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Synthesis and crystal structure of the first amino-1,3a,4,6a-tetraazapentalenes

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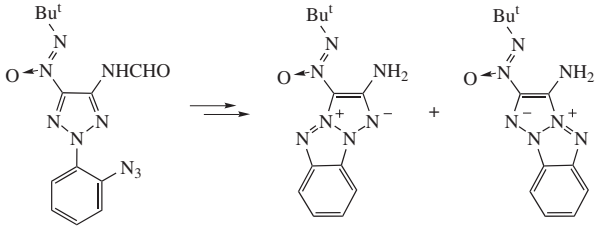
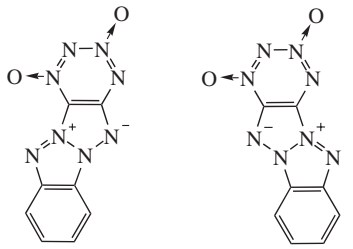
Synthesis of the first amino- and formylamino-1,3a,4,6a-tetraazapentalenes *via* thermolysis of the corresponding 4-amino- and 4-formylamino-2-(2-azidophenyl)-2*H*-[1,2,3]-triazoles has been elaborated. The crystal structures of 2-amino-3-(*tert*-butyl-*NNO*-azoxy)-1*H*-[1,2,3]triazolo[2,1-*a*]-[1,2,3]benzotriazol-1-id-4-ium and 3-amino-2-(*tert*-butyl-*NNO*-azoxy)-1*H*-[1,2,3]triazolo[2,1-*a*][1,2,3]benzotriazol-1-id-4-ium have been established using X-ray diffraction analysis.



Keywords: tetraazapentalenes, 1,2,3-triazoles, azides, cyclization, X-ray, differential scanning calorimetry.

We investigate systematically 1,2,3,4-tetrazine 1,3-dioxides (TDO)[1–3] as promising high energy density materials,[4–7] 1,3a,4,6a-tetraazapentalenes being also known as representatives of this type of substances.[4,8–11] We have recently developed an approach to the synthesis of compounds **1a** and **1b**,[12] in which the above 1,2,3,4-tetrazine 1,3-dioxide and 1,3a,4,6a-tetraazapentalene polynitrogen moieties are fused with each other. Aminotriazole **2** as a key precursor for them was converted to TDO **3** and further to products **1a**,**b** (Scheme 1). A notable drawback of this approach is that the thermolysis of compound **3** results in a mixture of isomers **1a** and **1b**, which are difficult to separate using chromatography or crystallization.

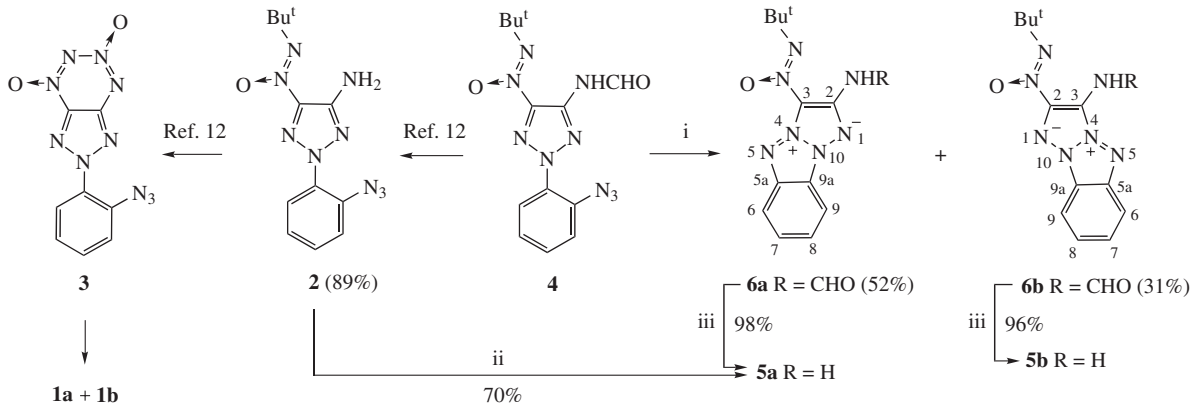
An alternative scheme for the synthesis of compounds **1** may include the formation of a tetraazapentalene system with amino and *tert*-butyl-*NNO*-azoxy groups at neighboring positions, followed by closure of the TDO cycle. However, the required amino-substituted tetraazapentalenes remained unknown so far; several attempts to obtain them by various methods[13] failed and were not resumed due to supposed instability of the products.



