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A new conjugated tripoid N_4 system containing furazan and triazolofurazan cores linked by a nitrogen bridge

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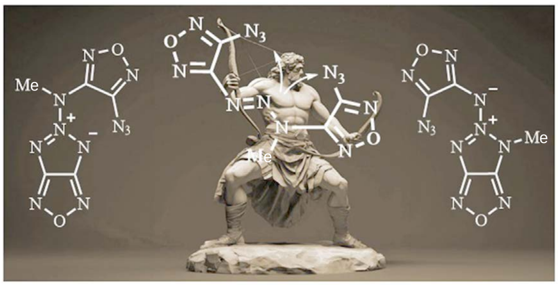
Two thermostable representatives of methyl-substituted triazolofurazan derivatives with zwitterionic N^+–N^- bonds were obtained *via* the thermal cyclization of *N,N′*-bis(azidofurazanyl)-*N*-methyltriazene. 5-(*N*-Azidofurazanyl-*N*-methylamino)triazolofurazan was the product of known intramolecular reaction of neighboring azido and azo groups. Its isomer with methyl group in the triazolofurazan core was formed in the course of new cyclization of azido and triazene groups representing an original N–N bond formation reaction giving an unusual zwitterionic heterocyclic system.



Keywords: 1,2,3-triazoles, 1,2,5-oxadiazoles, triazolofurazans, azides, triazenes, thermal cyclization, X-ray.

Recently, our research group has paid attention to the study of 5-(R-amino)triazolofurazans as well as their salts (Figure 1). A key feature of these heterocyclic compounds is the presence of a flat six π-electron conjugated tripoid (Y-shaped) N_4 fragment (colored red in Figure 1). For systems of this type, extra stabilization is suggested due to the so-called Y-aromaticity.[1] Moreover, the N_4 fragment contains three N–N bonds, which leads to high values of the enthalpy of formation, which is one of the main energy parameters of high-energy materials. In our previous papers,[2,3] it was shown that 5-(R-amino)triazolofurazans were relatively thermostable, which allowed them to be used for the design of new energetic materials by variation of R-substituent.

In this work, we obtained two new compounds having conjugated tripoid N_4 systems. The first one is known 5-(furazanylamino)triazolofurazan **1** (FATF). The second compound belongs to a family of new heterocyclic system with exocyclic amide moiety, namely, *N*-(4-azido-1,2,5-oxadiazol-3-yl)-*N*-(4-methyl-4*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazol-5-ium-5-yl)amide **2** (Scheme 1). The key compound in our synthetic scheme is bis(azidofurazanyl)triazene **4**. There are a few examples of such triazenes with the following furazan ring substituents: Me,[4,5] Ph,[6] NO_2,[7] NH_2,[8,9] Ph, BzNH,[10] and CON_3.[5] They were previously obtained by diazotization of the corresponding amines with sodium nitrite in mineral acid media. In our case this method turned out to be unsuccessful. We obtained bis(azidofurazanyl)triazene **4** in 66% yield by treating a dichloromethane solution of 3-amino-4-azidofurazan **3** with $NOBF_4$ (1 equiv.) at 20 °C for 30 min. Note that compound **4** is sensitive to mechanical stimuli and explodes in porcelain mortar under slight pressure from the pestle. Methylation of this triazene with diazomethane (diethyl ether solution) gave *N*-methylated compound **5** in 85% yield.

Thermolysis of methyltriazene **5** in boiling acetonitrile for 40 h resulted in cyclization to give a mixture of two products in a ratio of about 1 : 1 (^{1}H NMR). Further separation of the mixture using preparative chromatography resulted in two individual compounds **1** and **2** (Scheme 2). The first of these was the known expected FATF **1**, obtained with a 48% yield and formed according to path *a*. The pathway to this compound involves the intramolecular reaction of adjacent azido and azo groups leading to the formation of a 1,2,3-triazole ring. It is a well-known reaction in furazan series.[2,11–13]

