Synthesis of amino-substituted 1,3-bis(*tert*-butyl-*NNO*-azoxy)benzenes
2.* 2-Amino and 2,4-diamino derivatives

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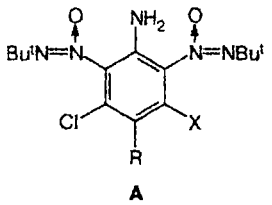
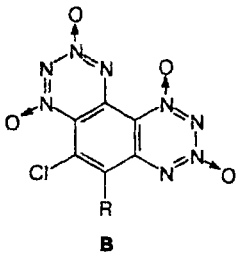
Oxidation of one of the amino groups of 2-bromo-4,6-dichloro-1,3-phenylenediamine to the nitroso group followed by its conversion into the *tert*-butyl-*NNO*-azoxy group afforded a derivative of *m*-(*tert*-butyl-*NNO*-azoxy)aniline, *viz.*, 2-bromo-3-(*tert*-butyl-*NNO*-azoxy)-4,6-dichloroaniline. Analogously, the second amino group was converted into the *tert*-butyl-*NNO*-azoxy group to form a derivative of 1,3-bis(*tert*-butyl-*NNO*-azoxy)benzene, *viz.*, 3-bromo-2,4-bis(*tert*-butyl-*NNO*-azoxy)-1,5-dichlorobenzene. The reaction of the latter with ammonia yielded 2-amino- and 2,4-diamino-substituted 1,3-bis(*tert*-butyl-*NNO*-azoxy)benzenes.

Key words: aromatic amino, azoxy, and nitroso compounds; *m*-nitrosoanilines; oxidation of the amino group.

As part of continuing studies of 1,2,3,4-tetrazines, we plan to synthesize compounds in which one benzene ring is fused with two 1,2,3,4-tetrazine-1,3-dioxide rings. The corresponding bis(*tert*-butyl-*NNO*-azoxy)anilines can serve as the initial compounds in the synthesis of the target compounds. Previously,[1] we have prepared 4-amino- and 4,6-diamino-substituted 1,3-bis(*tert*-butyl-*NNO*-azoxy)benzenes, which are intermediates in the synthesis of benzo[1,2-*e*:4,5-*e*]bis[1,2,3,4]tetrazine-1,3,7,9-tetraoxide. The present work is devoted to the synthesis of 2-amino- and 2,4-diamino-substituted 1,3-bis(*tert*-butyl-*NNO*-azoxy)benzenes (**A**), which can be used as the starting compounds for the synthesis of benzo[1,2-*e*:3,4-*e*]-bis[1,2,3,4]tetrazine-1,3,7,9-tetraoxides (**B**).



A



B

X = NH_2, Cl; R = H, Br

tert-Butyl-*NNO*-azoxybenzenes are generally prepared from the corresponding nitroso compounds and *N*,*N*-dibromo-*tert*-butylamine according to the Kovacic method.[2] Therefore, the corresponding nitrosobenzenes are the key compounds in our study.

Structures **A** were synthesized starting from 2-bromo-4,6-dichloro-1,3-phenylenediamine (**2**), which was prepared by bromination of 4,6-dichloro-1,3-phenylenediamine (**1**) under the standard conditions. Initially, we intended to apply the approach which has been used previously for preparing 1,5-bis(*tert*-butyl-*NNO*-azoxy)-2,4-dichlorobenzene.[1] This approach involves oxidation of phenylenediamine **1** to a dinitroso compound followed by the reaction with *N*,*N*-dibromo-*tert*-butylamine. However, the introduction of the bromine atom led to a substantial change in the reactivity of phenylenediamine **2** and we failed to prepare the dinitroso derivative by oxidation with Caro's acid or organic peracids. Hence, it was impossible to form two *tert*-butyl-*NNO*-azoxy groups in one step, as has been performed previously,[1] and we introduced these groups stepwise.

Peroxymaleic acid was found to be the optimum reagent for oxidation of one amino group of phenylenediamine **2** to the nitroso group. Under the action of this acid, *m*-nitrosoaniline **3** was obtained in 50% yield (Scheme 1).

The data on *m*-nitrosoanilines are scarce in the literature. In addition to compound **4**, which we have prepared previously,[1] only *N*-acetyl derivatives of *m*-nitrosoanilines[3] and amino-substituted nitrosophenols have been reliably described (see, for example, Ref. 4).

