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Endo- and exocyclic N-alkylation of 1- and 5-aminotetrazoles with *t*-BuOH–$HClO_4$: synthesis of mono-, di-, and tri-*tert*-butyl substituted aminotetrazolium salts

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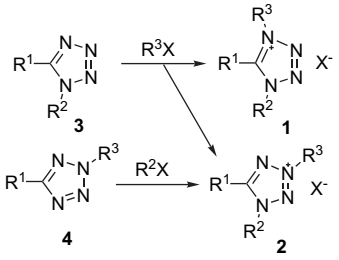
ABSTRACT

A new method for the synthesis of 1,3,5-trisubstituted aminotetrazolium salts based on alkylation of 1- and 5-aminotetrazoles with the *t*-BuOH–$HClO_4$ system is presented. Depending on the structure of the tetrazole substrate and reaction conditions, alkylation proceeds at the endocyclic nitrogen atoms as well as at the 1- and 5-amino groups giving mono-, di-, and tri-*tert*-butyl substituted tetrazolium salts. An X-ray diffraction investigation of 3-*tert*-butyl-1,5-bis(*tert*-butylamino)tetrazolium perchlorate and 5-amino-1,3-di-*tert*-butyltetrazolium chloride was carried out.

1. Introduction

Tetrazolium salts are widely used in different areas of science and technology.[1,2] In recent years, tetrazolium salts containing amino substituents at the C- and N-atoms of the heteroring have attracted considerable interest. Therefore, salts based on 1,4-disubstiuted 5-aminotetrazolium (**1**, R^1=NH_2; R^2=Me; R^3=Me, NH_2) and 3(4)-amino-1,5-dimethyltetrazolium (**1** and **2**, R^1=R^2=Me; R^3=NH_2) cations were found to be potential candidates for use as energetic ionic liquids. The above cations and also those obtained by protonation of 5-amino- and 1,5-diaminotetrazoles, are attractive as a constituent part of high-energetic compounds.[3] Moreover, some functionally substituted aminotetrazolium salts are valuable intermediates in the synthesis of tetrazolium *C*- and *N*-aminides,[4,5] 3*H*- and 2*H*-imidazo[1,2-*d*]tetrazoles.[6]

Methods for the preparation of aminotetrazolium salts are rather restricted.[1,5] The simplest synthesis is based on quaternization of the corresponding aminotetrazoles with alkyl iodides and α-halogeno carbonyl compounds in organic solvents. However, it reveals some problems. The main one is the lack of selectivity of this reaction due to the ambident character of the tetrazole ring. As a consequence, the quaternization of 1-mono- and 1,5-disubstituted tetrazoles **3**, including aminosubstituted ones, yields a mixture of isomeric 1,4-di-(1,4,5-tri)- and 1,3-di-(1,3,5-tri)-substituted tetrazolium salts **1** and **2** (Scheme 1). Individual isomers can be isolated from these mixtures by fractional crystallization. Less accessible 2-substituted tetrazoles **4** give only salts **2** under the action of alkylating agents. Due to the low basicity of tetrazoles **4**, they need more harsh conditions of quaternization. Moreover, the yield of salts is rather low. It should be noted that the amino substituent at C- or N-atoms of the heteroring remains unchanged under quaternization.



Scheme 1.

Recently, an effective method of quaternization of tetrazoles has been developed.[1] It is based on the use of alcohols (e.g., *tert*-butyl and diacetone alcohols, *iso*-propyl alcohol, 1-phenylethanol, adamantan-1-ol, and α-ferrocenylsubstituted alcohols) generating stable carbocations as alkylating agents. These processes are carried out in strong mineral acids (perchloric, sulfuric, tetrafluoroboric, etc.) or biphasic systems. The direction of quaternization cannot