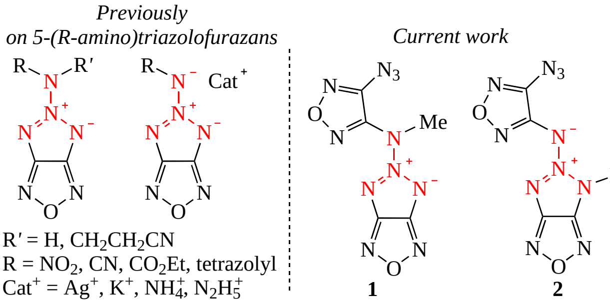
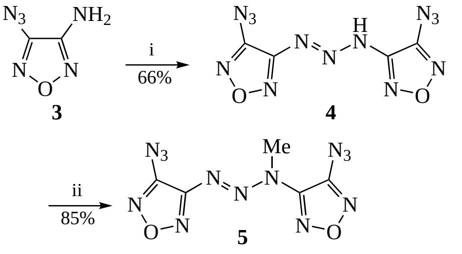
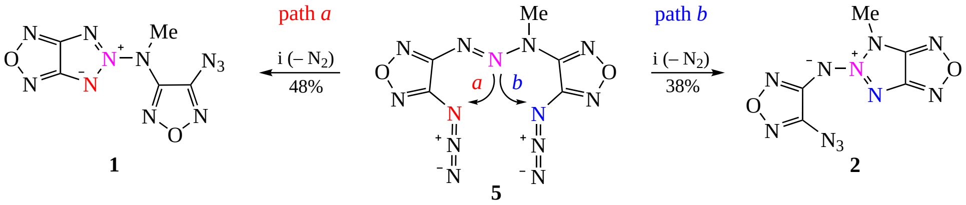


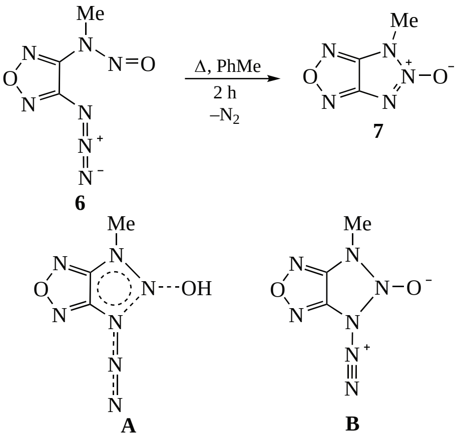
Figure 1 Structures of 5-(R-amino)triazolofurazans under study.



Scheme 1 *Reagents and conditions*: i, $NOBF_4$, CH_2Cl_2, 20 °C; ii, CH_2N_2/Et_2O, MeCN, room temperature.



Scheme 2 *Reagents and conditions*: i, MeCN, Δ, 40 h.



Scheme 3

Pathway *b* affording amide **2** in 38% yield is a previously unknown type of thermal cyclization and a new kind of N–N bond formation reaction, leading to the first example of heterocyclic system containing inner substituted tripoid N_4 fragment (structure discussion see below). This reaction is similar to the synthesis of 4-methyl-4*H*-[1,2,3]triazolo[4,5-*c*]-[1,2,5]oxadiazole 5-oxide (TFO **7**) which was first purposefully obtained in our group by thermal cyclization of furazan **6** (Scheme 3).[14] The mechanism of the latter cyclization can be single-stage, including a cyclic transition state **A**, or possibly two-stage, including an intermediate **B**. The mechanism of formation of amide **2** could be similar since the transition states of these two reactions are isoelectronic. Quantum chemical calculations are planned to clarify this process.

All compounds obtained were characterized by IR (KBr), multinuclear (^{1}H, ^{13}C, ^{14}N) NMR spectroscopy recorded in acetone-d$_6$ and HRMS (for details see Online Supplementary Materials). Due to the symmetry of the triazolofurazan core in FATF **1** the C^{3a} and C^{6a} atoms are equivalent and are observed in the ^{13}C NMR spectra as a single peak with δ = 162.3 ppm, which correlates to ^{13}C NMR data of the 5-(R-amino)triazolofurazans obtained earlier (see Figure 1).[2,3] Two signals (148.0 and 159.7 ppm) related to the triazolofurazan core are recorded in amide **2**. These signals are close to the signals observed in the Me-substituted TFO **7** (Figure 2).

^{14}N NMR spectra in acetone-d$_6$ solutions of both FATF **1** and amide **2** are similar to each other and contain broadened signals ($\Delta\nu_{1/2} \approx 500$ Hz) related to N^1 and N^3 atoms of the furazan ring with δ = 20 and 0 ppm, as well as very broadened signals with $\delta \approx -310$ ppm related to N–Me. Narrow signals of the azide group at $\delta \approx -145$ ppm ($\Delta\nu_{1/2} \approx 50$ Hz) with a shoulder at $\delta \approx -142$ ppm are also present. The narrow peaks of N^5 atom in both cases are observed at $\delta \approx -65$ ppm ($\Delta\nu_{1/2} \approx 230$ Hz). The main difference between ^{14}N NMR spectra of FATF **1** and amide **2** is the presence of the broadened signal at $\delta \approx -96$ ppm ($\Delta\nu_{1/2}$ = 760 Hz) related to N^4 and N^6 in the case of FATF **1**.

