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Oxidation and Reductive Bromination of Bis(4-*tert*-butylphenyl)aminoxyl

V. A. Golubev and V. D. Sen'

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast,142432 Russia
e-mail: vgolubev@icp.ac.ru

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Abstract—One-electron oxidation of bis(4-*tert*-butylphenyl)aminoxyl with antimony pentachloride and bromine leads to the formation of oxoammonium salts with anions $SbCl_6^-$ and Br_3^- respectively. The salt with the Br_3^- anion converted at heating into a mixture of bromodiphenylamines which formed also from the aminoxyl as a result of previously unknown reaction of three-electron reductive bromination. The mechanisms of these reactions were assumed.

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Oxoammonium salts are used as selective stoichiometric oxidants and as catalysts of alcohols oxidation [1–5]. These catalysts found an industrial application in the synthesis of pharmaceuticals [6]. The essential drawback of the oxoammonium salts is their low stability that restricts their practical application. Aiming at the search for stable oxoammonium salts we investigated the oxidation of bis-(4-*tert*-butylphenyl)aminoxyl (**I**) with antimony pentachloride and bromine.

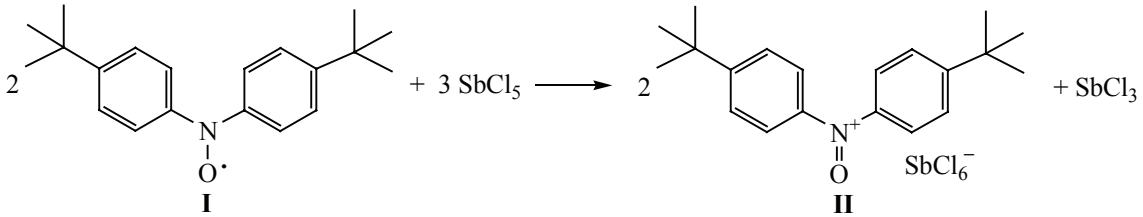
The antimony pentachloride quantitatively oxidized aminoxyl **I** to oxoammonium salt **II** (Scheme 1).

The dark brown crystals of salt **II** are well soluble in MeCN and $CHCl_3$ forming dark red solutions whose color is due to the strong absorption band of the oxoammonium cation, λ_{max} 505 nm (ε 16900 l mol^{-1} cm^{-1}). At room temperature this salt is sufficiently stable both in the crystalline state and in solution, yet it fast decomposes at heating and has no precise melting point. In the ^{1}H NMR spectrum of salt **II** under the effect of the oxoammonium group the signals of *ortho*- and *meta*-benzene protons and of the *tert*-butyl groups are shifted downfield by 1.1, 0.4, and 0.13 ppm as compared with the corresponding signals in the spectrum of the respective amine.

Bromine readily oxidizes aminoxyl **I** into oxoammonium salt **III** (Scheme 2).

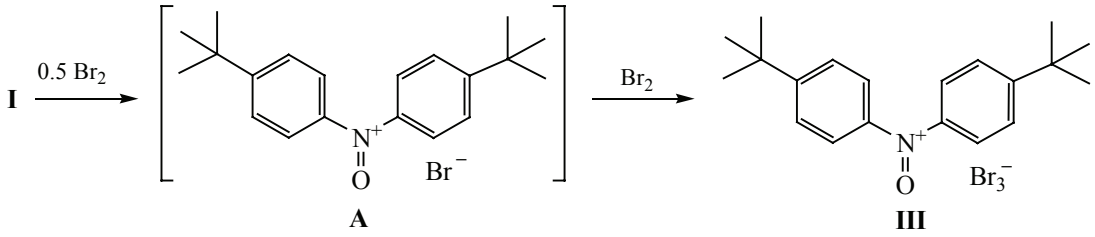
Primarily formed bromide **A** adds a molecule Br_2 converting into more stable tribromide **III**. When the bromination of aminoxyl **I** is carried out in CCl_4 at –20°C the dark brown crystalline modification of salt **III** formed in 92% yield. When aminoxyl **I** is brominated at ~20°C, in a 41% yield copper-red crystalline modification of salt **III** is obtained. Both modifications have no precise melting point and decompose in the range 110–130°C. IR spectra of the crystalline modifications of salt **III** essentially differ by the band intensity, and the UV spectra of both modifications are identical and qualitatively coincide with the UV spectrum of hexachloroantimonate **II**. The IR spectrum of the latter is similar to the spec-

Scheme 1.



I **II**

Scheme 2.



trum of the dark brown modification of tribromide **III**. ^{1}H NMR spectrum of tribromide **III** contains broadened signals of all protons. The broadening is apparently due to the equilibrium between the oxoammonium cation and aminoxyl **I**.