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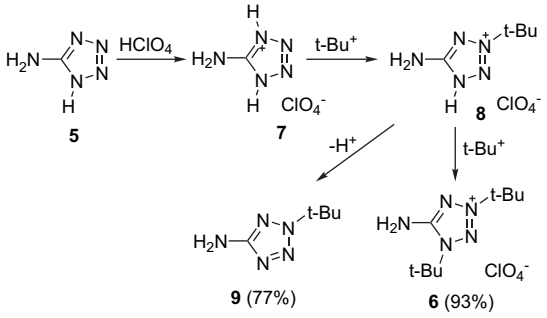
always be predicted unequivocally, since it depends on many factors, including the nature of the alkylating reagent, medium acidity, and reaction time. In spite of the fact that substituents at the heteroring also have an influence on the selectivity of quaternization, only tetrazole and its *C*- and *N*-alkyl and aryl derivatives were investigated as substrates in the above mentioned processes.

In the present work, we examined the behavior of 1- and 5-aminotetrazoles in the *t*-BuOH–$HClO_4$ system in order to study the effect of the amino substituent on the selectivity of acid catalyzed quaternization of tetrazole derivatives and to develop a novel method for synthesis of aminotetrazolium salts. It should be noted that previously we used the mentioned system for the selective synthesis of 1,3-disubstituted tetrazolium salts **2** (R^1=H) from 2-monosubstituted tetrazoles **4**,[7] as well as from tetrazole and 1-monosubstituted tetrazoles **3**.[8]

2. Results and discussion

We found that 5-aminotetrazole **5** reacts with *tert*-butyl alcohol in 70% perchloric acid regioselectively with formation of 1,3-di-*tert*-butylsubstituted tetrazolium salt **6**. High yield (76–93%) of salt **6** is achieved after 1 h of reaction time at room temperature using 2.5–3.5 equiv of *tert*-butyl alcohol. The selectivity of quaternization is explained by the complete protonation of tetrazole **5** at the most nucleophilic N4 atom resulting in the formation of the 1*H*-4*H*-5-aminotetrazolium cation **7** with only N2 and N3 atoms accessible for electrophilic attack.[1] Interaction of **7** with the *tert*-butyl cation generated from the alcohol leads to 5-amino-1*H*-3-*tert*-butyltetrazolium perchlorate **8**. Further attack of the latter with carbocation gives salt **6** (Scheme 2).

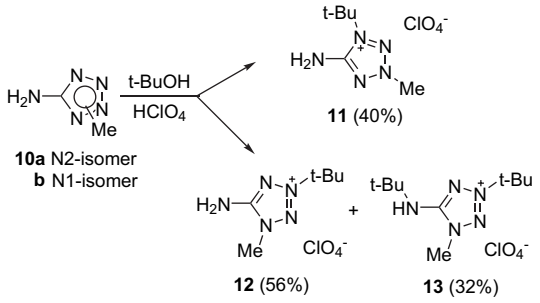


Scheme 2.

This mechanism is proposed by analogy with the mechanism of exhaustive alkylation of 5-R-tetrazole (R=H, Me, Ph).[8] N4 protonation of tetrazole **5** is confirmed by X-ray analysis of 5-aminotetrazolium nitrate.[9] Moreover, salt **8** was found to arise as a single product under reaction with 1 equiv of alcohol. The latter salt was characterized in the form of the appropriate base **9**.

Isomeric *N*-methyl-5-aminotetrazoles **10** reacted with the *t*-BuOH–$HClO_4$ system in different ways. Thus, under action of an equimolar amount of *tert*-butyl alcohol, the *N*2-isomer **10a** undergoes quaternization at the N4 endocyclic atom giving only salt **11**, whereas the *N*1-isomer **10b** is alkylated additionally at the amino group giving salts **12** and **13** with a molar ratio 90:10 (Scheme 3). The increase of alkylating agent content up to 2.5–3 equiv leads to an increase of the portion of salt **13** in the resulting mixture to 20–32 mol %. Selectivity of alkylation is reversed under the addition of chloroform. In the biphasic $HClO_4$–$HCCl_3$ system 4 h interaction of **10b** with *tert*-butyl alcohol (2.5 equiv) results in the formation of salts **12** and **13** in a molar ratio 15:85. Pure salts were isolated by recrystallization of the resulting mixtures.