Compounds **3** and **4** differ substantially in stability. Unlike unstable compound **4**, nitrosoaniline **3**, which contains the bromine atom between the amino and nitroso groups, is quite stable and can be stored at room temperature over a long period.

* For Part 1, see Ref. 1.

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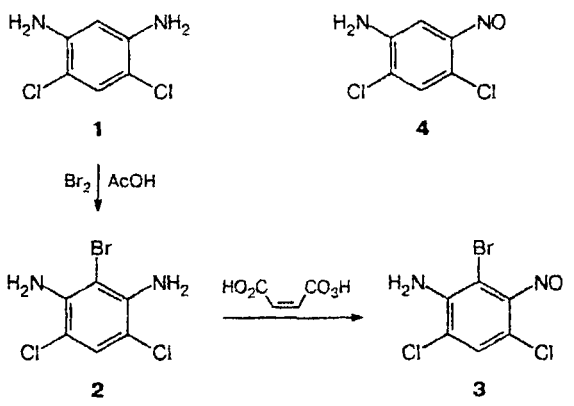
Scheme 1



The structure of compound **3** was established by NMR spectroscopy. The dependences of the ^{1}H NMR spectra on the temperature, the concentration, and the solvent were studied. It was found that monomer **3** and the *cis* and *trans* forms of dimers **3′** and **3″** exist in dynamic equilibrium (Table 1). The relative amount of the dimers increases as the concentration and the polarity of the solvent increase and decreases as the temperature increases. In the ^{1}H NMR spectra measured in $CDCl_3$, the signals of dimers **3′** and **3″** coincide and appear as a singlet. However, the ^{1}H NMR spectra measured in polar solvents ($(CD_3)_2SO$ or a 1 : 1 $(CD_3)_2SO/(CD_3)_2CO$ mixture) have two signals with close chemical shifts, which, most likely, belong to the *cis* and *trans* forms of the dimers. The ^{13}C NMR spectra of the dimers have also a double set of almost all signals. The ratio between the *cis* and *trans* forms (1 : 1) is virtually independent of the concentration and the solvent. The study of the monomer—dimer equilibrium made it possible to unambiguously assign the ^{13}C NMR signals to the monomer and dimer.

m-Nitrosoanilines **3** and **4** are characterized by a yellow-orange color both in the solid state and in solutions, which is untypical of nitroso compounds. The visible region of the electronic spectra of compound **4** (in CH_2Cl_2) has a rather intense absorption band with the maximum at 440 nm. It can be stated with assurance that this band belongs to the nitroso compound rather than to the dimer because the ^{1}H and ^{13}C NMR spectra unambiguously indicate that nitrosoaniline **4** exists in the monomeric form in solution at room temperature.[1] A solution of compound **3** can contain a small amount of dimers. However, an absorption band in the spectrum of compound **3** is also observed at 440 nm, which, apparently, indicates that this band belongs to the monomeric form. The interpretation of the spectra of *m*-nitrosoanilines calls for additional studies. Presently, it can be only suggested that the above-mentioned absorption band does not belong to the $n_N \rightarrow \pi^*$ electron transition of the nitroso group because this band in the spectra of aromatic nitroso compounds is weak and is observed in the region of 680—780 nm,[5] and there are no evident factors which could cause such a substantial shift of this band to the short-wavelength region.

Nitrosoaniline **3** reacted with *N,N*-dibromo-*tert*-butylamine to form product **5** in 63% yield. In this case, the amino group was not involved in the reaction.

A stronger oxidizing agent, such as trifluoroperacetic acid, was required for further oxidation of aniline **5** to nitroso compound **6**. Although the reaction was accompanied by substantial peroxidation and resinification, product **6** was obtained in 48% yield. Solutions of this nitroso compound develop a typical green color.

It was demonstrated by ^{1}H NMR spectroscopy that the solvent has a substantial effect on the dimer—monomer equilibrium of nitroso compound **6** (Table 2). In a solution of $CDCl_3$, compound **6** exists at a low concentration exclusively in the monomeric form, while in a DMSO-d_6 solution, **6** exists both in the dimeric and monomeric forms. This study allowed us to assign the signals to the monomeric or dimeric forms of the nitroso compound.

