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CONDENSED TETRAZOLO-1,3,5-TRIAZINES. 4*. SYNTHESIS OF SALTS OF 5-AMINO-TETRAZOLO[1,5-*a*]-1,3,5-TRIAZIN-7-ONE

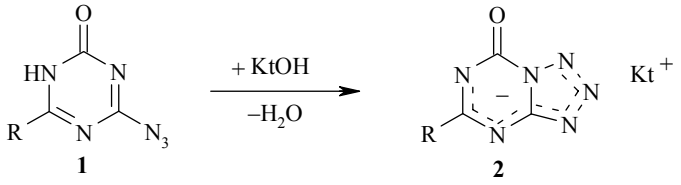
V. V. Bakharev[1], A. A. Ghidaspov[1], D. B. Krivolapov[2], E. V. Mironova[2], and I. A. Litvinov[2]

2-Amino-4-azido-1,3,5-triazin-6(1H)-ones were synthesized by successive substitution of the trinitromethyl groups in 2-amino-4,6-bis(trinitromethyl)-1,3,5-triazines under the influence of azide and nitrite ions. Interaction of 2-amino-4-azido-1,3,5-triazin-6(1H)-ones with bases led to the azido-tetrazole tautomeric conversion give salts of 5-aminotetrazolo[1,5-a]-1,3,5-triazin-7-one.

Keywords: 2-amino-4-azido-1,3,5-triazin-6(1H)-one, 2-amino-4,6-bis(trinitromethyl)-1,3,5-triazines, salts of 5-aminotetrazolo[1,5-*a*]-1,3,5-triazin-7-one, azido-tetrazole tautomeric conversion.

Interest in the synthesis of the heterocyclic structures of 5-amino-tetrazolo[1,5-*a*]-1,3,5-triazin-7-ones is because they are 5,8-diaza-analogs of guanine (2-aminoimidazo[4,5-*d*]pyrimidin-6-one), one of the structural blocks of nucleic acids [2]. Synthetic routes developed earlier for the synthesis of the tetrazolo[1,5-*a*]-1,3,5-triazin-7-one structure was based on the substitution of trinitromethyl group in the tetramethyl ammonium salt of 2-hydroxy-4,6-bis(trinitromethyl)-1,3,5-triazine under the influence of the azide ion, which was accompanied by lactim-lactam and azido-tetrazole tautomeric conversions [3]. A series of derivatives of this new heterocycle were obtained on the basis of reactions of 5-trinitromethyltetrazolo[1,5-*a*]-1,3,5-triazin-7-ones [3,4].

In contrast to [3], other means for the synthesis of salts of 5-R-tetrazolo[1,5-*a*]-1,3,5-triazin-7-ones are studied in this paper. Theoretically to obtain salts of 5-R-tetrazolo[1,5-*a*]-1,3,5-triazin-7-ones it is necessary to form the 2-R-4-azido-1,3,5-triazin-6(1H)-one **1**, which on conversion into a salt should lead to a salt of 5-R-tetrazolo[1,5-*a*]-1,3,5-triazin-7-one **2** as a result of an azido-tetrazolo rearrangement:



1 **2**

2-Dimethyl(diethyl)amino-4,6-bis(trinitromethyl)-1,3,5-triazines **3a,b** [3] were chosen as the starting materials for the synthesis of 5-aminotetrazol[1,5-*a*]-1,3,5-triazin-7-ones.

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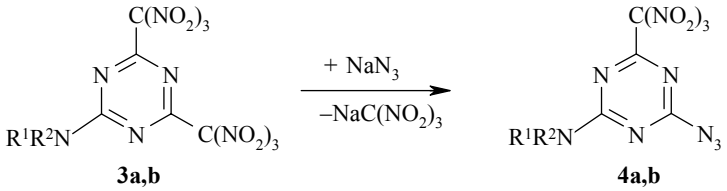
* For paper 3 see [1].

[1] Samara State Technical University, Samara 443100, Russia; e-mail: knil@sstu.smr.ru. [2] A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Science Center of the Russian Academy of Sciences, Kazan 420088, Tatarstan Republic. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1211-1219, August, 2006. Original article submitted February 22, 2006.

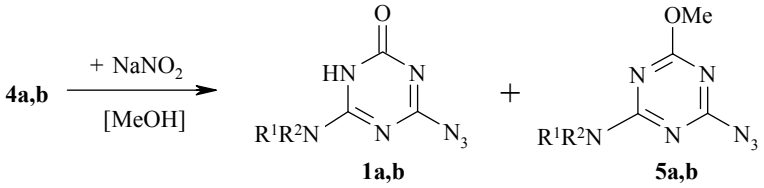
4-Azido-2-dimethyl(diethyl)amino-6-trinitromethyl-1,3,5-triazines **4a,b** were obtained from compounds **3a,b** by a known method [3].