At the bromination of aminoxyl **I** alongside with oxoammonium salt **III** products of three-electron reduction of aminoxyl **I**, amine **IV** and its bromoderivatives **V–VIII**, were obtained (Scheme 3).

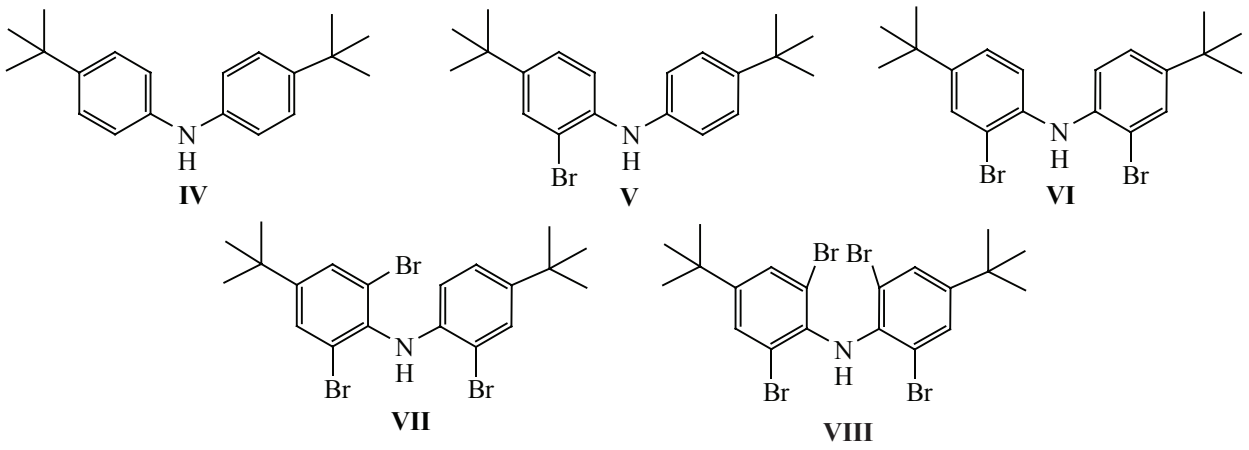
The ratio between the products of oxidation and reduction of aminoxyl **I** depend on the bromination temperature. At –20°C the fraction of the reduction products equals 8%. The main among them, dibromoamine **VI**, tribromoamine **VII**, and amine **IV**, formed in the yields 6.4, 1.0, and 0.5 mol% respectively. At ~20°C the fraction of the products of aminoxyl **I** reduction grew to ~50%. The main among them, dibromoamine **VI**, tribromoamine **VII**, and amine **IV**, formed in the yields 20, 19, and 3 mol% respectively. Bromoamines **VI, VII** were isolated in the pure state, and bromoamines **V, VIII** and amine **IV** were identified by chromatography by the retention volumes and also by UV spectra. To prove the structure of bromoamines **V–VIII** we synthesized these compounds by an independent method, the bromination of amine **IV**. The composition and structure of bromoamines were confirmed by elemental analysis, NMR, UV, IR, and mass spectra (see EXPERIMENTAL). The location of the bromine atoms in bromoamines **V–VIII** was established using NMR spectra ^{1}H – ^{1}H NOE based on the effect of intensification of the signals belonging to *tert*-butyl groups and benzene protons.

The bromination of benzene, its derivatives and other arenes is known to proceed by the mechanism of electrophilic substitution [7]. Evidently this mechanism operates in the formation of bromoamines **V – VIII** at the bromination of amine **IV** (Scheme 4).

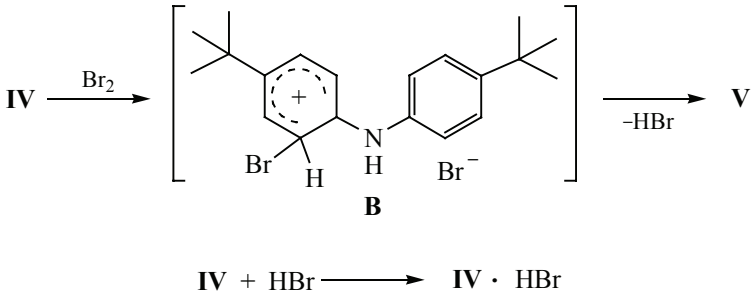
Bromine adds to amine **IV** with the formation of carbocation **B** that reacts with the anion Br– giving bromoamine **V** and HBr. The latter with excess amine **IV** affords ammonium salt **IV**·HBr. However this mechanism of electrophilic substitution does not explain the reduction of the nitroxyl into amino group at the bromination of aminoxyl **I**.