As expected, nitroso compound **6** reacted with *N,N*-dibromo-*tert*-butylamine to form bis(*tert*-butyl-*NNO*-azoxy)benzene **7** (Scheme 2).

Table 1. Dependence of the ratio between monomer **3** and dimers **3′** and **3″** according to the ^{1}H and ^{13}C NMR spectral data on the concentration and the solvent at 30 °C

Solvent	Concentration* /mol L^{-1}	**3** : **3′** : **3″** Ratio
$(CD_3)_2SO$	0.05	1 : 1 : 1
	0.5	2 : 5 : 5
$(CD_3)_2SO/(CD_3)_2CO$, 1 : 1	0.05	3 : 1 : 1
$CDCl_3$	0.05	4 : 1 : 1
	0.2	3 : 2 : 2
	0.2	4 : 1 : 1**

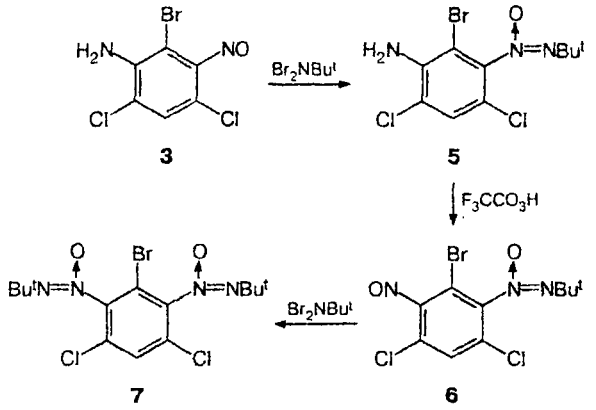
* Concentration per monomer.
** At 50 °C.

Table 2. Dependence of the ratio between monomer **6** and dimers **6′** and **6″** according to the ^{1}H NMR spectral data on the concentration and the solvent at 30 °C

Solvent	Concentration* /mol L^{-1}	**6** : **6′** : **6″** Ratio
$(CD_3)_2SO$	0.07	2 : 1 : 1
	0.2	1 : 1 : 1
$CDCl_3$	0.03	>95% **6**
	0.2	>95% **6****
	0.4	2 : 1***

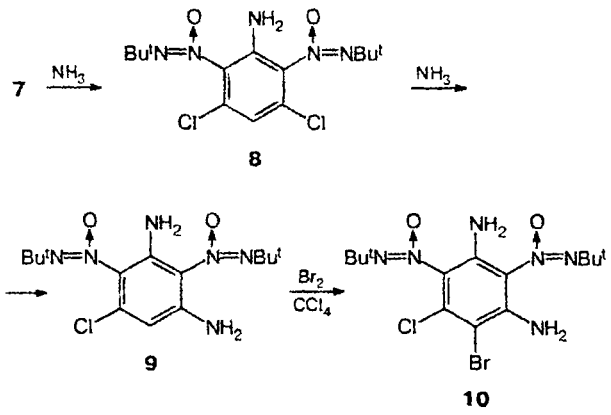
* Concentration per monomer.
** At 50 °C.
*** In $CDCl_3$, the signals of monomers **6′** and **6″** are indistinguishable.

Scheme 2



The reaction of compound **7** with ammonia was performed as described previously[1] in an autoclave at 170—180 °C using toluene as the solvent. Under these conditions, the bromine atom was selectively replaced to give aniline **8**. Under more drastic conditions, the chlorine atom was also replaced to yield diamino derivative **9** (Scheme 3).

Scheme 3



The structures of compounds **7**, **8**, and **9** were confirmed by ^1H, ^{13}C, and ^{14}N NMR spectroscopy (see Experimental). In particular, a characteristic signal of the *N*-oxide nitrogen atom of the azoxy group is clearly seen in the ^{14}N NMR spectra at δ from −53 to −60 with a half-width of 150—190 Hz (*cf.* Refs. 1 and 6).

With the aim of extending the variety of the target products, we synthesized brominated derivative **10**. Note that the reaction of compound **9** with one equivalent of bromine to form compound **10** proceeded smoothly only in nonpolar solvents (for example, in CCl_4). In polar solvents (for example, in AcOH), the *tert*-butyl-*NNO*-azoxy group was unexpectedly replaced by the bromine atom. This reaction has been considered in detail in Ref. 7.