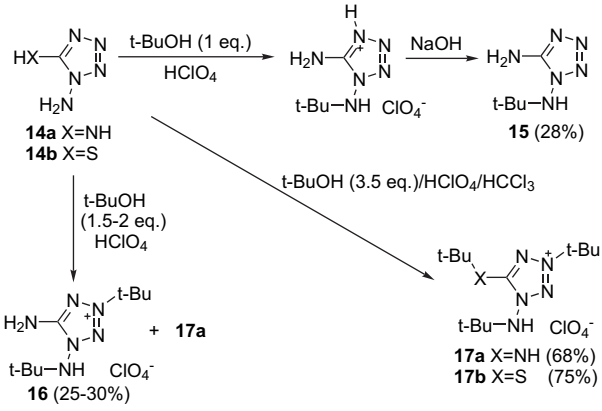
Observed selective N3 quaternization of the tetrazole ring of **10b** is due to blocking the N4 position because of protonation. The site



Scheme 3.

of protonation is confirmed by X-ray analysis of salts obtained by the interaction of tetrazole **10b** with acids.[3j,10] It should be noted that only salts **6** and **11** were isolated under the alkylation of tetrazoles **5** and **10a** with an excess of *tert*-butyl alcohol (2–4 equiv) in biphasic system. The corresponding products of the amino group alkylation were not detected. The observed distinction can be explained by steric hindrance from the neighboring bulky 1-*tert*-butyl group in salts **6** and **11** formed.

The amino group at the N1 atom of 1,5-diaminotetrazole **14a** undergoes alkylation as well as the C5 amino group and endocyclic N3 atom. At first the 1-amino group is alkylated and 5-amino-1-(*tert*-butylamino)tetrazole **15** is isolated under alkylation with 1 equiv of *tert*-butyl alcohol followed by alkalization of the reaction mixture. Di-*tert*-butyl substituted salt **16** and trisubstituted one **17a** were isolated as the major products under the action of 1.5–2 equiv and 2.5–3.5 equiv of *tert*-butyl alcohol, respectively. Maximum content (~90%) of salt **17a** in resulting mixture of salts was achieved under alkylation of tetrazole **14a** in a biphasic $HClO_4$–$HCCl_3$ system using 3.5 equiv of alkylating agent (Scheme 4). The observed higher reactivity of the 1-amino group in comparison with the 5-amino group is in agreement with data on complex formation of tetrazole **14a**. Thus, in complex with copper(II) chloride, **14a** acts as a bridging ligand coordinated through the N4 atom of the tetrazole ring and the nitrogen atom of the 1-amino group.[11] The passivity of the 5-amino group is due to its conjugation with the π-system of the tetrazole ring, whereas the nitrogen atom of the 1-amino group is sp^3 hybridized and is not conjugated.[12] Therefore, initial N4 protonation of tetrazole **14a** deactivates the 5-amino group since the positive charge is delocalized not only in the N1–C5–N4 fragment of heteroring but also on the 5-amino group.[13]

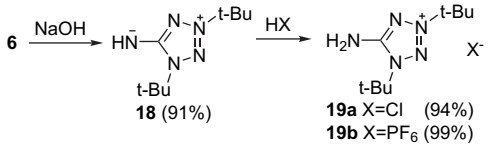


Scheme 4.

The investigated *t*-BuOH–$HClO_4$ system can also alkylate the thiol group of 5-thiotetrazoles. Thus, under alkylation of 1-amino-5-thiotetrazole **14b** with excess *tert*-butyl alcohol in a biphasic

system, 1,3,5-trisubstituted tetrazolium salt **17b** was synthesized in high yield (75%).

