Synthesis of 1,2,3,4-tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxides

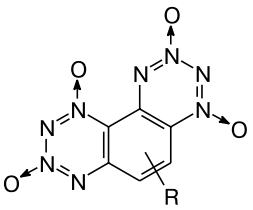
A. E. Frumkin, A. M. Churakov, Yu. A. Strelenko, and V. A. Tartakovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5328. E-mail: churakov@ioc.ac.ru

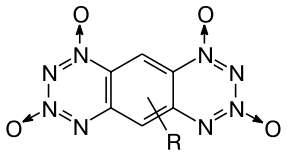
1,2,3,4-Tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxides, which possess anthracene-type annulation of the benzene ring with two 1,2,3,4-tetrazine 1,3-dioxide fragments, were obtained for the first time from aminobenzenes containing *tert*-butyl-*NNO*-azoxy groups in appropriate positions. Complete assignments of the signals in the ^{1}H, ^{13}C, and ^{14}N NMR spectra of the compounds obtained were carried out.

Key words: benzo-1,2,3,4-tetrazines, *N*-oxides, *N*-nitroamines, azoxy compounds, ^{13}C NMR spectroscopy.

Benzo-1,2,3,4-tetrazine 1,3-dioxides (BTDO) fused with a second 1,2,3,4-tetrazine 1,3-dioxide (TDO) ring are of interest as a new class of polynitrogen heterocycles with pronounced electrophilic properties. Angularly fused compounds **A** with the phenanthrene-type annulation of the rings have been obtained by us earlier.[1] Here we propose methods for the synthesis of linearly fused compounds **B** with the anthracene-type annulation.



A



B

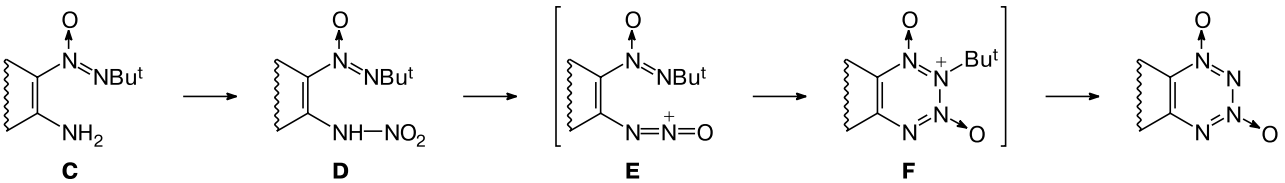
Previously,[2] we have developed several versions of the synthesis of BTDO from *o*-(*tert*-butyl-*NNO*-azoxy)anilines **C**. One of them[3] involves treatment of these azoxyanilines with an excess of a nitrating reagent (N_2O_5 or NO_2BF_4). Presumably, the reaction proceeds through intermediate oxodiazonium ion **E** (generated under the action of the nitrating reagent on *N*-nitroamine **D**), which undergoes cyclization into cation **F** with subsequent elimination of the *tert*-butyl cation to give the target TDO ring (Scheme 1). Another route to BTDO[4] involves treatment of *N*-nitroamine **D** with phosphoric anhydride. Supposedly, this reaction is also mediated by oxodiazonium ion **E**. We used both the methods to obtain compounds **B**.

Results and Discussion

Step-by-step cyclization. The first approach to the synthesis of 1,2,3,4-tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxides (TBTTO) involves sequential formation of two TDO rings. Treatment of azoxyaniline **1** with nitric anhydride gave compound **2** (Scheme 2). In a reaction of the latter with ammonia, the Cl atom was easily replaced by an amino group to form amino derivative **3**. The second TDO ring was also closed under the action of N_2O_5. Treatment of compound **3** with this cyclization reagent yielded TBTTO **4** and nitro-TBTTO **5**.