Experimental

The IR spectra were recorded on a Perkin—Elmer 577 spectrometer. The electronic absorption spectra (EAS) were obtained on a Specord UV VIS spectrophotometer. The mass spectra were measured on a Kratos MS-30 instrument (EI, 70 eV); only signals from the ^{35}Cl and ^{79}Br isotopes are given for fragments containing chlorine and bromine atoms. The ^1H, ^{13}C, and ^{14}N NMR spectra were obtained on a Bruker AM-300 spectrometer operating at 300.13, 75.5, and 21.5 MHz, respectively. The chemical shifts in the ^{14}N NMR spectra are given in the δ scale relative to nitromethane. The assignment of the signals in the ^{13}C NMR spectra was made using procedures for obtaining spectra with selective decoupling of signals of individual protons and selective polarization transfer (SPT) from the protons as well as with the use of calculational techniques (an additive scheme). The course of the reactions was monitored by TLC on Silufol UV-254 plates; silica gel was used for column chromatography.

2,4-Dichloro-5-nitrosoaniline,[1] 4,6-dichloro-1,3-phenylenediamine,[8] and *N,N*-dibromo-*tert*-butylamine[9] were prepared according to procedures reported previously.

2-Bromo-4,6-dichloro-1,3-phenylenediamine (2). A solution of bromine (7.2 g, 45 mmol) in AcOH (15 mL) was added with stirring to a solution of 4,6-dichloro-1,3-phenylenediamine (**1**) (8.0 g, 45 mmol) in AcOH (100 mL) at 20 °C. The reaction mixture was stirred for 20 min. The precipitate that formed was filtered off, washed with water, and dried in air. Recrystallization of the residue from AcOH afforded phenylenediamine **2** in a yield of 10 g (87%), m.p. 145—146 °C. Found (%): C, 28.11; H, 1.93; Br+Cl, 58.79; N, 11.22. $C_6H_5BrCl_2N_2$. Calculated (%): C, 28.16; H, 1.97; Br, 31.22; Cl, 27.71; N, 10.95. IR (KBr), ν/cm^{-1}: 3300, 3420 (NH_2). ^1H NMR ($(CD_3)_2SO$), δ: 5.26 (s, 4 H, NH_2); 7.20 (s, 1 H, CH). ^{13}C NMR ($(CD_3)_2SO$), δ: 94.5 (C-2); 104.8 (C-4, C-6); 127.2 (C-5); 141.2 (C-1, C-3). MS, *m/z*: 254 $[M]^+$.

2-Bromo-4,6-dichloro-3-nitrosoaniline (3). Peroxymaleic acid was prepared according to a known procedure.[10] Finely dispersed maleic anhydride (5.1 g, 52 mmol) was gradually added with vigorous stirring to a solution of 90% H_2O_2 (1.2 mL, 44 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The reaction mixture was stirred for 0.5 h, during which the temperature was gradually increased to 20 °C. The resulting solution was added with stirring to a solution of phenylenediamine **2** (5 g, 20 mmol) in CH_2Cl_2 (100 mL). The reaction mixture was stirred for 3 h and kept for 12 h. The solution was decanted, washed with water until the aqueous layer became transparent, and dried ($MgSO_4$). Then the solvent was evaporated *in vacuo*. The residue was washed on a filter with cold MeOH and dried in air. Aniline **3** was obtained in a yield of 2.7 g (50%) as orange crystals, m.p. 146—147 °C (from $CHCl_3$). Found (%): C, 26.58; H, 1.06; Br+Cl, 55.58; N, 10.30. $C_6H_3BrCl_2N_2O$. Calculated (%): C, 26.70; H, 1.12; Br, 29.60; Cl, 26.27; N, 10.38. EAS, visible region (CH_2Cl_2, λ_{max}/nm (lgε)): 440 (3.17). IR (KBr), ν/cm^{-1}: 3300, 3370, 3420, 3475 (NH_2). ^1H NMR ($CDCl_3$, *c* 0.05 mol L^{-1}), δ: 4.94 (br.s, 2 H, NH_2); 7.43 (s, 1 H, CH). ^1H NMR ($(CD_3)_2SO$, *c* 0.05 mol L^{-1}), δ: 6.20 (br.s, 2 H, NH_2); 7.73 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$, *c* 0.2 mol L^{-1}, 50 °C), δ: 106.9 (C-2); 112.4 (C-4, ^2J = 5.6 Hz); 123.5 (C-6, ^2J = 5.7 Hz); 130.3 (C-5); 141.9 (C-1, ^3J = 7.1 Hz); 158.2 (C-3, ^3J = 7.1 Hz). MS, *m/z*: 268 $[M]^+$.