3a,b **4a,b**

3, 4 a $R^1 = R^2 = Me$; **b** $R^1 = R^2 = Et$

Subsequent reaction of the azides **4a,b** with sodium nitrite in methanol gave 4-azido-2-dimethyl(diethyl)amino-1,3,5-triazin-6(1H)-ones **1a,b** in 60-65% yield with 4-azido-2-dimethyl(diethyl)amino-6-methoxy-1,3,5-triazines **5a,b** as side products in 10-15% yield.

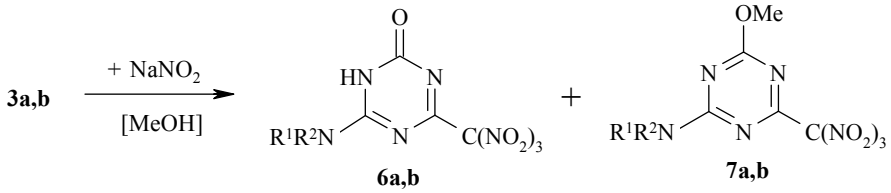


1a,b **5a,b**

1, 5 a $R^1 = R^2 = Me$; **b** $R^1 = R^2 = Et$

Separation of the products was not difficult because the lactams **1a,b** form sodium salts which are soluble in water, from which, after filtration of the methoxy derivatives **5a,b**, they can be separated by acidification to pH 2-3.

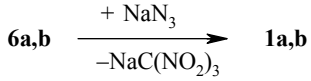
The order of insertion of the azide and oxo groups may be reversed. Treatment of compounds **3a,b** with sodium nitrite in methanol gave 2-dimethyl(diethyl)amino-4-trinitromethyl-1,3,5-triazin-6(1H)-ones **6a,b** (55-60% yield) with 2-dimethyl(diethyl)amino-4-methoxy-6-trinitromethyl-1,3,5-triazines **7a,b** (25-30% yield) as impurities.



6a,b **7a,b**

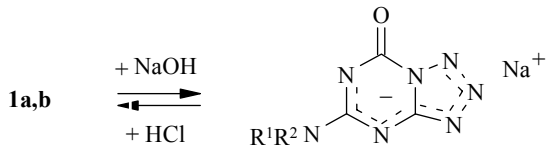
6, 7 a $R^1 = R^2 = Me$; **b** $R^1 = R^2 = Et$

The azido derivatives **1a,b** were obtained in 80-85% yield on reaction of the trinitromethyl derivatives **6a,b** with sodium azide in acetone (acetonitrile).



Deprotonation of the azido derivatives **1a,b** to convert them into salts by treatment of their aqueous suspensions with an equimolar amount of sodium hydroxide gave the required sodium salts of 5-dimethyl(diethyl)aminotetrazol[1,5-*a*]-1,3,5-triazin-7-ones **2a,b** according to IR and ^{1}H NMR data. The

process is reversible. Treatment of aqueous solutions of the sodium salts of 5-dimethyl(diethyl)aminotetrazol[1,5-*a*]-1,3,5-triazin-7-ones **2a,b** with acid gave the reverse rearrangement of the tetrazolo unit to the azide with the formation of the azido derivatives **1a,b**.



1,2 a $R^1 = R^2 = Me$; **b** $R^1 = R^2 = Et$

The structure of compound **2a** was confirmed by X-ray crystallography (Fig. 1, Tables 1-3).

TABLE 1. Bond Lengths (*d*) in the Anion of Structure **2a**

Bond	*d*, Å	Bond	*d*, Å
N(2)–C(3)	1.346(4)	N(4)–C(5)	1.359(3)
N(2)–N(7)	1.366(3)	N(9)–C(3)	1.344(3)
N(2)–C(1)	1.428(3)	N(9)–N(8)	1.375(4)
N(6)–C(1)	1.327(4)	N(7)–N(8)	1.290(4)
N(6)–C(5)	1.363(4)	N(10)–C(5)	1.346(4)
O(13)–C(1)	1.234(3)	N(10)–C(12)	1.446(4)
N(4)–C(3)	1.329(3)	N(10)–C(11)	1.453(4)