Only nitro derivative **5** was isolated in the individual state from the mixture of products **4** and **5**. This was done by extraction with CH_2Cl_2. To obtain pure compound **4**, we employed the second way of cyclization that prevents

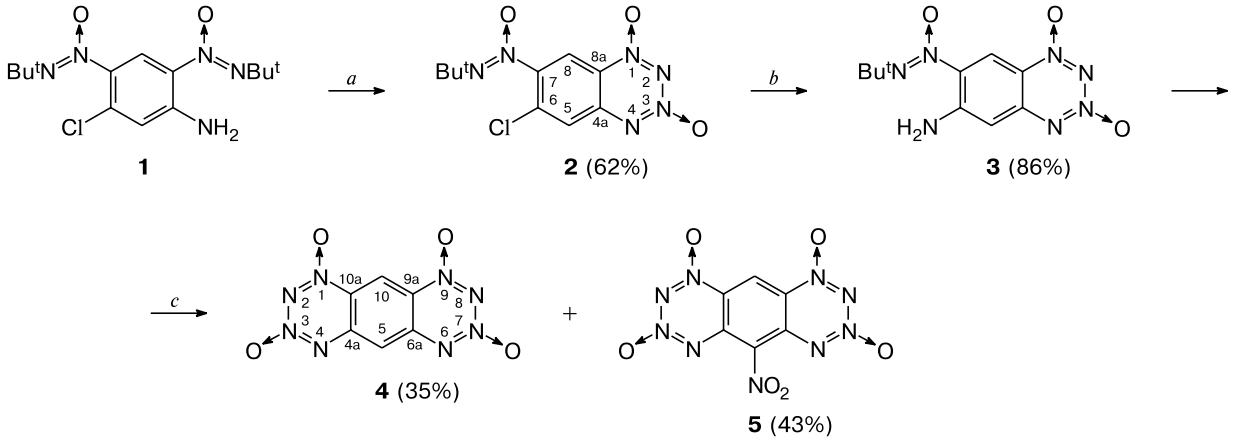
Scheme 1



C **D** **E** **F**

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1595—1599, September, 2006.

Scheme 2

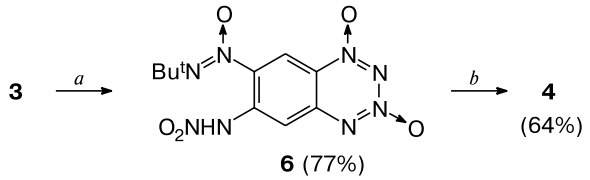


Reagents and conditions: *a*. N_2O_5, MeCN, –30 °C; *b*. NH_3, DMSO, 60 °C, 3 h; *c*. N_2O_5, MeCN, –30 °C.

the formation of products directly nitrated in the ring, *viz.*, treatment of an appropriate nitramine with P_4O_{10}.

Nitramine **6** was obtained from amino derivative **3** under the action of an equivalent of NO_2BF_4 at –20 °C. The reaction of this nitramine with P_4O_{10} gave compound **4** in 64% yield (Scheme 3). Note that the resulting compound required no additional purification.

Scheme 3



Reagents and conditions: *a*. BF_4NO_2, MeCN, –20 °C; *b*. P_4O_{10}, MeCN, 20 °C, 2 h.

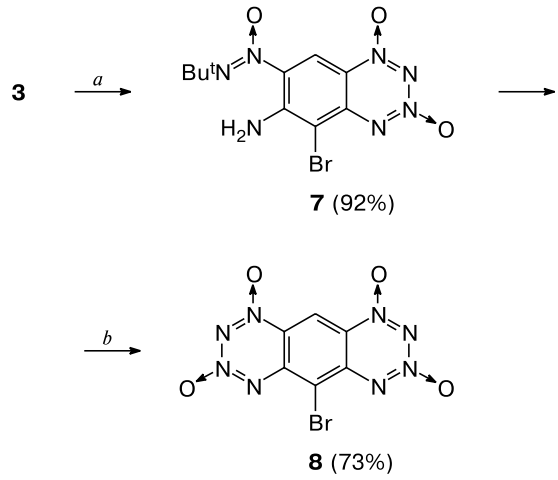
Bromination of BTDO **3** under standard conditions followed by treatment of the resulting BTDO **7** with N_2O_5 afforded bromo-TBTTO **8** (Scheme 4).

Single-step cyclization. The second approach to the synthesis of TBTTO involves the formation of two tetrazine 1,3-dioxide rings in one step. Treatment of phenylenediamine **9** with N_2O_5 gave, as in the first way, a mixture of compounds **4** and **5** (Scheme 5).

This method was used to obtain TBTTO **8** in good yield by treating phenylenediamine **10** with N_2O_5 (Scheme 6). For the synthesis of compounds **5** and **8**, this method is preferred to step-by-step cyclization.