1a **1b**

Here we present the first synthesis of amino-substituted tetraazapentalenes.

Aminotriazole **2**, which was obtained from (formylamino)-triazole **4** by its reaction with methanol in the presence of methanesulfonic acid according to known procedure (see Scheme 1),[12] became a key starting compound in our synthetic approach. In general, thermolysis of precursors with 1,2,3-triazole ring and azide group at the *ortho* positions is one of the methods



Scheme 1 *Reagents and conditions*: i, 1,2-dichlorobenzene, 180 °C, 1 h; ii, 1,2-dichlorobenzene, 150 °C, 3.5 h; iii, $MeSO_3H$, MeOH, 50 °C, 30 min.

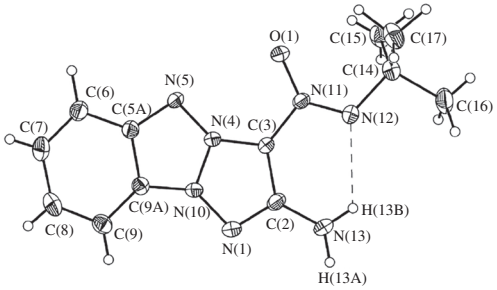


Figure 1 Molecular structure of aminotetraazapentalene **5a**. Non-hydrogen atoms are represented as thermal ellipsoids of atom displacements at 50% probability level.

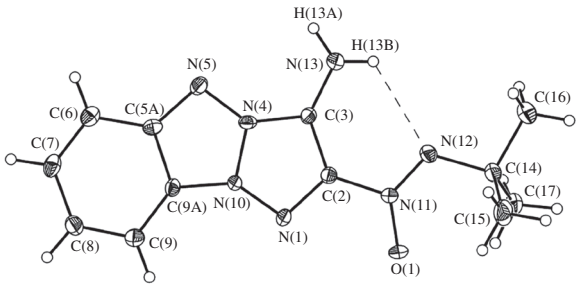


Figure 2 Molecular structure of aminotetraazapentalene **5b**. Non-hydrogen atoms are represented as thermal ellipsoids of atom displacements at 50% probability level.

for the preparation of tetraazapentalenes[14–17] and is typically carried out in 1,2-dichlorobenzene, in DMF or without a solvent. Thus, for cyclization of aminotriazole **2** we used 1,2-dichlorobenzene. The reaction occurred at 150 °C within 3.5 h, affording aminotetraazapentalene **5a** in 70% yield with no isomer **5b**.

The cyclization of formylaminotriazole **4** was carried out in 1,2-dichlorobenzene at 180 °C for 1 h, resulting in a mixture of (formylamino)tetraazapentalenes **6a** and **6b** in 52 and 31% yields, respectively. Deformylation of compounds **6a** and **6b** was performed in methanol in the presence of methanesulfonic acid at 50 °C for 30 min, leading to aminotetraazapentalenes **5a** and **5b** in quantitative yields (see Scheme 1).

Tetraazapentalenes **5a**,**b** as well as **6a**,**b** are high-melting crystalline compounds. According to differential scanning calorimetry data, isomer **5a** with the temperature of decomposition onset equal to 240 °C is thermally more stable than isomer **5b** with the corresponding temperature value of 193 °C. The chemical resistance of these compounds probably originates from the presence of *tert*-butyl-*NNO*-azoxy group as a strong electron-withdrawing substituent adjacent to the amino group. Previous failure to synthesize compounds of this type can be explained by the electron-donating methyl group or weak electron-withdrawing chloro substituent in the starting structures.[13]

According to quantum chemical calculations using B3LYP/6-311++g(d,2p) method,[18] tetraazapentalene **5a** is more thermodynamically stable than compound **5b** by 3 kcal mol^{-1}.