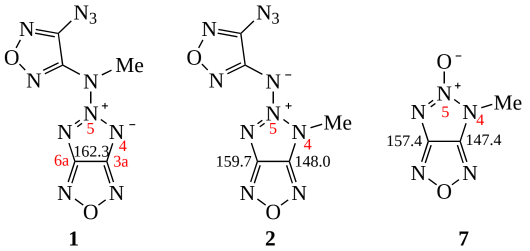


Figure 2 ^{13}C NMR signals of C^{3a} and C^{6a} atoms in compounds **1**, **2**, **7**.

The structure of molecule **2** was ultimately confirmed by single crystal X-ray diffraction analysis (Figure 3).[†] All bond lengths and angles are within the expected ranges, as confirmed by the Mogul geometry check,[15] with the exception of the uncommon N(5)–N(7) bond and bond angles in the annulated heterocycles, which lack correct reference values but are still typical of systems with this heterocycle reported earlier.[2,3,16] Note that the molecule adopts a nearly flat conformation in the crystal, which may indicate significant conjugation throughout the system of π-bonds.

Thermal stability of the compounds was assessed by tracking the signals of thermogravimetry (TG) and differential scanning calorimetry (DSC). As a first measure of thermal stability, the extrapolated onset of decomposition peak was used. Note that more precise conclusion can be drawn only after kinetic analysis of decomposition process.[17] FATF **1** and amide **2** manifest close thermal stability, but FATF **1** first melts at 43 °C and then decays at 150 °C, while amide **2** decomposes without melting at 158 °C. It is likely that such thermal stability is related to the heat resistance of azido group in azidofurazanyl fragment, since most of the organic azides decompose at *ca*. 150 °C.[18,19]

In conclusion, this work is a link in a chain of 5-(R-amino)-triazolofurazans study and high nitrogen compounds,[20,21] demonstrating that the 5-(amino)triazolofurazan core is a

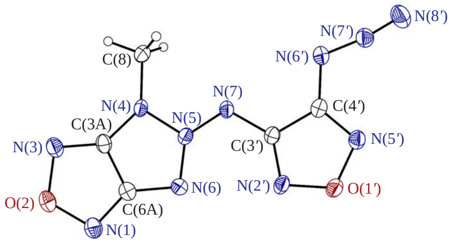


Figure 3 General view of **2** in crystal in thermal ellipsoid representation (p = 50%). Selected bond lengths (Å): N(1)–O(2) 1.4012(14), O(2)–N(3) 1.4302(14), N(1)–C(6A) 1.3114(16), N(3)–C(3A) 1.3038(16), C(3A)–N(4) 1.3554(16), N(6)–C(6A) 1.3776(16), N(4)–N(5) 1.3999(14), N(5)–N(6) 1.3379(14), C(3A)–C(6A) 1.4054(17), N(4)–C(8) 1.4489(17), N(5)–N(7) 1.2934(13), N(7)–C(3′) 1.3778(15), O(1′)–N(2′) 1.3947(13), O(1′)–N(5′) 1.4000(14), N(2′)–C(3′) 1.3180(16), N(5′)–C(4′) 1.3035(16), N(6′)–N(7′) 1.2646(15), N(6′)–C(4′) 1.3912(16), N(7′)–N(8′) 1.1211(14), C(3′)–C(4′) 1.4305(17).

[†] *Crystal data for* **2**. Space group $P2_1/c$, a = 9.5378(5), b = 12.6092(6) and c = 8.7911(4) Å, β = 115.720(2)°, V = 952.50(8) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.738 g cm^{-3}, R_1 = 0.0387 [for 1939 reflections with $2\theta < 60°$ and $I > 2\sigma(I)$], wR_2 = 0.0989, GOF = 1.016. The experiment was performed on a Bruker Smart Apex II diffractometer equipped with a Proton II detector at 120 K using MoKα radiation (λ = 0.71072 Å).

CCDC 2353656 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

promising scaffold for the creation of new energetic compounds. Two new heat resistant representatives of this class, compounds **1** and **2**, were obtained by the thermal cyclization of methyltriazene **5**. FATF **1** was the product of a well-known intramolecular reaction of adjacent azido and azo groups. Compound **2** was the result of the previously unknown type of thermal cyclization of azido and triazene groups, which exhibited an original method of N–N bond formation. This compound is a zwitterionic system with conjugated tripoid N_4 fragment.

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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.2024.10.029.

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