−325.70 (87.1)

Note. For the conditions used for recording the spectra, see Table 1. *a* ^{15}N NMR, δ −16.81 (N—Bu^t; SPT from CH_3). *b* ^{15}N NMR, δ −15.10 (N—Bu^t; SPT from CH_3). *c* ^{14}N NMR, δ −23±10 (N—Bu^t, $\Delta\nu_{0.5}$ > 1000 Hz).

(δ −45 to −55). A signal for the second N atom of the azoxy group was observed by us in the ^{15}N NMR spectra of some of the compounds (δ −15 to −25) with the aid of the INEPT technique, which also allows one to record the triplet for the NH_2 group with a characteristic spin-spin coupling constant $J_{^1H,^{15}N} \approx 90$ Hz.

Experimental

IR spectra were recorded on a UR-20 spectrometer; mass spectra were obtained on a Varian CH-6 instrument. ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra based on natural isotope abundances were recorded on a Bruker AM-300 spectrometer operating at 300.13, 75.5, 21.5, and 30.4 MHz, respectively. The chemical shifts in the ^{14}N and ^{15}N NMR spectra are given in the δ scale relative to nitromethane; the $^1J_{^{15}N,^1H}$ spin-spin coupling constants were measured using the INEPT technique. The reactions were monitored by TLC (Silufol UV-254); column chromatography was performed on silica gel.

N,N-Dibromo-*tert*-butylamine,[7] 2,4-dibromoaniline,[8] 2,4,6-tribromonitrosobenzene[9] (**4b**), and *ortho*-nitronitrozobenzene[10] were prepared by the previously reported procedures.

Reactions of nitroso compounds with *N,N*-dibromo-*tert*-butylamine (general procedure). A solution of *N,N*-dibromo-*tert*-butylamine in dichloromethane (50 mL) was added at 20 °C to a stirred suspension of a nitroso compound (0.05 mol) in dichloromethane (300 mL). The mixture was stirred until the nitroso compound dissolved and kept for 6—16 h (the reaction was monitored by TLC, visualization of chromatograms was carried out by spraying with a 1 % solution of diphenylamine followed by 2—3 min at 100 °C; nitroso compounds appear as brown spots). The solvent was evaporated *in vacuo*, and the residue was washed with a solution of sodium sulfite to remove excess *N,N*-dibromo-*tert*-butylamine and recrystallized if needed.

2-(*tert*-Butyl-*NNO*-azoxy)nitrobenzene (1). Yield 95 %, m.p. 50—51 °C (from hexane). Found (%): C, 53.74; H, 5.81; N, 19.02. $C_{10}H_{13}N_3O_3$. Calculated (%): C, 53.81; H, 5.87; N, 18.82. ^{1}H NMR (acetone-d_6), δ: 1.43 (s, 9 H, 3 Me); 7.79 (m, 1 H, H(4), $^3J_{H(4),H(3)}$ = 8.12 Hz, $^3J_{H(4),H(5)}$ = 7.62 Hz, $^4J_{H(4),H(6)}$ = 1.30 Hz); 7.80 (m, 1 H, H(6), $^3J_{H(6),H(5)}$ = 8.03 Hz, $^5J_{H(6),H(3)}$ = 0.40 Hz); 7.87 (m, 1 H, H(5), $^4J_{H(5),H(3)}$ = 1.29 Hz); 8.05 (m, 1 H, H(3)). ^{13}C NMR (acetone-d_6), δ: 25.39 (Me); 60.50 (CMe_3); 125.62, 126.14, 131.98, 139.90 (CH); 143.64 (C—N(O)); 143.94 (C—NO_2). ^{14}N NMR (acetone-d_6), δ: −13.88±1 (NO_2, $\Delta\nu_{0.5}$ = 50 Hz); −55.65±1 (N(O), $\Delta\nu_{0.5}$ = 30 Hz). IR (KBr), ν/cm^{-1}: 1340, 1525 (NO_2); 1490 (N(O)=N). MS, *m/z*: 208 $[M-CH_3]^+$.