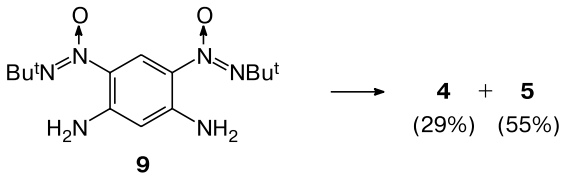
Confirmation of the TBTTO structure. The structure of TBTTO was unambiguously confirmed by physicochemical studies. The mass spectra (EI, 70 eV) of compounds **4**, **5**, and **8** contain molecular ion peaks. The

Scheme 4



Reagents and conditions: *a*. Br_2, AcOH/AcONa, 20 °C, 5 min; *b*. N_2O_5, MeCN,–30 °C.

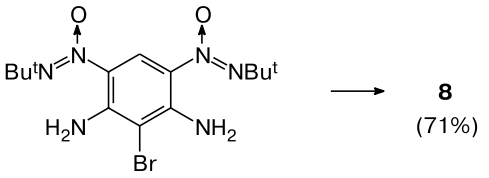
Scheme 5



Reagents and conditions: N_2O_5, MeCN, –30 °C.

^{14}N NMR spectra (Table 1) show narrow signals for the N(1) and N(3) atoms in the ranges typical of benzotetrazine 1,3-dioxides. For instance, for unsubstituted benzotetrazine 1,3-dioxide, which is the simplest repre-

Scheme 6



Reagents and conditions: N_2O_5, MeCN, −30 °C.

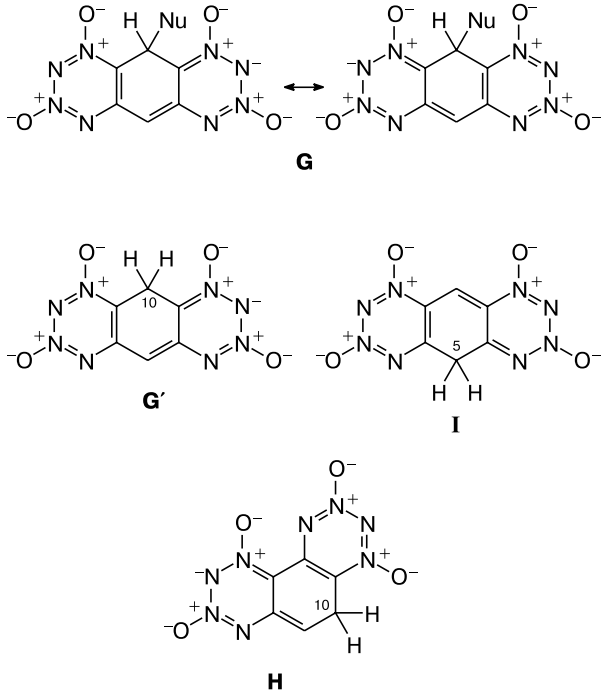
sentative of this series, the chemical shifts of the N(1) and N(3) atoms are δ −41 ($\Delta\nu_{1/2}$ = 20 Hz) and −48 ($\Delta\nu_{1/2}$ = 30 Hz), respectively.[2] The ^{13}C NMR spectra (Table 2) contain four signals for the benzene ring, which prove the symmetrical structures of the products.

Stability of TBTTO. The thermal stabilities of linearly fused TBTTO **B** under consideration are comparable with those of angularly fused TBTTO **A** obtained earlier.[1] When heated on a Kofler hot stage, linearly fused TBTTO began to decompose without melting at 140—160 °C. These compounds are very sensitive to nucleophiles, including water. For this reason, water treatment of the reaction mixture should be excluded during their isolation.

In DMSO containing trace amounts of water, TBTTO decompose instantaneously. Because of this, we recorded their NMR spectra in CD_3CN. These solutions are stable for one to two days. Solutions of TBTTO in CH_2Cl_2 are even more stable; however, these compounds are substantially less soluble in this solvent. When stored in the solid state, TBTTO gradually resinify even at a low temperature (−10 °C). Both solid compounds and their solutions can be appreciably stabilized by adding small amounts of an acid (*e.g.*, CF_3COOH).

1,2,3,4-Tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxides, especially nitro derivative **5**, are broken down by silica gel, which precluded their purification by preparative chromatography. At the same time, the purity of TBTTO can be checked by TLC (Silufol UV-254) in benzene—ether (10 : 1) as an eluent containing 0.05% CF_3COOH.