The main product of the reductive bromination of

Scheme 3.



Scheme 4.



aminoxyl **I**, tribromoamine **VII**, forms along the simple stoichiometric equation

$$\mathbf{I} + 1.5\ Br_2 \rightarrow \mathbf{VII} + H_2O. \quad (1)$$

In keeping with this stoichiometry the nitroxyl group is reduced to amino group by three hydrogen atoms of benzene rings that are substituted by bromine. Apparently the reductive bromination occurs as a result of successive addition of bromine atoms to aminoxyl **I** (Scheme 5).

Bromine atoms add to benzene ring of aminoxyl **I** with the formation of nitrone **C** that isomerizes into hydroxylamine **D**. As a result the nitroxyl group of aminoxyl **I** undergoes the one-electron reduction into the hydroxyamino group. The addition of the second bromine atom to the benzene ring of hydroxylamine **D** provides adduct **E** that via water elimination converts into aminyl radical **F**. Therewith hydroxylamine **D** undergoes the one-electron reduction into aminyl **F**. The addition of the third bromine atom to aminyl **F** gives imine **G** that isomerizes into bromoamine **VII**. Thus the successive addition of three bromine atoms leads to the three-electron reduction of aminoxyl **I** to tribromoamine **VII**. The sum of these successive reaction is the stoichiometric equation (1).

The second product of the reductive bromination of aminoxyl **I**, dibromoamine **VI**, formed apparently by the reaction of the intermediate bromohydroxylamine **D** with hydrogen bromide (Scheme 6).

Bromohydroxylamine **D** like the other *N*,*N*-diarylhydroxylmines [8] by reaction with HBr converts into salt **H**, which through imine **I** isomerizes into the final dibromoamine **VI**. The conversion of aminoxyl **I** into dibromoamine **VI** is described by a stoichiometric equation

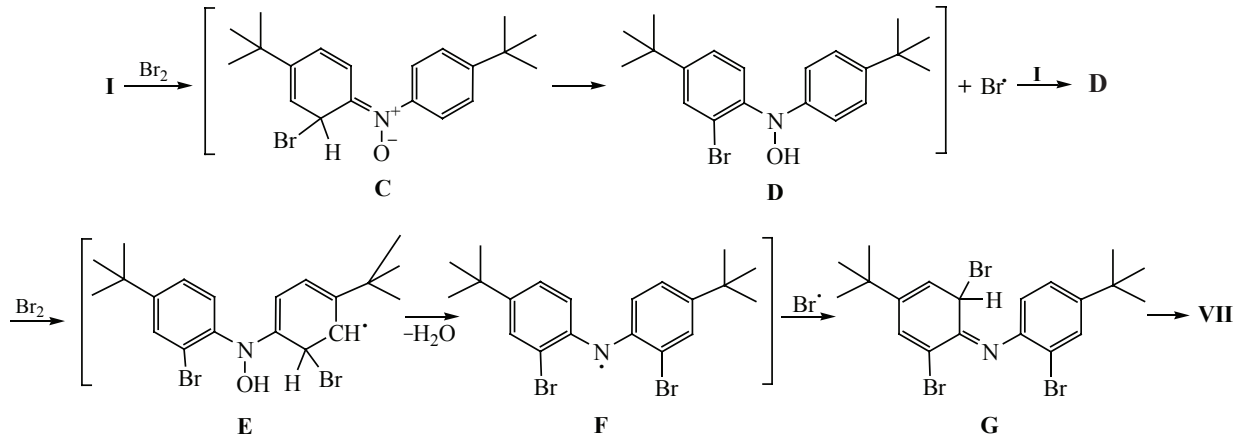
$$\mathbf{I} + 0.5Br_2 + HBr \rightarrow \mathbf{VI} + H_2O. \quad (2)$$

Hydrogen bromide can form in the reaction of intermediate nitrone **C** or hydroxylamine **D** with bromine (Scheme 7).

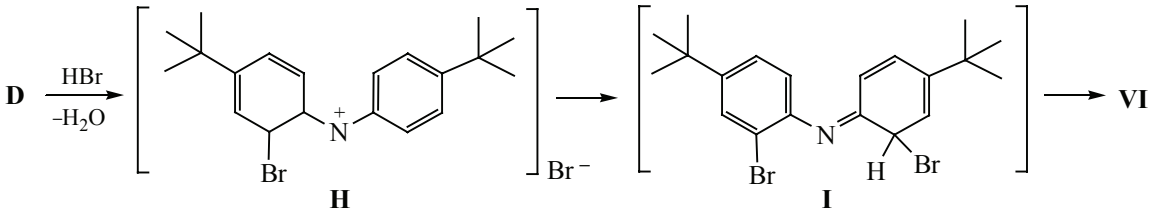
Amine **IV** evidently forms at the disproportionation of aminoxyl **I** under the action of HBr:

$$4\mathbf{I} + 3HBr \rightarrow \mathbf{IV} + 3\mathbf{A} + H_2O \quad (3)$$

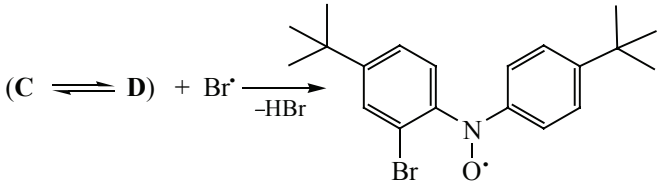
Scheme 5.



Scheme 6.



Scheme 7.



This disproportionation is characteristic of all diarylnitroxyls [8]. Bromoamine **V** and tetrabromoamine **VIII** form in small amounts apparently by the bromination of amine **IV** and tribromoamine **VII** respectively.

We also studied the stability of oxoammonium salt **III** with Br_3^- anion. In an acetonitrile solution this salt decomposes completely within ~8 h at room temperature and within ~5 min in the boiling solution. The main decomposition products are tribromoamine **VII** and dibromoamine **VI** which form in the yields 61 and 37 mol% respectively.

The following stoichiometric equation corresponds to the conversion of salt **III** into tribromoamine **VII**:

$$\mathbf{III} \rightarrow \mathbf{VII} + H_2O. \quad (4)$$

The result of this transformation is the four-electron reduction of oxoammonium group of the cation into amino group. Nominally the oxoammonium group is reduced by Br_3^- anion and three benzene hydrogen atoms which are replaced by three bromine atoms. Apparently the first stage of the decomposition of salt **III** consists in adding Br_3^- anion to one of the benzene rings of salt **III** cation with the formation of the intermediate nitrone **C** that undergoes the isomerization into bromohydroxylamine **D.**

$$\mathbf{III} \rightarrow (\mathbf{C} \rightarrow \mathbf{D}) + Br_2. \quad (5)$$

As a result of this reaction the oxoammonium group of salt **III** suffers a two-electron reduction into a hydroxyamine group. Further transformation of bromohydroxylamine **D** into tribromoamine **VII** and dibromoamine **VI** proceeds along Schemes 5 and 6 respectively.

Therefore during the reaction of aminoxyl **I** with bromine two processes occur simultaneously: One-electron oxidation of aminoxyl **I** to oxoammonium salt **III** and three-electron reductive bromination of aminoxyl **I** with the formation of bromoamines **VI, VII**. The first process is typical for all nitroxyl radicals, yet the reductive bromination was observed for the first time. Presumably the reductive bromination is a reaction characteristic of all diarylnitroxyls. The thermal decomposition of oxoammonium salt **III** proceeds as the reaction between the oxoammonium cation and Br_3^- anion. As a result the four-electron reductive bromination of this cation occurs affording as the products bromoamines **VI, VII**.

EXPERIMENTAL

Bis(4-*tert*-butylphenyl)aminoxyl (**I**) was obtained by procedure [9] and crystallized from methanol, mp 137°C. Bis(4-*tert*-butylphenyl)amine (**IV**) was obtained by procedure [10] and crystallized from methanol, mp 108°C. The chromatographic analysis was performed on a chromatograph Milikhrom equipped with an UV detector (column 2 × 64 mm, Separon C18, 5 μm). The preparative TLC was carried out on plates 200 × 200 mm with a layer of silica gel G 1.5 mm thick, with fluorescent indicator. IR reflection spectra were registered on a spectrometer Spectrum 100, absorption spectra were recorded on a spectrophotometer Specord 75IR. NMR spectra were taken on a spectrometer Bruker AIII, 500 MHz, UV spectra were measured on a spectrophotometer Specord UV-VIS. Electron impact mass spectra (70 eV) were re-

corded on an GC-MS instrument Finnigan. Melting points were determined on a heating block PNMK.