It should be noted that the synthesized aminotetrazolium perchlorates are convenient precursors for tetrazolium-5-aminides and aminotetrazolium salts with diverse anions. Base treatment of salt **6** gave the corresponding conjugate base **18**, which was reversively protonated by hydrochloric or hexafluorophosphoric acids to give salts **19** (Scheme 5).



Scheme 5.

The obtained salts were attributed to 1,3,5-trisubstituted tetrazolium salts according to ^{13}C NMR spectroscopic chemical shifts of the endocyclic carbon atom C5, in accordance with data on the related 5-aminotetrazolium[3d,6,14] and 5-thiotetrazolium[1,15] salts. The chemical shift of C5 for 1,3-disubstituted 5-aminotetrazolium salts is observed at 155.8–158.3 ppm. At the same time, analogous signals for 1,4-disubstituted 5-aminotetrazolium salts **1** (R^1=NH_2) appear at 147.5–148.5 ppm.

The structures of salts **17a** and **19a** were also unambiguously confirmed by X-ray structural analysis of single crystals (Figs. 1 and 2). In salts **17a** and **19a**, the ring reveals the differentiation of bonds showing the longest bond N1–C5 and the shortest one N2–N3. These results show agreement with structural data of other 1,3,5-trisubstituted tetrazolium salts [Cambridge Structural Database (CSD), Version 5.29 of November 2007].[16] There are classic hydrogen bonds in the crystal structure of both compounds. In salt **17a**, there are polymeric chains, running along the *c* axis, due to N–H···O hydrogen bonds. In compound **19a**, N–H···Cl hydrogen bonds result in the formation of centrosymmetric dimers (Supplementary data).

3. Conclusions

We have shown that 1- and 5-aminotetrazoles can be readily alkylated with the *t*-BuOH–$HClO_4$ system and alkylation can proceed at the endocyclic nitrogen atom as well as at the amino group, depending on the structure of the substrate and the reaction conditions. This method is an efficient tool for the introduction of lipophilic and easily removable *tert*-butyl group[1] into aminotetrazoles and for the synthesis of aminotetrazolium salts, which are gaining increasing interest in the chemistry of energetic materials. Moreover, the synthesized aminotetrazolium salts are convenient precursors for mesoionic 5-aminotetrazole derivatives. As a whole, the described system has a potential for alkylation of nitrogen heterocycles. Our investigations in this direction are in progress.

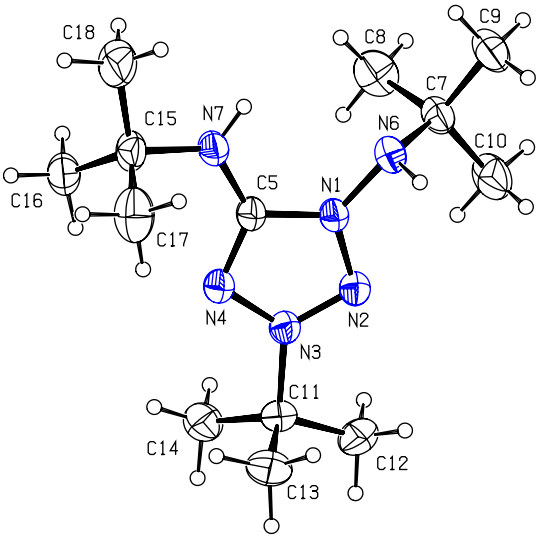


Figure 1. Tetrazolium cation in the structure of salt **17a**. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): N1–N2 1.338(3), N1–C5 1.363(3), N2–N3 1.290(2), N3–N4 1.341(3), N4–C5 1.325(3).