2,4-Dibromo(*tert*-butyl-*NNO*-azoxy)benzene (5a). Yield 96 %, oil. Found (%): C, 35.84; H, 3.59; Br, 47.38; N, 8.19. $C_{10}H_{12}Br_2N_2O$. Calculated (%): C, 35.74; H, 3.60; Br, 47.56; N, 8.34. ^{1}H NMR ($CDCl_3$), δ: 1.47 (s, 9 H, 3 Me); 7.32 (d, 1 H, H(6), ^3J = 8.0 Hz); 7.47 (dd, 1 H, H(5), ^3J = 8.0 Hz, ^4J = 2.0 Hz); 7.77 (d, 1 H, H(3), ^4J = 2.0 Hz). ^{13}C NMR ($CDCl_3$), δ [the calculated chemical shifts are given in brackets]: 25.51 (CH_3); 60.16 (CMe_3); 115.76 [118.1] (C(2), $^3J_{^{13}C,^1H}$ = 8.5 Hz, $^2J_{^{13}C,^1H}$ = 4.0 Hz, $^4J_{^{13}C,^1H}$ = 1.6 Hz); 123.18 [126.9] (C(4), $^3J_{^{13}C,^1H}$ = 11.9 Hz, $^2J_{^{13}C,^1H}$ = 4.1 and 3.0 Hz); 125.52 [125.5] (C(6)); 131.22 [130.1] (C(5)); 136.05 [134.9] (C(3)); 148.31 [150.5] (C(1)). ^{14}N NMR ($CDCl_3$), δ: −51.7±2 (N(O), $\Delta\nu_{0.5}$ = 120 Hz). MS, *m/z* (the ratio between the integral intensities): 334, 336, 338 $[M]^+$ (1 : 2 : 1).

2,4,6-Tribomo(*tert*-butyl-*NNO*-azoxy)benzene (5b). Yield 94 %, m.p. 97—98 °C (from hexane). Found (%): C, 30.02; H, 2.69; Br, 57.84; N, 2.16. $C_{10}H_{11}Br_3N_2O$. Calculated (%): C, 28.95; H, 2.67; Br, 57.77; N, 2.67. ^{1}H NMR ($CDCl_3$), δ: 1.50 (s, 9 H, Me); 7.73 (s, 2 H, C_6H_2). ^{13}C NMR ($CDCl_3$), δ: 25.47 (Me); 60.80 (CMe_3); 116.90 (C(2), C(6)); 122.75 (C(4)); 134.95 (C(3), C(5)); 147.01 (C(1)). ^{14}N NMR ($CDCl_3$), δ: −55.4±2 (N(O), $\Delta\nu_{0.5}$ = 120 Hz). IR (KBr), ν/cm^{-1}: 1480 (N(O)=N). MS, *m/z* (the ratio between the integral intensities): 412, 414, 416, 418 $[M]^+$ (1 : 3 : 3 : 1).

2-(*tert*-Butyl-*NNO*-azoxy)aniline (2). At ≤10 °C, a solution of $SnCl_2 \cdot 2H_2O$ (41.3 g, 183 mmol) in 35 mL of conc. HCl was added dropwise to a stirred solution of compound **1** (11.81 g, 53 mmol) in methanol (150 mL) and the mixture was kept for 30 min at ≤20 °C and for an additional 30 min without cooling, at 20—24 °C. The reaction mixture was poured into 1500 mL of water, neutralized with a NaOH solution to pH 7, and extracted with ether (4×250 mL). The

extract was dried ($MgSO_4$), the solvent was evaporated *in vacuo*, and the remaining oil was purified by chromatography (using petroleum ether as the eluent). The oil crystallized after seeding. The yield of compound **2** was 6.85 g (67 %), m.p. 30—31 °C (lit[2]: oil). MS, *m/z*: 193 $[M]^+$.