The structures of tetraazapentalenes **5a**,**b** and **6a**,**b** were confirmed by ^{1}H, ^{13}C, ^{14}N NMR and IR spectra as well as by mass spectrometry. Their ^{14}N NMR spectra contain signals in the area of –61 to –66 ppm assigned to the *N*-oxide nitrogen atoms of the *tert*-butyl-*NNO*-azoxy group. The high-resolution mass spectra (ESI) reveal peaks of the corresponding molecular ions.

The structures of aminotetraazapentalenes **5a** and **5b** were also confirmed by single-crystal X-ray diffraction analysis (Figures 1 and 2).†

† *Crystal data for* **5a**. $C_{13}H_{16}Cl_3N_7O$ (M = 392.68), triclinic, space group $P\bar{1}$, at 173 K: a = 6.932(2), b = 8.552(3) and c = 15.570(5) Å, α = = 82.768(7)°, β = 83.838(7)°, γ = 82.171(7)°, V = 903.4(5) Å^3, Z = 2, Z' = 1, d_{calc} = 1.444 g cm^{-3}, μ(MoKα) = 5.23 mm^{-1}, F(000) = 404. Total of 10444 reflections were collected (4359 independent reflections, R_{int} = = 0.0338) and used in refinement, which converged to wR_2 = 0.2200, GOF = 0.952 for all independent reflections [R_1 = 0.0711 was calculated for 2871 reflections with $I > 2\sigma(I)$]. $2q_{max}$ was 56° (completeness 99.8%). Residual electron density r_{max}/r_{min} was 0.294/–0.318 e Å^{-3}.

Crystal data for **5b**. $C_{13}H_{16}Cl_3N_7O$ (M = 392.68), monoclinic, space group $P2_1/c$, at 120 K: a = 6.3531(10), b = 15.839(3) and c = 17.705(3) Å, β = 96.093(4)°, V = 1771.5(5) Å^3, Z = 4, Z' = 1, d_{calc} = 1.472 g cm^{-3}, μ(MoKα) = 5.34 mm^{-1}, F(000) = 808. A total of 16078 reflections were collected (4281 independent reflections, R_{int} = 0.0921) and used in refinement which converged to wR_2 = 0.1220, GOF = 1.040 for all independent reflections [R_1 = 0.0565 was calculated for 2493 reflections with $I > 2\sigma(I)$]. $2q_{max}$ was 56° (completeness 100%). Residual electron density r_{max}/r_{min} was 0.318/–0.377 e Å^{-3}.

The crystals of compounds **5a** and **5b** were grown from $CHCl_3$ as solvates with single $CHCl_3$ molecule. According to X-ray diffraction data, the tetraazapentalene system, amino and azoxy groups are arranged in the same plane for both structures. The H(13B)···N(12) distance is 2.235 Å for compound **5a** and 2.371 Å for compound **5b**, which is less than the sum of van der Waals radii for the N and H atoms and thus indicates the presence of a hydrogen bond.

In summary, a method for the synthesis of the first representatives of amino-1,3a,4,6a-tetraazapentalenes **5a**,**b** has been developed, their X-ray diffraction data has been collected, and the thermal stability has been revealed. Investigations towards further transformation of compounds **5a**,**b** to the corresponding TDOs **1a** and **1b** are underway.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.03.002.

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X-ray diffraction data were recorded using a SMART APEX II area-detector diffractometer (graphite monochromator, ω-scan technique) with MoKα-radiation (0.71073 Å). The structures were solved by direct methods using SHELXS[19] and were refined on F^2 using SHELXL-2014/2017.[19,20] The structure **5a** contained strongly disordered $CHCl_3$ molecules which were removed by the SQUEEZE tool.[21]

CCDC 1852709 and 1852710 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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