Bis(4-*tert*-butylphenyl)oxoammonium hexachloroantimonate (II). A solution of 168 mg (0.56 mmol) of $SbCl_5$ in 2 ml of CCl_4 was added to a solution of 107 mg (0.36 mmol) of aminoxyl **I** in 2 ml of CCl_4 cooled to –15°C in a bath filled with ice mixed with salt. The separated precipitate was filtered off, washed with CCl_4, dried, and purified by reprecipitation from $CHCl_3$ with hexane. Yield 220 mg (96%), dark brown crystals, t.decomp. 115–120°C. UV spectrum (MeCN), λ_{max}, nm (ε, l mol^{-1}·cm^{-1}): 505 (16900), 370 (6270), 320 (6040), 308 (6170), 269 (12900). IR spectrum (reflection), cm^{-1}: 3099 (CH_{aryl}); 2970, 2908, 2873 (CH_3); 1580 (aryl), 1476, 1440, 1424, 1366, 1347, 1327, 1312, 1256, 1173, 1104, 1026, 851, 815, 714, 679. ^{1}H NMR spectrum ($CDCl_3$ + $SbCl_5$), δ, ppm: 1.43 s[18H, $C(CH_3)_3$], 7.89 br.d (4H, $H^{3,5}$, *J* 8.7 Hz), 8.09 br.d (4H, $H^{2,6}$, *J* 8.8 Hz). Found, %: C 38.21; 3.78; Cl 33.24; N 2.22. $C_{20}H_{26}Cl_6NOSb$. Calculated, %: C 38.08; H 4.15; Cl 33.72; N 2.22.

Bromination of bis(4-*tert*-butylphenyl)aminoxyl (I). *a*. At ~20°C. A solution of 287 mg (1.8 mmol) of bromine in 3.6 ml of CCl_4 was added to a solution of 347 mg (1.17 mmol) of aminoxyl **I** in 5 ml of CCl_4. Immediately a precipitate of bis(4-*tert*-butylphenyl)oxoammonium tribromide (**III**) separated that was filtered off, washed with CCl_4, and dried in a vacuum. Yield 259 mg (41%), copper-red flake crystals, t.decomp. 120–125°C.

The solution was evaporated in a vacuum to obtain as a residue 316 mg of resinous solid whose HPLC showed the following result (80% aqueous MeCN, λ 210 nm), V_{sp}, μL (I_{rel}, %): 470 (2.5), 950 (6.2) (**IV**), 1360 (2) (**V**), 2170 (100) (**VII**), 3200 (90) (**VI**), 3600 (1.5) (**VIII**). The data of the quantitative HPLC analysis revealed that the mixture consisted of 117 mg (19%) of tribromoamine **VII**, 104 mg (20%) of dibromoamine **VI**, 10 mg (3%) of amine **IV**, 6 mg (1%) of tetrabromoamine **VIII**, and 4 mg (1%) of bromoamine **V**.

The resinous product was washed with MeOH (3 × 5 ml), thereafter remained 219 mg of solid colorless substance that was separated on four chromatographic plates with silica gel eluting with hexane. From the first chromatographic zone we isolated 95 mg of dibromoamine **VI**, colorless crystals, mp 163°C (*i*-PrOH). From the second zone 90 mg of tribromoamine **VII** was obtained, colorless crystals, mp 182°C (heptane).

b. At –20°C. A solution of 315 mg (1.97 mmol) of bromine in 3 ml of CCl_4 was added to a solution of 387 mg (1.31 mmol) of aminoxyl **I** in 5 ml of CCl_4 cooled to –20°C (bath filled with ice with salt). Immediately a fine crystalline precipitate of tribromide **III** separated that was filtered off, washed with CCl_4, and dried in a vacuum. Yield 641 mg (92%), dark brown crystals, t.decomp. 110–130°C.

The solution was evaporated in a vacuum to obtain a residue of 50 mg of a compounds mixture whose HPLC showed the following result (MeCN, λ 210 nm), V_{sp}, μL (I_{rel}, %): 240 (13) (**IV**), 300 (7.6) (**VII**), 400 (100) (**VI**), 705 (1.3). The data of the quantitative HPLC analysis revealed that the mixture consisted of 36.4 mg (6.4%) of dibromoamine **VI**, 6.7 mg (1%) of tribromoamine **VII**, and 1.9 mg (0.5%) of amine **IV**.

Bis(4-*tert*-butylphenyl)oxoammonium tribromide (III). *a*. Copper-red crystalline modification forms in the reaction of aminoxyl **I** with Br_2 in CCl_4 at ~20°C. Copper-red plate crystals, t.decomp. 120–125°C (CCl_4). UV spectrum (MeCN), λ_{max}, nm (ε, l mol^{-1}cm^{-1}): 506 (23000), 370 (8700), 316 sh (8800), 269 (54000). IR spectrum (reflection), cm^{-1}: 3071 (CH_{aryl}); 2963, 2904, 2869 (CH_3); 1585, 1520 (aryl); 1478, 1446, 1425, 1406, 1366, 1333, 1255, 1181, 1109, 1026, 851, 829, 753, 714, 679. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 1.33 br.s (18H, CH_3), 7.31 br.s (4H, $H^{3,5}$), 7.74 br.s (4H, $H^{2,6}$). Found, %: C 45.06; H 4.95; Br 44.12; N 2.73. $C_{20}H_{26}Br_3NO$. Calculated, %: C 44.81; H 4.89; Br 44.71; N 2.61.