The high reactivity of linearly fused TBTTO toward nucleophiles can be explained by the very easy formation of an anionic σ-complex of the type **G**, in which the negative charge is symmetrically partitioned between two TDO rings. Such complexes are thermodynamically more stable than analogous anionic σ-complexes of the type **H** generated from angularly fused TBTTO **A**.



According to our quantum-chemical HF/6-31G(d) calculations, σ-complex **G′** is more stable than σ-complex **H** (by 23 kcal mol^{-1}). The relative total energies of the isomers are 0 (**G′**), 23 (**H**), and 28 kcal mol^{-1} (**I**) (the energy of the thermodynamically most stable isomer was taken to be zero). To simplify the calculations, the hydrogen atom in compounds **G′**, **H**, and **I** was considered a nucleophile.

Anionic σ-complex **G′** is substantially more stable than isomeric anionic σ-complex **I** arising from an attack of a nucleophile at position 5, because the charge distribution along the nitrogen chain in the tetrazine ring of the latter σ-complex is much worse. This explains, at least

Table 1. ^{1}H and ^{14}N NMR spectra (CD_3CN) of compounds **4**, **5**, and **8**

Compound	^{1}H NMR δ		^{14}N NMR δ ($\Delta\nu_{1/2}$/Hz)		
	H(5)	H(10)	N(1), N(9)	N(3), N(7)	NO_2
4	8.27 (s)	9.10 (s)	−39 (40)	−46 (70)	—
5	—	9.25 (s)	−40 (50)	−45 (70)	−28 (40)
8	—	9.18 (s)	−39 (60)	46 (100)	—

Table 2. ^{13}C NMR spectra (CD_3CN) of compounds **4**, **5**, and **8**

Compound	δ (*J*/Hz)			
	C(5)	C(4a), C(6a)	C(9a), C(10a)	C(10)
4	119.9	146.9 ($^3J_{H(10)}$ = 5.8, $^2J_{H(5)}$ = 2.5)	128.7 (br.s)	115.1
5	123.4 (br.s)	140.0	128.1 (br.s)	117.2
8	110.7	146.1 ($^3J_{H(10)}$ = 6.3)	129.6 (br.s)	113.4

partly, our failure to replace the Br atom in position 5 of TBTTO by a nucleophile. For instance, treatment of bromo-TBTTO **8** with morpholine yielded a difficult-to-separate mixture of products. In this respect, TBTTO differ greatly from bromobenzotetrazine 1,3-dioxides, from which the Br atom can be normally displaced by a nucleophile, regardless of its position in the ring.[2]

Experimental

^{1}H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13, 75.5, and 21.5 MHz, respectively). Chemical shifts were measured with reference to Me_4Si (^{1}H and ^{13}C) or $MeNO_2$ (^{14}N; the external standard; high-field chemical shifts are negative). IR spectra were recorded on a UR-20 instrument. Mass spectra were recorded on a Varian MAT-311A instrument (EI, 70 eV). For fragments containing bromine and chlorine atoms, the peaks due to the ^{35}Cl and ^{79}Br isotopes are given only. The course of the reactions was monitored by TLC on Silufol UV-254 plates.

To assign the signals in the ^{1}H and ^{13}C NMR spectra, we used 2D C—H correlation spectroscopy and selective proton decoupling, selective polarization transfer (SPT) from protons, and NOE techniques.

Compounds **1**, **9**, and **10** were prepared according to the published procedures;[5] N_2O_5 was prepared from conc. HNO_3 and P_4O_{10} (see Ref. 6) in a flow of dry argon and evacuated (15 Torr) at 0 °C to remove N_2O_4.