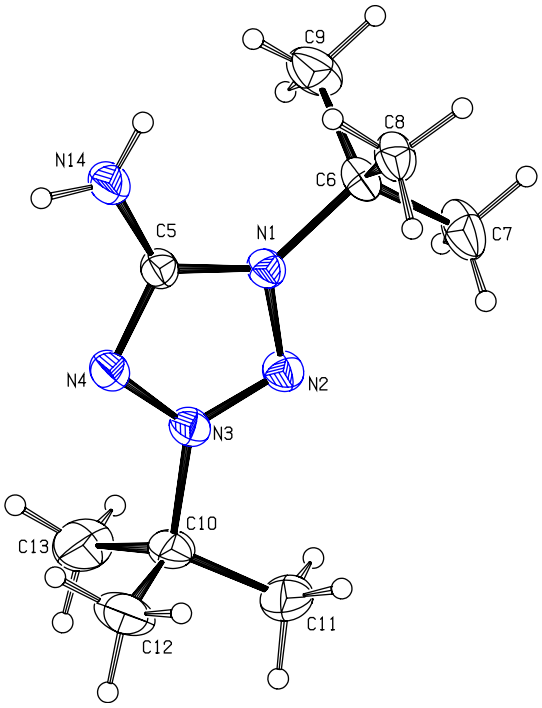


Figure 2. Tetrazolium cation in the structure of salt **19a**. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): N1–N2 1.3396(17), N1–C5 1.3700(18), N2–N3 1.2837(17), N3–N4 1.3337(18), N4–C5 1.3355(19).

4. Experimental

4.1. General

All reagents and solvents were obtained from commercial sources and used without purification. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $(CD_3)_2SO$. IR spectra were recorded with a Bruker Equinox 55 spectrometer using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) technique. The pure sample was placed on the crystal of the ATE unit and the spectra were collected in the range of 600–4000 cm^{-1}. Melting points were determined using melting point apparatus. Initial 5-amino-*N*-methyltetrazoles **10**,[17] 1,5-diaminotetrazole **14a**,[11] and 1-amino-5-thiotetrazole **14b**[18] were prepared according to the literature procedures.

4.1.1. 5-Amino-1,3-di-tert-butyltetrazolium perchlorate ***6***

tert-Butyl alcohol (4 mL, 42 mmol) was added with stirring to 5-aminotetrazole monohydrate (1.96 g, 28 mmol) dissolved in 70% perchloric acid (7.5 mL). The obtained solution was kept at room temperature for 1 h, diluted with water (2–3 mL), and filtered to give **6** (3.31 g, 93%) as white crystals. Mp 161–162 °C from water. ^1H NMR δ (ppm): 8.07 (s, 2H, NH_2), 1.67 (s, 9H, *t*-Bu), 1.66 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 156.5 (CN_4), 69.0 (CMe_3), 63.9 (CMe_3), 28.0

(Me), 26.8 (Me). ν_{max} 3408, 3331, 3275, 3217, 2994, 1651, 1589, 1464, 1408, 1375, 1284, 1230, 1188, 1163, 1076, 835, 785, 740, 623 cm^{-1}. Anal. Calcd for $C_9H_{20}ClN_5O_4$: C, 36.3; H, 6.8; N, 23.5. Found: C, 36.4; H, 6.6; N, 23.9.

4.1.2. 5-Amino-2-tert-butyltetrazole **9**

tert-Butyl alcohol (1.2 mL, 13 mmol) was added with stirring to 5-aminotetrazole monohydrate (1.96 g, 12 mmol) dissolved in 70% perchloric acid (5 mL). The obtained solution was kept at room temperature for 1 h. Salt **8** precipitated as a white solid. Alkalization of reaction mixture with aqueous NaOH till pH=8–9 and following filtration gave **9** (1.3 g, 77%) as white crystals. Mp 115–116 °C from water. ^{1}H NMR δ (ppm): 5.90 (s, 2H, NH_2), 1.51 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 167.2 (CN_4), 62.6 (CMe_3), 29.2 (Me). Anal. Calcd for $C_5H_{11}N_5$: C, 42.5; H, 7.8; N, 49.6. Found: C, 42.7; H, 7.6; N, 49.8.