b. Dark brown crystalline modification forms in the reaction of aminoxyl **I** with Br_2 in CCl_4 at –20°C. Dark brown crystals, t.decomp. 110–130°C (CCl_4). UV spectrum (MeCN), λ_{max}, nm (ε, l mol^{-1}cm^{-1}): 506 (23000), 370 (8700), 316 sh (8800), 269 (54000). IR spectrum (reflection), cm^{-1}: 3092 (CH_{aryl}); 2966, 2904, 2869 (CH_3); 1576 (aryl); 1487, 1436, 1422, 1399, 1365, 1334, 1311, 1249, 1167, 1102, 1024, 852, 813, 712. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 1.33 br.s (18H, CH_3), 7.31 br.s (4H, $H^{3,5}$), 7.74 br.s (4H, $H^{2,6}$). Found, %: C 44.78; H 4.81; Br 44.37; N 2.49. $C_{20}H_{26}Br_3NO$. Calculated, %: C 44.81; H 4.89; Br 44.71; N 2.61.

***N*-(2-Bromo-4-*tert*-butylphenyl)-*N*-(4'-*tert*-butylphenyl)amine (V).** A solution of 329 mg (2.06 mmol) of bromine in 4 ml of CCl_4 was added within 10 min to a solution of 1.16 g (4.12 mmol) of amine **IV** in 4 ml of CCl_4 cooled to –20°C (bath filled with ice with salt). The reaction mixture was stirred for 5 min at cooling and 10 min at ~20°C. The separated precipitate of amine **IV** hydrobromide (720 mg) was filtered off, and the solution

was evaporated in a vacuum. The residue was dispersed in 4 ml of MeOH, filtered off, washed with MeOH, and dried in a vacuum. Yield 531 mg of a mixture of bromoamine **V** and dibromoamine **VI**. The mixture was separated by column chromatography (30 × 200 mm, silica gel KSK, 40–50 μm, elution with heptane). The composition of eluate was monitored by TLC. The evaporation of the eluate of the second zone afforded 320 mg (22%) of bromoamine **V**. Colorless crystals, mp 90°C (MeCN). UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1}cm^{-1}): 286 (21800), 238 sh (7530), 202 (40140). IR spectrum (reflection), cm^{-1}: 3415 (NH), 3049 (CH_{aryl}); 2960, 2902, 2864 (CH_3); 1604, 1518 (aryl); 1478, 1463, 1390, 1362, 1320, 1264, 1117, 1037, 879, 842, 710. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s [9H, 4-C(CH_3)$_3$], 1.32 s [9H, 4'-C(CH_3)$_3$], 5.93 s (1H, NH), 7.07 d.m (2H, H$^{2',6'}$, *J* 8.6 Hz), 7.17 m (2H, H^{5,6}), 7.32 d.m (2H, H$^{3',5'}$, *J* 8.6 Hz), 7.51 br.d.d (1H, H^3, *J* 0.9, 1.5 Hz). ^{1}H–^{1}H NOE NMR spectrum ($CDCl_3$): the intensification of NMR signals indicated the interaction between protons 4-C(CH_3)$_3$ (δ 1.28) s H^3 (δ 7.51) and H^5 (δ 7.17); 4'-C(CH_3)$_3$ (δ 1.32) s H$^{3'}$ and H$^{5'}$ (δ 7.32). Mass spectrum, *m*/*z* (I_{rel}, %): 363 (2.7), 362 (17.8), 361 (97.7), 360 (17.5), 359 (100) [*M*]$^+$; 347 (15.5), 346 (58.8), 345 (16.6), 344 (54.3) [*M* – CH_3]$^+$. Found, %: C 54.92; H 5.75; Br 36.69; N 3.19. $C_{20}H_{26}BrN$. Calculated, %: C 54.69; H 5.74; Br 36.38; N 3.19. [*M*]$^+$ 363.13 (2.2), 362.13 (21.5), 361.12 (99.5), 360.13 (21.9), 359.12 (100).