4-Bromo-2-(*tert*-butyl-*NNO*-azoxy)aniline (3a). At 20 °C, a solution of bromine (1.6 g, 10 mmol) in glacial acetic acid (5 mL) was added dropwise to an intensely stirred solution of azoxyaniline **2** (1.93 g, 10 mmol) and AcONa (0.85 g, 10.4 mmol) in glacial AcOH (10 mL). After 5 min, the reaction mixture was poured into 100 mL of water and extracted with ether (2×50 mL). The extract was dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. Recrystallization of the solid residue from petroleum ether gave 1.71 g (63 %) of bromoaniline **3a**, m.p. 72 °C. Found (%): C, 44.28; H, 5.21; Br, 29.44; N, 15.27. $C_{10}H_{14}BrN_3O$. Calculated (%): C, 44.13; H, 5.19; Br, 29.36; N, 15.44. MS, *m/z* (the ratio between the integral intensities): 271, 273 $[M]^+$ (1 : 1). The mother liquor was concentrated, and the residue was chromatographed (a petroleum ether—ethyl acetate mixture (19 : 1) was used as the eluent). An additional 0.77 g of compound **3a** was isolated, the overall yield was 2.48 g (91 %).

4,6-Dibromo-2-(*tert*-butyl-*NNO*-azoxy)aniline (3b). At 20 °C, a solution of bromine (3.2 g, 20 mmol) in AcOH (5 mL) was added dropwise to a stirred solution of azoxyaniline **2** (1.93 g, 10 mmol) and AcONa (1.7 g, 20.7 mmol) in glacial AcOH (10 mL). After 5 min the reaction mixture was poured into 100 mL of water and extracted with petroleum ether (2×50 mL). The extract was concentrated *in vacuo* to 15 mL. Chromatography (with petroleum ether as the eluent) gave 3.27 g (93 %) of dibromoaniline **3b**, m.p. 49—51 °C. Found (%): C, 34.40; H, 3.69; Br, 45.41; N, 11.74. $C_{10}H_{13}Br_2N_3O$. Calculated (%): C, 34.22; H, 3.73; Br, 45.52; N, 11.97. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3350, 3420 (NH_2). MS, *m/z* (the ratio between the integral intensities): 349, 351, 353 $[M]^+$ (1 : 2 : 1).

2,4-Dibromonitrosobenzene (4a). A mixture of ammonium persulfate (45.6 g, 0.2 mol) and conc. H_2SO_4 (66 g) was stirred for 1 h at 20 °C, and poured onto 400 g of ice, and 1200 mL of water was added. 2,4-Dibromoaniline (10 g, 39.8 mmol) was added to the resulting solution of Caro's acid,[11] the mixture was stirred for 4 h at 20 °C, and the precipitate was filtered off, washed with water, distilled with steam, and dried in a desiccator over P_4O_{10} to give 6.35 g (60 %) of dibromonitrosobenzene **4a**, m.p. 50—51 °C. Found (%): C, 27.13; H, 1.08; Br, 60.14; N, 4.98. $C_6H_3Br_2NO$. Calculated (%): C, 27.20; H, 1.14; Br, 60.33; N, 5.29. ^1H NMR ($CDCl_3$, 30 °C), δ: 6.05 (d, 1 H, H(6), ^3J = 8.5 Hz); 7.41 (dd, 1 H, H(5), ^3J = 8.5 Hz, ^4J = 2.2 Hz); 8.14 (d, 1 H, H(3), ^4J = 2.2 Hz). ^{13}C NMR ($CDCl_3$, 30 °C), δ: 109.91 (C(6)); 130.71 (C(3)); 132.05 and 133.58 (C(2) and C(4)); 137.35 (C(5)); 159.37 (C(1)). At −40 °C, additional paired signals of dimers **4a′** and **4a″** appear (the second signal prevails), δ: 139.72/139.93 (C(1)); 117.86/118.78 (C(2)); 125.81/126.83 (C(4)). ^{15}N NMR ($CDCl_3$, 30 °C), δ: 516.75 (N=O); at −40 °C, an additional signal of dimers appears, δ: −77.66 (N(O)=N(O)). MS, *m/z* (the ratio between the integral intensities): 263, 265, 267 $[M]^+$ (1 : 2 : 1).