4.1.3. 5-Amino-1-tert-butyl-3-methyltetrazolium perchlorate **11**

tert-Butyl alcohol (0.6 mL, 6 mmol) was added with stirring to the solution of tetrazole **10a** (0.40 g, 4 mmol) in 1.5 mL of 70% perchloric acid. The mixture was kept at room temperature for 6 h, diluted with water (3 mL), cooled to 0 °C, and filtered to give **11** (0.41 g, 40%) as white crystals. Mp 129–130 °C (dec) from water. ^{1}H NMR δ (ppm): 8.10 (s, 2H, NH_2), 4.31 (s, 3H, Me), 1.65 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 156.6 (CN_4), 63.9 (CMe_3), 42.9 (Me), 26.7 (3Me). Anal. Calcd for $C_6H_{14}ClN_5O_4$: C, 28.2; H, 5.5; N, 27.4. Found: C, 28.4; H, 5.3; N, 27.8.

4.1.4. 5-Amino-3-tert-butyl-1-methyltetrazolium perchlorate **12**

tert-Butyl alcohol (0.3 g, 4 mmol) was added with stirring to the solution of tetrazole **10b** (0.40 g, 4 mmol) in 1.5 mL of 70% perchloric acid. The mixture was kept at room temperature for 1 h, diluted with water (3 mL), cooled to 0 °C, and filtered to give mixture of **12** and **13** (0.75 g, molar ratio 90:10), which was recrystallized from propanol-2/chloroform (2:1) to give **12** (0.57 g, 56%) as white crystals. Mp 113–115 °C. ^{1}H NMR δ (ppm): 8.24 (s, 2H, NH_2), 3.92 (s, 3H, Me), 1.67 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 158.3 (CN_4), 69.0 (CMe_3), 34.9 (Me), 28.0 (3Me). Anal. Calcd for $C_6H_{14}ClN_5O_4$: C, 28.2; H, 5.5; N, 27.4. Found: C, 28.3; H, 5.0; N, 27.7.

4.1.5. 3-tert-Butyl-5-tert-butylamino-1-methyltetrazolium perchlorate **13**

tert-Butyl alcohol (0.75 g, 10 mmol) was added with stirring to the solution of tetrazole **10b** (0.40 g, 4 mmol) in mixture of 3 mL of 70% perchloric acid and 3 mL of chloroform. The mixture was stirred at room temperature for 6 h, diluted with water (5 mL). Chloroform was removed under steam of air. Aqueous solution was cooled to 0 °C and filtered to give mixture of **12** and **13** (0.56 g, molar ratio 15:85), which was recrystallized from water to give **13** (0.4 g, 32%) as white crystals. Mp 125–126 °C. ^{1}H NMR δ (ppm): 7.84 (s, 1H, NH), 3.96 (s, 3H, Me), 1.70 (s, 9H, *t*-Bu), 1.41 (s, 9H, *t-Bu*–NH); ^{13}C NMR δ (ppm): 156.1 (CN_4), 69.1 (CMe_3), 53.7 (CMe_3), 35.1 (Me), 28.1 (3Me), 27.9 (3Me). Anal. Calcd for $C_{10}H_{22}ClN_5O_4$: C, 38.5; H, 7.1; N, 22.5. Found: C, 38.8; H, 6.8; N, 22.8.

4.1.6. 5-Amino-1-(tert-butylamino)tetrazole **15**

tert-Butyl alcohol (0.6 g, 8 mmol) was added with stirring to the solution of tetrazole **14a** (0.8 g, 8 mmol) in 2 mL of 70% perchloric acid. The mixture was kept at room temperature for 1 h. Alkalization of reaction mixture with aqueous NaOH till pH=8–9, following filtration and recrystallization from chloroform gave **15** (0.35 g, 28%) as white crystals. Mp 165 °C (dec). ^{1}H NMR δ (ppm): 6.65 (s, 1H, NH), 6.43 (s, 2H, NH_2), 1.06 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 156.0 (CN_4), 56.2 (CMe_3), 27.9 (3Me). Anal. Calcd for $C_5H_{12}N_6$: C, 38.5; H, 7.7; N, 53.8. Found: C, 38.7; H, 7.5; N, 54.0.