Bis(2-bromo-4-*tert*-butylphenyl)amine (VI). A solution of 1.6 g (10 mmol) of bromine in 2 ml of CCl_4 was added within 12 min while stirring and cooling to –20°C (bath of ice with salt) to a solution of 2.81 g (10 mmol) of amine **IV** in 10 ml of CCl_4. The reaction mixture was stirred for 15 min at cooling, the separated precipitate of amine **IV** hydrobromide was filtered off, the reaction solution was evaporated in a vacuum. The residue was dispersed in 10 ml of MeOH, the precipitate was filtered off and washed with hot MeOH (3 × 5 ml), and after drying it was twice recrystallized from *i*-PrOH. Yield 1.3 g (30%), colorless crystals, mp 163°C, sublimed at temperature >150°C. UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1}cm^{-1}): 287 (22700), 236 sh (9300), 208 (39900). IR spectrum (reflection), cm^{-1}: 3389 (NH), 3038 (CH_{aryl}); 2961, 2900, 2866 (CH_3); 1601, 1519 (aryl); 1331, 1262, 1116, 1036, 882, 814, 712; (c CCl_4): 3380 (NH), 3030 (CH_{aryl}); 2956, 2898, 2862 (CH_3); 1605, 1510 (aryl); 1315, 1265, 1115, 1040, 880. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 s [18H, C(CH_3)$_3$], 6.26 s (1H, NH), 7.21 m (4H, H^{5,6}), 7.56 br.d.d (2H, H^3, *J* 0.7, 1.8 Hz). ^{1}H–^{1}H NOE NMR spectrum ($CDCl_3$): the intensification of NMR signals indicated the interaction between protons 4-C(CH_3)$_3$ (δ 1.30) with H^3 (δ 7.56) and H^5 (δ 7.21). Mass spectrum, *m*/*z* (I_{rel}, %): 442 (12.0), 441 (49.4), 440 (22.8), 439 (100), 438 (15.2), 437 (49.1) [*M*]$^+$; 427 (13.5), 426 (53.9), 425 (19.5), 424 (98.7), 423 (11.9), 422 (51.4) [*M* – CH_3]$^+$. Found, %: C 54.92; H 5.75; Br 36.69; N 3.19. $C_{20}H_{25}Br_2N$. Calculated, %: C 54.69; H 5.74; Br 36.38; N 3.13. [*M*]$^+$ 443.04 (1.1), 442.03 (10.7), 441.03 (51.0), 440.04 (21.9), 439.03 (100), 438.04 (11.3), 437.04 (51.4).

***N*-(2,6-Dibromo-4-*tert*-butylphenyl)-*N*-(2'-bromo-4'-*tert*-butylphenyl)amine (VII).** A solution of 2.15 g (13.5 mmol) of bromine in 2 ml CCl_4 was added within 7 min at stirring to a solution of 1.28 g (4.55 mmol) of amine **IV** in 8 ml of CCl_4. The reaction mixture was boiled for 70 min. The solvent was evaporated in a vacuum, the residue was dispersed in 10 ml of hot MeOH. The insoluble precipitate was filtered off, washed with MeOH, and after drying it was twice recrystallized from heptane. Yield 1.05 g (45%), colorless plate crystals, mp 182°C, sublimed at temperature >140°C. UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1}cm^{-1}): 286 (9380), 234 sh (18400), 208 (69300). IR spectrum (reflection), cm^{-1}: 3355 (NH), 3039 (CH_{aryl}); 2962, 2902, 2865 (CH_3); 1610, 1541, 1506 (aryl); 1476, 1383, 1313, 1263, 1037, 868, 815, 736, 712. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 s [9H, 4'-C(CH_3)$_3$], 1.32 s [9H, 4-C(CH_3)$_3$], 5.96 s (1H, NH), 6.29 d (1H, H$^{6'}$, *J* 8.5 Hz), 7.10 d.d (1H, H$^{5'}$, *J* 2.2, 8.5 Hz), 7.52 d (1H, H$^{3'}$, *J* 2.2 Hz), 7.60 s (2H, H^{3,5}). ^{1}H–^{1}H NOE NMR spectrum ($CDCl_3$): the intensification of NMR signals indicated the interaction between protons 4-C(CH_3)$_3$ (1.32) s H^3 and H^5 (δ 7.60); 4'-C(CH_3)$_3$ (δ 1.27) s H$^{3'}$ (δ 7.52) and H$^{5'}$ (δ 7.10). Mass spectrum, *m*/*z* (I_{rel}, %): 522 (7.1), 521 (34.2), 520 (20.1), 519 (96.1), 518 (20.3), 517 (100), 516 (9.9) and 515 (40.9) [*M*]$^+$; 506 (19.8), 505 (13.8), 504 (56.2), 503 (12.3), 502 (53.6), 501 (1.1), 500 (12.5) [*M* – CH_3]$^+$. Found, %: C 46.30; H 4.44; Br 46.27; N 2.69. $C_{20}H_{24}Br_3N$. Calculated, %: C 46.36; H 4.67; Br 46.26; N 2.70. [*M*]$^+$ 521.94 (6.9), 520.94 (33.8), 519.95 (21.5), 518.94 (99.7), 517.95 (21.9), 516.94 (100), 515.95 (7.5), 514.95 (34.3).