Synthesis of the starting reagents

7-(*tert*-Butyl-*NNO*-azoxy)-6-chlorobenzo-1,2,3,4-tetrazine 1,3-dioxide (2). Nitric anhydride (3 g, 27.8 mmol) was added at −30 °C to a solution of azoxyaniline **1** (3 g, 9.2 mmol) in dry MeCN (20 mL). The reaction mixture was stirred at −30 °C for 30 min. The precipitate was filtered off, washed with a small amount of cold MeCN and then with water, and dried in air. The yield of compound **2** was 1.7 g (62%), yellow crystals, m.p. 253—255 °C (from ether). Found (%): C, 40.54; H, 3.67; Cl, 11.53; N, 28.29. $C_{10}H_{11}ClN_6O_3$. Calculated (%): C, 40.21; H, 3.71; Cl, 11.87; N, 28.14. IR (KBr), ν/cm^{-1}: 1420, 1510 (N_4O_2); 1495 (N(O)=NBu^t). ^{1}H NMR (DMSO-d$_6$), δ: 1.48 (s, 9 H, 3 Me); 8.46 (s, 1 H, H(5)); 8.81 (s, 1 H, H(8)). ^{13}C NMR (DMSO-d$_6$), δ: 25.2 (Me); 60.4 (C$\underline{\text{C}}$Me$_3$); 115.5 (C(8)); 126.2 (C(5)); 127.5 (br.s, C(8a), ^3J = 7.4 Hz, ^2J = 3.9 Hz); 135.0 (C(6), ^3J = 9.1 Hz, ^2J = 4.3 Hz); 143.5 (C(4a), ^3J = 5.9 Hz, ^2J = 2.2 Hz); 146.5 (br.s, C(7), ^3J = 8.3 Hz, ^2J = 4.1 Hz). ^{14}N NMR (acetone-d$_6$), δ: −56 ($\underline{\text{N}}$(O)=NBu^t, $\Delta\nu_{1/2}$ = 85 Hz); −45 ($\Delta\nu_{1/2}$ = 75 Hz); −40 ($\Delta\nu_{1/2}$ = 50 Hz) (N(3), N(1)). MS, *m/z*: 298 [M]$^+$.

6-Amino-7-(*tert*-butyl-*NNO*-azoxy)-1,2,3,4-tetrazine 1,3-dioxide (3). Gaseous NH_3 was bubbled at 60 °C for 3 h through a solution of compound **2** (1.5 g, 5.0 mmol) in dry DMSO (10 mL) until compound **2** was completely consumed (monitoring by TLC with benzene as an eluent). The reaction mixture was cooled to 20 °C and diluted with water (30 mL). The precipitate was filtered off, washed with water, and dried in air. The yield of compound **3** was 1.2 g (86%), red crystals, m.p. 262—263 °C (decomp.; from acetone). Found (%): C, 42.79; H, 4.62; N, 35.31. $C_{10}H_{13}N_7O_3$. Calculated (%): C, 43.01; H, 4.69; N, 35.11. IR (KBr), ν/cm^{-1}: 1450 (N_4O_2); 1515 (N(O)=NBu^t); 3325, 3435 (NH_2). ^{1}H NMR (DMSO-d$_6$), δ: 1.46 (s, 9 H, 3 Me); 6.98 (s, 1 H, H(5)); 7.80 (br.s, 2 H, NH_2); 8.53 (s, 1 H, H(8)). Irradiation of the sample at the frequency of the signal for NH_2 gave rise to the Overhauser effect (NOE) for the signal of H(5). ^{13}C NMR (DMSO-d$_6$), δ: 25.4 (Me); 60.0 (C$\underline{\text{C}}$Me$_3$); 104.0 (C(5)); 117.1 (C(8)); 118.8 (C(8a), ^3J = 7.9 Hz, ^2J = 3.8 Hz); 136.2 (br.s, C(7)); 144.6 (C(4a), ^3J = 6.1 Hz, ^2J = 2.2 Hz); 149.9 (C(6), ^3J = 6.8 Hz). ^{14}N NMR (acetone-d$_6$), δ: −53 ($\underline{\text{N}}$(O)=NBu^t, $\Delta\nu_{1/2}$ = 50 Hz); −43 ($\Delta\nu_{1/2}$ = 70 Hz); −41 ($\Delta\nu_{1/2}$ = 90 Hz) (N(1) and N(3)). MS, *m/z*: 279 [M]$^+$.