4.1.7. 5-Amino-3-tert-butyl-1-tert-butylaminotetrazolium perchlorate **16**

tert-Butyl alcohol (0.45 g, 6 mmol) was added with stirring to the solution of tetrazole **14a** (0.40 g, 4 mmol) in 2 mL of 70% perchloric acid. The mixture was kept at room temperature for 1 h, diluted with water (3 mL), cooled to 0 °C, and filtered to give mixture of **16** and **17a** (0.45 g, molar ratio 90:10). Mixture of salts (0.6 g, molar ratio 80:20) was obtained then more amount of *tert*-butyl alcohol (0.6 g, 8 mmol) was used. Mixtures were recrystallized from chloroform to give pure **16** (yield 25–30%) as white crystals. Mp 112–113 °C (dec). ^{1}H NMR δ (ppm): 8.25 (s, 2H, NH_2), 7.45 (s, 1H, NH), 1.70 (s, 9H, *t*-Bu), 1.17 (s, 9H, *t-Bu*–NH); ^{13}C NMR δ (ppm): 158.1 (CN_4), 70.0 (CMe_3), 57.7 (CMe_3), 27.9 (3Me), 27.1 (3Me). Anal. Calcd for $C_9H_{21}ClN_6O_4$: C, 34.6; H, 6.8; N, 26.9. Found: C, 34.7; H, 6.9; N, 27.1.

4.1.8. 3-tert-Butyl-1,5-bis(tert-butylamino)tetrazolium perchlorate **17a**

tert-Butyl alcohol (1.05 g, 14 mmol) was added with stirring to the solution of tetrazole **14a** (0.40 g, 4 mmol) in mixture of 3 mL of 70% perchloric acid and 3 mL of chloroform. The mixture was stirred at room temperature for 6 h, diluted with water (5 mL). Chloroform was removed under steam of air. Aqueous solution was cooled to 0 °C and filtered to give mixture of **16** and **17a** (1.3 g, molar ratio 10:90), which was recrystallized from water to give **17a** (1.0 g, 68%) as white crystals suitable for X-ray analysis. Mp 144–145 °C. ^{1}H NMR δ (ppm): 7.63 (s, 1H, NH), 7.46 (s, 1H, NH), 1.73 (s, 9H, *t*-Bu), 1.41 (s, 9H, *t-Bu*–NH–$C_{(5)}$), 1.17 (s, 9H, *t-Bu*–NH–$N_{(1)}$); ^{13}C NMR δ (ppm): 155.8 (CN_4), 70.2 (CMe_3), 58.1 (CMe_3), 53.8 (CMe_3), 28.4 (3Me), 27.9 (3Me), 27.1 (3Me). Anal. Calcd for $C_{13}H_{29}ClN_6O_4$: C, 42.3; H, 7.9; N, 22.8. Found: C, 42.7; H, 7.59; N, 23.3.

4.1.9. 3-tert-Butyl-1-tert-butylamino-5-tert-butylsulfanyl-tetrazolium perchlorate **17b**

Compound **17b** was synthesized in a manner similar to the synthesis of salt **17a** using tetrazole **14b** (0.58 g, 4 mmol). Obtained mixture was recrystallized from water–acetonitrile system to give **17b** (1.1 g, 75%) as white crystals. Mp 131–132 °C (dec). ^{1}H NMR δ (ppm): 8.00 (s, 1H, NH), 1.80 (s, 9H, *t-Bu*–S), 1.65 (s, 9H, *t-Bu*–NH–$C_{(5)}$), 1.19 (s, 9H, *t-Bu*–NH–$N_{(1)}$); ^{13}C NMR δ (ppm): 161.7 (CN_4), 72.2 (CMe_3), 59.0 (CMe_3), 52.8 (CMe_3), 30.1 (3Me), 28.1 (3Me), 27.3 (3Me). Anal. Calcd for $C_{13}H_{28}ClN_5O_4S$: C, 40.5; H, 7.3; N, 18.2. Found: C, 40.4; H, 7.2; N, 18.5.