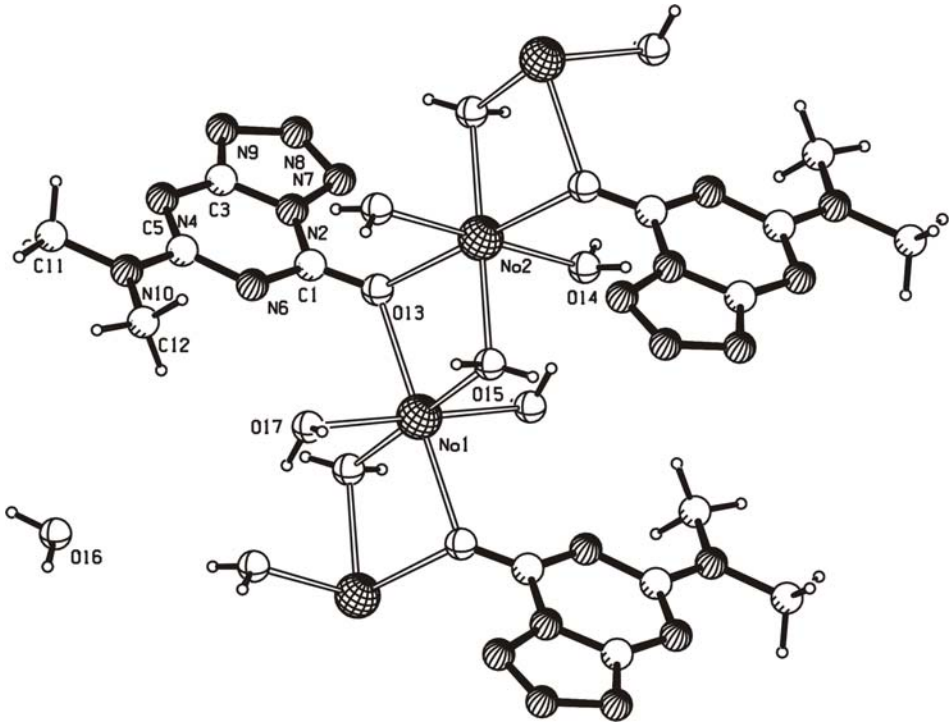


Fig. 1. Molecular and crystal structure of compound **2a**.

TABLE 2. Bond Angles (ω) In the Anion of Structure **2a**

Angle	ω, deg.	Angle	ω, deg.
C(3)–N(2)–N(7)	110.7(2)	N(10)–C(5)–N(4)	116.6(2)
C(3)–N(2)–C(1)	121.7(2)	N(10)–C(5)–N(6)	116.9(2)
N(7)–N(2)–C(1)	127.6(2)	N(4)–C(5)–N(6)	126.5(2)
C(1)–N(6)–C(5)	120.4(2)	N(4)–C(3)–N(9)	128.4(2)
C(3)–N(4)–C(5)	112.8(2)	N(4)–C(3)–N(2)	124.1(2)
C(3)–N(9)–N(8)	104.2(2)	N(9)–C(3)–N(2)	107.5(2)
N(8)–N(7)–N(2)	103.7(2)	O(13)–C(1)–N(6)	127.1(2)
C(5)–N(10)–C(12)	121.2(2)	O(13)–C(1)–N(2)	118.3(2)
C(5)–N(10)–C(11)	120.5(2)	N(6)–C(1)–N(2)	114.6(2)
C(12)–N(10)–C(11)	118.1(2)	N(7)–N(8)–N(9)	113.8(2)

TABLE 3. Torsion Angles (φ) in the Anion of Structure **2a**

Angle	φ, deg.	Angle	φ, deg.
O(13)–C(1)–N(6)–C(5)	-177.18(26)	N(4)–C(3)–N(9)–N(8)	179.45(27)
O(13)–C(1)–N(2)–N(7)	-0.80(38)	C(3)–N(9)–N(8)–N(7)	0.93(28)
O(13)–C(1)–N(2)–C(3)	178.55(25)	N(9)–N(8)–N(7)–N(2)	-0.84(27)
C(1)–N(6)–C(5)–N(10)	177.19(23)	N(8)–N(7)–N(2)–C(1)	179.84(23)
N(6)–C(5)–N(10)–C(12)	-4.91(37)	N(8)–N(7)–N(2)–C(3)	0.42(27)
N(6)–C(5)–N(10)–C(11)	-178.69(24)	N(7)–N(2)–C(3)–N(4)	-179.91(24)
N(4)–C(5)–N(10)–C(12)	175.87(24)	C(3)–N(2)–C(1)–N(6)	-1.14(35)
N(4)–C(5)–N(10)–C(11)	2.09(37)	C(1)–N(2)–C(3)–N(9)	-179.32(22)
C(1)–N(6)–C(5)–N(4)	-3.68(41)	C(1)–N(2)–C(3)–N(4)	0.63(41)
N(6)–C(5)–N(4)–C(3)	2.88(39)	C(5)–N(6)–C(1)–N(2)	2.48(34)
C(5)–N(4)–C(3)–N(9)	178.61(27)	N(7)–N(2)–C(3)–N(9)	0.13(30)
C(5)–N(4)–C(3)–N(2)	-1.34(38)	N(6)–C(1)–N(2)–N(7)	179.50(23)

The tetrazole ring in salts **2a,b** is formed by closing the azide group at atom N(2) of the 1,3,5-triazine in the direction of the carbonyl group C(1)–O(13). The nature of the substituent at position 5 of the 1,3,5-triazine ring (the electron-withdrawing trinitromethyl group [3] or the electron-donating dialkylamino groups in compound **2a,b**) does not affect the direction of cyclization during the azido-tetrazolo tautomeric conversion.