Dimers 3′ and 3″. ^{1}H NMR ($(CD_3)_2SO$, *c* 0.05 mol L^{-1}), δ: 6.20 (br.s, 2 H, NH_2); 7.78/7.79* (both s, each 1 H, CH); the **3′/3″** ratio is 1 : 1. ^{1}H NMR ($CDCl_3$), δ: 4.82 (br.s, 2 H, NH_2); 7.48 (s, 1 H, CH). ^{13}C NMR ($(CD_3)_2SO$, *c* 0.2 mol L^{-1}, 50 °C), δ: 103.2/103.4 (C-2 or C-4, ^4J = 2.4 Hz); 114.0/114.2 (C-4 or C-2, ^2J = 4.6 Hz); 119.8/119.9 (C-6, ^2J = 4.9 Hz); 129.3/129.4 (C-5); 137.85 (C-3, ^3J = 8.5 Hz); 143.2/143.3 (C-1, ^3J = 7.3 Hz); the **3′/3″** ratio is 1 : 1. ^{13}C NMR ($CDCl_3$, *c* 0.2 mol L^{-1}), δ: 129.6/129.7 (C-5). The **3′/3″** ratio is 1 : 1.

2,4-Dichloro-5-nitrosoaniline (4). EAS, visible region (CH_2Cl_2, λ_{max}/nm (lgε)): 440 (3.30).

2-Bromo-3-(*tert*-butyl-*NNO*-azoxy)-4,6-dichloroaniline (5). *N,N*-Dibromo-*tert*-butylamine (2.75 g, 12 mmol) was added with stirring to a solution of aniline **3** (2.5 g, 9.3 mmol) in CH_2Cl_2 (100 mL) and MeCN (100 mL) at 20 °C and then the reaction mixture was kept for 12 h. The solvent and excess *N,N*-dibromo-*tetr*-butylamine were distilled off *in vacuo*. Chromatography (benzene as the eluent) gave aniline **5** in a yield of 2.0 g (63%) as a yellow oil. Found (%): C, 35.11; H, 3.61; Br+Cl, 43.45; N, 12.20. $C_{10}H_{12}BrCl_2N_3O$. Calculated (%): C, 35.22; H, 3.55; Br, 23.43; Cl, 20.79; N, 12.32. IR (KBr), ν/cm^{-1}: 1495 (N(O)=N); 3380, 3480 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 1.50 (s, 9 H, 3 Me); 4.71 (br.s, 2 H, NH_2); 7.33 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 25.5 (Me); 60.7 (<u>C</u>Me$_3$); 102.6 (C-2, ^4J = 1.6 Hz); 114.8 (C-4, ^2J = 4.7 Hz); 118.7 (C-6, ^2J = 4.2 Hz); 129.0 (C-5); 141.3 (C-1, ^3J = 7.2 Hz); 145.6 (br, C-3, ^3J = 9.4 Hz). ^{14}N NMR ($CDCl_3$), δ: −56 (N(O), $\Delta\nu_{1/2}$ = 140 Hz). MS, *m/z*: 339 $[M]^+$.