Bis(2,6-dibromo-4-*tert*-butylphenyl)amine (VIII). A solution of 1.3 g (8 mmol) of bromine in 1 ml of CCl_4 was added within 5 min at stirring to a solution of 1.13 g (4 mmol) of amine **IV** in 4 ml of CCl_4. The reaction mixture was boiled for 2 h, then 0.64 g (4 mmol) of bromine was added, and the mixture was boiled for 0.5 h more. On cooling the solvent was evaporated, the residue was

dispersed in 10 ml of MeOH. The precipitate of bromoamines was filtered off, washed with MeOH, and dried in a vacuum. To the obtained mixture of bromoamines 4 ml of CCl_4 and 0.64 g (4 mmol) of bromine were added, and the mixture was boiled for 1 h. The solvent was evaporated, the residue was dispersed in 5 ml of MeOH. The precipitate was filtered off, washed with MeOH, and after drying it was twice recrystallized from *i*-PrOH. Yield 1.65 g (69%), colorless crystals, mp 208–209°C, sublimed at temperature > 170°C. UV spectrum (EtOH), λ_{max}, nm (ε, l·mol^{-1}cm^{-1}): 294 (13600), 257 (9030), 216 (45960). IR spectrum (reflection), cm^{-1}: 3383 (NH), 3039 (CH_{aryl}); 2963, 2902, 2867 (CH_3); 1589, 1549, 1535, 1501, 1489 (aryl); 1460, 1383, 1313, 1262, 871, 736, 701. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 s [18H, $C(CH_3)_3$], 5.76 s (1H, NH), 7.48 s (4H, $H^{3,5}$). ^{1}H–^{1}H NOE NMR spectrum ($CDCl_3$): the intensification of NMR signals indicated the interaction between protons 4-$C(CH_3)_3$ (δ 1.29) s H^3 and H^5 (δ 7.48). Mass spectrum, *m*/*z* (I_{rel}, %): 601 (17.6), 600 (10.5), 599 (54.1), 598 (19.3), 597 (100), 596 (10.2), 595 (54.8), 594 (3.9), 593 (18.1) $[M]^+$; 586 (10.3), 585 (1.7), 584 (33.1), 583 (15.0), 582 (75.6), 581 (8.9), 580 (32.8), 578 (9.7) [$M - CH_3$]. Found, %: C 40.17; H 3.66; Br 53.13; N 2.38. $C_{20}H_{23}Br_4N$. Calculated, %: C 40.24; H 3.88; Br 53.53; N 2.35. [*M*] 601.85 (3.5), 600.85 (17.3), 599.85 (14.3), 598.85 (67.2), 597.86 (22.0), 596.85 (100), 595.86 (15.0), 594.85 (68.5), 593.86 (3.9), 592.86 (17.6).

Bis(4-*tert*-butylphenyl)amine hydrobromide (IV)·HBr formed as a precipitate at the bromination of amine **IV** in CCl_4 (see above). Colorless needle crystals, t.decomp. 185–200°C. IR spectrum (reflection), cm^{-1}: 3064 (CH_{aryl}); 2963, 2902, 2868 (CH_3); 2701, 2632, 2577, 2468 (NH_2); 1608, 1551, 1511 (aryl); 1477, 1408, 1271, 1203, 1178, 1111, 1017, 865, 838, 795. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s [18H, $C(CH_3)_3$], 7.41 d.m (4H, H^m, *J* 8.8 Hz), 7.60 d.m (4H, H^O, *J* 8.8 Hz), 12.8 br.s (2H, NH_2). Found, %: C 66.15; H 7.45; Br 22.12; N 4.05. $C_{20}H_{27}N$·HBr. Calculated, %: C 66.29; H 7.79; Br 22.05; N 3.87.

Themal decomposition of bis(4-*tert*-butyl-phenyl) oxoammonium tribromide (III). A solution of 0.1 g (0.19 mmol) of tribromide **III** in 0.25 ml of MeCN was heated to boiling. The brown-red color of the solution turned light brown, and colorless crystals precipitated. The precipitate was filtered off, washed with MeCN, and dried in a vacuum. Yield of the precipitate 85 mg. HPLC of the precipitate (MeCN, λ 210 nm), V_{sp}, μL (I_{rel}, %): 240 (1.7) (**IV**), 300 (100) (**VII**), 400 (39) (**VI**), 700 (0.2). The data of the quantitative HPLC analysis revealed that the precipitate contained 61.5, 37.5, 0.4 mol% of tribromoamine **VII**, dibromoamine **VI**, and amine **IV** respectively.

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