4.1.10. 1,3-di-tert-Butyltetrazolium-5-aminide **18**

A solution of perchlorate **6** (0.3 g, 1 mmol) in 15 mL chloroform was shaked with aqueous sodium hydroxide (1 N, 5 mL). An intense yellow color immediately developed. The organic layer was separated, dried with anhydrous sodium sulfate, and concentrated. The residue was recrystallized from hexane to give **18** (0.18 g, 91%) as light-yellow crystals. Mp 69–70 °C. ^{1}H NMR δ (ppm): 4.31 (br s, 1H, NH), 1.59 (s, 9H, *t*-Bu), 1.54 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 162.1 (CN_4), 65.2 (CMe_3), 58.9 (CMe_3), 28.1 (Me), 26.5 (Me). ν_{max} 3323, 2989, 2972, 2940, 2912, 2872, 1602, 1456, 1393, 1368, 1305, 1207, 1163, 1138, 1073, 1030, 985, 940, 841, 783, 727, 690, 658 cm^{-1}. Anal. Calcd for $C_9H_{19}N_5$: C, 54.8; H, 9.7; N, 35.5. Found: C, 54.5; H, 9.6; N, 35.9.

4.1.11. 5-Amino-1,3-di-tert-butyltetrazolium chloride **19a**

Hydrochloric acid (36%, 0.2 mL) was added with stirring to base **18** (0.1 g, 0.5 mmol) dissolved in 5 mL of methanol. The obtained solution was concentrated to give **19a** (0.11 g, 94%) as white crystals. Monocrystals of **21a** suitable for X-ray analysis were grown from toluene/chloroform mixture (1:1). Mp 161–162 °C. ^{1}H NMR δ (ppm): 8.23 (s, 2H, NH_2), 1.64 (s, 9H, *t*-Bu), 1.63 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 156.7 (CN_4), 69.2 (CMe_3), 64.2 (CMe_3), 28.2 (Me), 27.0 (Me). Anal. Calcd for $C_9H_{20}ClN_5$: C, 46.3; H, 8.6; N, 30.0. Found: C, 46.6; H, 8.6; N, 29.8.

4.1.12. 5-Amino-1,3-di-tert-butyltetrazolium hexafluorophosphate ***19b***

Hexafluorophoshoric acid (54%, 0.2 mL) was added with stirring to base **18** (0.1 g, 0.5 mmol) dissolved in 3 mL of water. Resulted precipitate was filtered to give **19b** (0.17 g, 99%) as white crystals. Mp 155–156 °C from water. ^{1}H NMR δ (ppm): 8.06 (s, 2H, NH_2), 1.63 (s, 9H, *t*-Bu), 1.62 (s, 9H, *t*-Bu); ^{13}C NMR δ (ppm): 156.7 (CN_4), 69.2 (CMe_3), 64.2 (CMe_3), 30.0 (Me), 28.2 (Me). ν_{max} 3497, 3389, 3300, 3227, 2991, 1647, 1462, 1410, 1377, 1230, 1184, 1163, 827, 738 cm^{-1}. Anal. Calcd for $C_9H_{20}N_5F_6P$: C, 31.5; H, 5.9; N, 20.4. Found: C, 31.6; H, 5.8; N, 20.6.

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Supplementary data

Experimental details of X-ray structural analysis, including crystal data and structure refinement details for salts **17a** and **19a**, and figures depicting hydrogen bonding in investigated structures are available via the Internet at http://www.sciencedirect.com/.

Crystallographic data for **17a** and **19a** have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 686488 and 686489. Copies of this information may be obtained free of charge from deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.06.095.

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