3-Bromo-2-(*tert*-butyl-*NNO*-azoxy)-1,5-dichloro-4-nitrosobenzene (6). Trifluoroperacetic acid was prepared according to a known procedure.[11] Trifluoroacetic anhydride (3.7 mL, 26 mmol) was added with stirring to a solution of 90% H_2O_2 (0.6 mL, 22 mmol) in CH_2Cl_2 (8 mL) at 0 °C. Then the reaction mixture was stirred for 0.5 h, during which the temperature was gradually increased to 20 °C. The resulting solution was added dropwise to a solution of aniline **5** (2.0 g, 6 mmol) in CH_2Cl_2 (50 mL) over 2 h. The addition was performed until the degree of conversion of the starting compound became equal to 90—95% (TLC control, benzene as the eluent). The reaction solution was washed with a large amount of water and dried ($MgSO_4$). The solvent was evaporated *in vacuo*. Chromatography gave colorless crystalline nitrobenzene **6** in a yield of 1.0 g (48%), m.p. 161—163 °C (from acetone). Found (%): C, 34.27; H, 2.83; Br+Cl, 41.43; N, 12.05. $C_{10}H_{10}BrCl_2N_3O_2$. Calculated (%): C, 33.83; H, 2.84; Br, 22.51; Cl, 19.97; N, 11.84. IR (KBr), ν/cm^{-1}: 1500 (N(O)=N). ^{1}H NMR ($CDCl_3$, *c* 0.2 mol L^{-1}, 50 °C), δ: 1.56 (s, 9 H, 3 Me); 7.65 (s, 1 H, CH). ^{1}H NMR ($(CD_3)_2SO$, *c* 0.07 mol L^{-1}), δ: 1.48 (s, 9 H, 3 Me); 8.30 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$, *c* 0.2 mol L^{-1}, 50 °C), δ: 25.6 (Me); 61.4 (<u>C</u>Me$_3$); 115.4 (C-3, ^4J = 1.9 Hz); 124.8 (C-1 or C-5, ^2J = 5.7 Hz); 132.1 (C-6); 132.7 (C-5 or C-1, ^2J = 3.8 Hz); 146.7 (br, C-2, ^3J = 9.5 Hz); 157.3 (C-4, ^3J = 5.7 Hz). ^{14}N NMR ($CDCl_3$), δ: −60 (<u>N</u>(O), $\Delta\nu_{1/2}$ = 150 Hz). MS, *m/z*: 353 $[M]^+$.

Dimers 6′ and 6″. ^{1}H NMR ($(CD_3)_2SO$, *c* 0.07 mol L^{-1}), δ: 1.47 (two coinciding singlets, each 9 H, Me); 8.43/8.44 (both s, each 1 H, CH). The **6′/6″** ratio was 1 : 1. ^{1}H NMR ($CDCl_3$, *c* 0.4 mol L^{-1}), δ: 1.51 (s, 9 H, 3 Me); 7.70 (s, 1 H, CH).

3-Bromo-2,4-bis(*tert*-butyl-*NNO*-azoxy)-1,5-dichlorobenzene (7). *N,N*-Dibromo-*tert*-butylamine (0.72 g, 3.1 mmol) was added with stirring to a green solution of compound **6** (1.0 g, 2.8 mmol) in CH_2Cl_2 (60 mL) at 20 °C and the reaction mixture was kept for 12 h. The solvent was evaporated *in vacuo*. Crystallization from MeOH afforded compound **7** in a yield of 1.0 g (83%) as colorless crystals, m.p. 147—149 °C. Found (%): C, 39.25; H, 4.42; Br+Cl, 34.92; N, 13.0. $C_{14}H_{19}BrCl_2N_4O_2$. Calculated (%): C, 39.46; H, 4.49; Br, 18.75; Cl, 16.64; N, 13.15. IR (KBr), ν/cm^{-1}: 1495 (N(O)=N). ^{1}H NMR ($CDCl_3$), δ: 1.50 (s, 18 H, 6 Me); 7.58 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 25.5 (Me); 61.1 (<u>C</u>Me$_3$); 112.5 (C-3, ^4J = 2.4 Hz); 128.3 (C-1, C-5, ^2J = 4.3 Hz); 130.6 (C-6); 145.7 (br, C-2, C-4, ^2J = 7.7 Hz). ^{14}N NMR ($CDCl_3$), δ: −60 (N(O), $\Delta\nu_{1/2}$ = 180 Hz). MS, *m/z*: 424 $[M]^+$.