7-(*tert*-Butyl-*NNO*-azoxy)-6-(*N*-nitroamino)-1,2,3,4-tetrazine 1,3-dioxide (6). Nitronium tetrafluoroborate (0.24 g, 1.8 mmol) was added at −20 °C to a stirred solution of compound **3** (0.28 g, 1.0 mmol) in dry MeCN (10 mL). The reaction mixture was stirred at −20 °C for 30 min until the starting reagent was completely consumed (monitoring by TLC with $CHCl_3$—EtOAc (5 : 1) as an eluent). The solvent was removed *in vacuo* at ≤0 °C. The product from the residue was extracted with CH_2Cl_2 and the extract was dried with $MgSO_4$ and concentrated *in vacuo*. The yield of compound **6** was 0.25 g (77%), brown crystals, m.p. 61—63 °C (from $CHCl_3$). Found (%): C, 37.27; H, 3.71; N, 34.40. $C_{10}H_{12}N_8O_5$. Calculated (%): C, 37.04; H, 3.73; N, 34.56. IR (KBr), ν/cm^{-1}: 1430, 1515, 3110 (NH). ^{1}H NMR (CD_2Cl_2), δ: 1.55 (s, 9 H, 3 Me); 8.67 (s, 1 H, H(5)); 9.12 (s, 1 H, H(8)); 14.10 (br.s, 1 H, NH). ^{13}C NMR (CD_2Cl_2), δ: 25.7 (Me); 62.2 (C$\underline{\text{C}}$Me$_3$); 114.8 (C(5)); 118.2 (C(8)); 123.5 (br.s, C(8a)); 136.8 (br.s, C(7)); 138.2 (C(6), ^3J = 7.9 Hz, ^2J = 2.3 Hz); 145.2 (C(4a), ^3J = 6.1 Hz, ^2J = 2.8 Hz). ^{14}N NMR (CD_2Cl_2), δ: −58 (1 N, $\underline{\text{N}}$(O)=NBu^t, $\Delta\nu_{1/2}$ = 75 Hz); −43 (3 N, N(1), N(3), NO_2, $\Delta\nu_{1/2}$ = 110 Hz). MS, *m/z*: 324 [M]$^+$.

6-Amino-5-bromo-7-(*tert*-butyl-*NNO*-azoxy)-1,2,3,4-tetrazine 1,3-dioxide (7). Sodium acetate (0.1 g, 1.3 mmol) was added to a suspension of compound **3** (0.30 g, 1.1 mmol) in glacial AcOH (8 mL). Then a solution of bromine (0.21 g, 1.3 mmol) in acetic acid (1 mL) was added dropwise at 20 °C with vigorous stirring. After 5 min, the reaction mixture was diluted with water (50 mL). The resulting precipitate was filtered off, washed with water, and dried. The yield of compound **7** was 0.36 g (92%), orange crystals, m.p. 252—256 °C (decomp.; from acetone). Found (%): C, 33.51; H, 3.22; Br, 22.07; N, 27.23. $C_{10}H_{12}BrN_7O_3$. Calculated (%): C, 33.54; H, 3.38; Br, 22.31; N, 27.38. IR (KBr), ν/cm^{-1}: 1430 br., 1490, 1510; 3205, 3400 (NH_2). ^{1}H NMR (acetone-d$_6$), δ: 1.53 (s, 9 H, 3 Me); 7.9 (br.s, 2 H, NH_2); 8.87 (s, 1 H, H(8)). ^{13}C NMR (DMSO-d$_6$), δ: 25.3 (Me); 60.3 (C$\underline{\text{C}}$Me$_3$); 97.3 (C(5)); 116.0 (C(8)); 120.1 (br.s, C(8a), ^2J = 4.1 Hz); 136.0 (br.s, C(7)); 143.3 (C(4a), ^3J = 6.1 Hz); 146.9 (C(6), ^3J = 7.2 Hz). ^{14}N NMR (acetone-d$_6$), δ: −54 ($\underline{\text{N}}$(O)=NBu^t, $\Delta\nu_{1/2}$ = 40 Hz); −43 ($\Delta\nu_{1/2}$ = 70 Hz); −41 ($\Delta\nu_{1/2}$ = 60 Hz) (N(3), N(1)). MS, *m/z*: 357 [M]$^+$.

Synthesis of 1,2,3,4-tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxides

1,2,3,4-Tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxide (4). Phosphoric anhydride (2 g) was added to a solution of nitramine **6** (0.16 g, 0.5 mmol) in dry MeCN (30 mL). The reaction mixture was stirred for 2 h until the starting reagent was completely consumed (monitoring by TLC with C_6H_6—EtOAc (5 : 1) as an eluent). The solvent was removed *in vacuo* and the product was extracted with dry THF. The extract was concen-

trated and the residue was washed with ether and dried *in vacuo*. The yield of compound **4** was 80 mg (64%), orange crystals, decomp. >160 °C (without melting). Found (%): C, 28.54; H, 0.97; N, 45.12. $C_6H_2N_8O_4$. Calculated (%): C, 28.81; H, 0.81; N, 44.80. IR (KBr), ν/cm^{-1}: 1413, 1488 (TDO ring). MS, *m/z*: 250 $[M]^+$.