The reaction of bromo(*tert*-butyl-*NNO*-azoxy)benzenes 5a,b with ammonia. A solution of compound **5** (5 mmol) in 50 mL of toluene was placed into a 150-mL steel autoclave, preliminarily cooled with liquid nitrogen, and 75 mL of liquid NH_3 was added. The mixture was heated for 8 h at 180—190 °C, at a pressure of 200 atm. The solvent was evaporated *in vacuo*, and the residue was chromatographed (using a petroleum ether—ethyl acetate mixture (19 : 1) as the eluent).

5-Bromo-2-(*tert*-butyl-*NNO*-azoxy)aniline (6a). The reaction yielded 0.08 g of unchanged **5a** (degree of conversion 95 %) and 0.95 g (74 % with respect to the converted **5a**) of aniline **6a**, m.p. 81.5—82 °C. Found (%): C, 44.29; H, 5.13; Br, 29.47; N, 15.24. $C_{10}H_{14}BrN_3O$. Calculated (%): C, 44.13; H, 5.19; Br, 29.36; N, 15.44. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3340, 3460 (NH_2). MS, *m/z* (the ratio between the integral intensities): 271, 273 $[M]^+$ (1 : 1).

3,5-Dibromo-2-(*tert*-butyl-*NNO*-azoxy)aniline (6b). The reaction yielded 0.14 g of unchanged **5b** (degree of conversion 95 %), 0.01 g (0.6 %) of **7**, and 1.35 g (82 % with respect to the converted **5b**) of aniline **6b**, m.p. 110—112 °C (from hexane). Found (%): C, 34.36; H, 3.74; Br, 45.59; N, 11.62. $C_{10}H_{13}Br_2N_3O$. Calculated (%): C, 34.22; H, 3.73; Br, 45.52; N, 11.97. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3340, 3420 (NH_2). MS, *m/z* (the ratio between the integral intensities): 349, 351, 353 $[M]^+$ (1 : 2 : 1).

3,5-Dibromo-4-(*tert*-butyl-*NNO*-azoxy)aniline (7). A solution of compound **5b** (2.07 g, 5 mmol) in 50 mL of ethanol saturated with ammonia was heated in a steel autoclave (150 mL) for 6 h at 160 °C. The solvent was evaporated *in vacuo*. Chromatography of the residue (with a petroleum ether—ethyl acetate mixture (19 : 1) as the eluent) afforded 1.79 g of unchanged **5b** and 0.13 g (55 % with respect to converted **5b**) of aniline **7**, m.p. 162—163 °C (from hexane). Found (%): C, 34.38; H, 3.60; Br, 45.72; N, 10.71. $C_{10}H_{13}Br_2N_3O$. Calculated (%): C, 34.22; H, 3.73; Br, 45.52; N, 11.97. ^1H NMR (DMSO-d_6), δ: 1.40 (s, 9 H, 3 Me); 5.95 br (s, 2 H, NH_2); 6.63 (s, 2 H, C_6H_2). ^{13}C NMR (DMSO-d_6), δ [the calculated chemical shifts are given in brackets]: 25.15 (Me); 59.40 ($\underline{C}Me_3$); 115.48 [118.6] (C(2), C(6)); 115.57 [120.6] (C(3), C(5), $^2J_{^{13}C,^1H} = {}^4J_{^{13}C,^1H}$ = 2.5 Hz); 137.21 [146.2] (C(4)); 150.72 [154.9] (C(1)). IR (KBr), ν/cm^{-1}: 1495 (N(O)=N); 3370, 3460 (NH_2). MS, *m/z* (the ratio between the integral intensities): 349, 351, 353 $[M]^+$ (1 : 2 : 1).

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