2,6-Bis(*tert*-butyl-*NNO*-azoxy)-3,5-dichloroaniline (8). A solution of compound **7** (1.6 g, 3.8 mmol) in toluene (18 mL) was placed into a 50-mL steel autoclave precooled with liquid nitrogen and then liquid NH_3 (10 mL) was added. The reaction mixture was heated at 130 °C for 8 h. After cooling of the reaction mixture, the precipitate was filtered off and the filtrate was concentrated *in vacuo*. Chromatography (benzene as the eluent) gave aniline **8** in a yield of 1.1 g (81%) as yellow crystals, m.p. 117—119 °C (from MeOH). Found (%): C, 46.16; H, 5.98; Cl, 19.63; N, 19.22. $C_{14}H_{21}Cl_2N_5O_2$. Calculated (%): C, 46.42; H, 5.84; Cl, 19.57; N, 19.33. IR (KBr), ν/cm^{-1}: 1490 (N(O)=N); 3385, 3490 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 1.49 (s, 18 H, 6 Me); 4.69 (br.s, 2 H, NH_2); 6.91 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 25.6 (Me); 60.8 (<u>C</u>Me$_3$); 119.1 (C-4); 128.0 (C-3, C-5); 134.5 (br, C-2, C-6); 136.4 (C-1). ^{14}N NMR ($CDCl_3$), δ: −60 (N(O), $\Delta\nu_{1/2}$ = 150 Hz). MS, *m/z*: 361 $[M]^+$.

2,4-Bis(*tert*-butyl-*NNO*-azoxy)-5-chloro-1,3-phenylenediamine (9). The reaction was performed as described above at 190 °C for 12 h. After chromatographic separation, aniline **8** was obtained in a yield of 0.4 g (29%) and phenylenediamine **9** was obtained in a yield of 0.5 g (39%) as orange crystals, m.p. 101—103 °C (from MeOH). Found (%): C, 49.35; H, 6.82; Cl, 9.92; N, 24.40. $C_{14}H_{23}ClN_6O_2$. Calculated (%): C, 49.05; H, 6.76; Cl, 10.34; N, 24.51. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3380, 3385, 3475, 3490 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 1.47 (s, 9 H, 3 Me); 1.48 (s, 9 H, 3 Me); 5.12 (br.s, 2 H, NH_2); 5.55 (br.s, 2 H, NH_2); 6.13 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 25.7, 26.2 (both Me); 60.0, 60.3 (both <u>C</u>Me$_3$); 105.8 (C-6); 121.7 (br, C-2); 127.6 (br, C-4); 129.2 (C-5); 137.8 (C-3); 142.7 (C-1). ^{14}N NMR ($CDCl_3$), δ: −53 (N(O), $\Delta\nu_{1/2}$ = 190 Hz). MS, *m/z*: 342 $[M]^+$.

4-Bromo-2,6-bis(*tert*-butyl-*NNO*-azoxy)-5-chloro-1,3-phenylenediamine (10). A solution of Br_2 (0.1 g, 0.6 mmol) in CCl_4 (1 mL) was added dropwise with intense stirring to a solution of phenylenediamine **9** (0.2 g, 0.6 mmol) in CCl_4 (5 mL) at 20 °C. The solvent was evaporated *in vacuo*. Chromatography (benzene as the eluent) of the residue gave compound **10** in a yield 0.17 g (69%) as yellow crystals, m.p. 90—92 °C (from hexane). Found (%): C, 39.75; H, 5.29; Br+Cl, 27.61; N, 19.79. $C_{14}H_{22}BrClN_6O_2$. Calculated (%): C, 39.87; H, 5.26; Br, 18.95; Cl, 8.41; N, 19.93. IR (KBr), ν/cm^{-1}: 1485 (N(O)=N); 3320, 3355, 3410, 3460 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 1.49 (s, 18 H, 6 Me); 5.30 (br.s, 2 H, NH_2); 5.66 (br.s, 2 H, NH_2). ^{13}C NMR ($CDCl_3$), δ: 25.5, 26.1 (both Me); 60.3, 60.5 (both <u>C</u>Me$_3$); 99.1 (C-4); 121.7 (br, C-2); 128.3 (br, C-6); 130.0 (C-5); 136.0 (C-1); 141.0 (C-3). ^{14}N NMR ($CDCl_3$), δ: −54 (N(O), $\Delta\nu_{1/2}$ = 170 Hz). MS, *m/z*: 420 $[M]^+$.

* Hereinafter, the signals of the corresponding atoms of the *cis* and *trans* dimers of the nitroso compounds are separated by slashes.

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