5-Nitro-1,2,3,4-tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxide (5). ***Procedure A.*** Nitric anhydride (100 mg, 0.93 mmol) was added at −30 °C to a suspension of compound **3** (100 mg, 0.36 mmol) in dry MeCN (3 mL). The reaction mixture was stirred at −30 °C for 30 min. The solvent was removed *in vacuo* and $CHCl_3$ (10 mL) was added to the residue. The precipitate was filtered off, washed with $CHCl_3$ (20 mL), and dried *in vacuo* to give orange crystals (77 mg). According to the ^{1}H NMR data, the product contained a 45 : 55 mixture of compounds **4** and **5** (35 and 43% yields, respectively). Organic material from this mixture was extracted with CH_2Cl_2 (4×10 mL). The extract was concentrated *in vacuo* and the residue was washed with a small amount of ether to give compound **5** (10 mg) as yellow crystals, decomp. >150 °C (without melting). Found (%): C, 23.99; H, 0.51; N, 42.29. $C_6HN_9O_6$. Calculated (%): C, 24.42; H, 0.34; N, 42.71. IR (KBr), ν/cm^{-1}: 1368, 1552 (NO_2); 1441, 1492 (TDO ring). MS, *m/z*: 295 $[M]^+$.

B. Nitric anhydride (170 mg, 1.6 mmol) was added at −30 °C to a solution of phenylenediamine **9** (100 mg, 0.32 mmol) in dry MeCN (3 mL). The reaction mixture was stirred at −30 °C for 30 min and then allowed to warm to 0 °C. The solvent was removed *in vacuo* and $CHCl_3$ (10 mL) was added to the residue. The resulting orange crystals were filtered off, washed with $CHCl_3$ (20 mL), and dried *in vacuo*. According to the ^{1}H NMR data, the crystals contained a mixture of compounds **4** (24 mg, 29%) and **5** (53 mg, 55%). Extraction with CH_2Cl_2 gave compound **5** (25 mg). The samples obtained by methods ***A*** and ***B*** were identical.

5-Bromo-1,2,3,4-tetrazino[5,6-*g*]benzo-1,2,3,4-tetrazine 1,3,7,9-tetraoxide (8). ***Procedure A.*** Nitric anhydride (95 mg, 0.89 mmol) was added at −30 °C to a suspension of compound **7** (120 mg, 0.34 mmol) in dry MeCN (3 mL). The reaction mixture was stirred at −30 °C for 30 min and concentrated *in vacuo*. Chloroform (10 mL) was added to the residue and the resulting precipitate was filtered off, washed with ether (20 mL), and dried *in vacuo*. The yield of compound **8** was 80 mg (73%), orange crystals, decomp. >160 °C (without melting). Found (%): C, 21.66; H, 0.47; Br, 24.20; N, 33.87. $C_6HBrN_8O_4$. Calculated (%): C, 21.90; H, 0.31; Br, 24.28; N, 34.06. IR (KBr), ν/cm^{-1}: 1428, 1488 (TDO ring). MS, *m/z*: 328 $[M]^+$.

B. Nitric anhydride (140 mg, 1.3 mmol) was added at −30 °C to a solution of phenylenediamine **10** (100 mg, 0.26 mmol) in dry MeCN (3 mL). The reaction mixture was stirred at −30 °C for 30 min and treated as described in procedure ***A***. The yield of compound **8** was 60 mg (71%). The samples obtained by methods ***A*** and ***B*** were identical.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32432).

References

1. A. E. Frumkin, A. M. Churakov, Yu. A. Strelenko, V. V. Kachala, and V. A. Tartakovsky, *Org. Lett.*, 1999, **1**, 721.
2. A. M. Churakov and V. A. Tartakovsky, *Chem. Rev.*, 2004, **104**, 2601.
3. A. M. Churakov, O. Yu. Smirnov, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Eur. J. Org. Chem.*, 2002, 2342.
4. A. E. Frumkin, A. M. Churakov, Yu. A. Strelenko, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 480 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 482].
5. A. E. Frumkin, A. M. Churakov, Yu. A. Strelenko, O. Yu. Smirnov, S. L. Ioffe, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1307 [*Russ. Chem. Bull., Int. Ed.*, 1999, **48**, 1295].
6. N. S. Gruenhut, M. Goldfrank, M. L. Cushing, and G. V. Caesar, *Inorg. Synth.*, 1950, **3**, 78.

Received June 14, 2006;
in revised form July 12, 2006