The molecule **2a** is planar (divergence from the plane does not exceed 0.078 Å), the dimethylamino group lies in the plane of the tetrazolo[1,5-*a*]-1,3,5-triazine. A comparison of the geometric parameters of the salt **2a** and the dipotassium salt of 5-dinitromethyltetrazolo[1,5-*a*]-1,3,5-triazin-7-one [2] showed that the differences in the bond lengths and angles in the cyclic tetrazolo[1,5-*a*]-1,3,5-triazine systems are not large – 0.01-0.02 Å and 1-2°. Maximum differences (0.04 Å and 3°) were observed in the 1,3,5-triazine ring about the substituent in position 5, apparently caused by the substituents (dimethylamino and dinitromethyl groups). Analysis of the bond lengths and bond angles in the 1,3,5-triazine and tetrazole rings of tetrazolo[1,5-*a*]-1,3,5-triazine systems in comparison with those in the structures of covalent 1,3,5-triazines [4], tetrazoles [5], and the sodium salt of tetrazole [6] showed that the whole conjugated cyclic system of the tetrazolo[1,5-*a*]-1,3,5-triazine was involved in the delocalization of the negative charge in the anion of compound **2a**.

The following additional points may be noted in the analysis of the crystal structure of compound **2a**. The two independent sodium cations occupy special positions, at centers of symmetry. The 5-dimethylaminotetrazolo[1,5-*a*]-1,3,5-triazine anions and four water molecules occupy general positions, corresponding to the stoichiometry of the compound. The sodium cations have practically undistorted octahedral coordination with bonds to four water molecules and two oxygen atoms of two molecules of

TABLE 4. Hydrogen Bond Parameters in the Crystal of Compound **2a**

D–H···A	D–H, Å	H···A, Å	D···A, Å	∠ DHA, deg.	Symmetry operation
O(14)–H(141)···N(9)	0.82	2.360	2.898(4)	124.0	$x, y, 1 + z$
O(14)–H(142)···O(16)	0.85	2.270	2.860(4)	127.0	$1 + x, -1 + y, z$
O(15)–H(151)···O(16)	0.85	2.040	2.884(4)	169.0	$1 - x, 1 - y, 1 - z$
O(15)–H(152)···N(4)	0.85	2.120	2.919(4)	157.0	$x, y, 1 + z$
O(16)–H(161)···O(15)	0.86	2.500	2.884(4)	108.0	$1 - x, 1 - y, 1 - z$
O(16)–H(162)···O(15)	0.85	2.500	2.884(4)	108.0	$1 - x, 1 - y, 1 - z$
O(17)–H(171)···O(16)	0.82	2.090	2.748(4)	137.0	$1 - x, 1 - y, 1 - z$
O(17)–H(172)···O(14)	0.85	1.980	2.818(4)	169.0	$1 - x, -y, 1 - z$

5-dimethylaminotetrazolo[1,5-*a*]-1,3,5-triazine-7-one. The carbonyl oxygen atoms and one water molecule form a bridge between the two independent sodium ions, two water molecules are coordinated to a sodium cations, and one does not participate in coordinate bonds but apparently stabilizes the crystal *via* hydrogen bonds. As a result a polymeric chains are formed from four-membered Na_2O_2 rings along the 0*y* axis. The four-membered Na_2O_2 rings are not planar: the fold angle along O(13)···O(15) is 22.1°.

Compound **2a** is a crystallohydrate, stabilized by a system of hydrogen bonds (Table 4). In the crystals of compound **2a** intermolecular hydrogen bonds between the 5-dimethylaminotetrazolo[1,5-*a*]-1,3,5-triazine-7-one anion and the water molecules of solvation as a result of which a two-dimensional network is formed – layers parallel to the *a*0*c* plane of the crystal.

In conclusion a new method for the synthesis of heterocyclic salts of the 5-dimethyl(diethyl)aminotetrazolo[1,5-*a*]-1,3,5-triazine-7-one system based on the successive substitution of the trinitromethyl groups in 2-dimethyl(diethyl)amino-4,6-bis(trinitromethyl)-1,3,5-triazines under the influence of azide and nitrite ions with subsequent treatment with base. It is shown that the azido-tetrazolo rearrangement: 2-dimetyl(diethyl)amino-4-azido-1,3,5-triazin-6(1H,6H)-ones **1a,b** – sodium salt of 5-dimethyl(diethyl)amino-tetrazolo[1,5-*a*]-1,3,5-triazin-7-ones **2a,b** , is reversible.

EXPERIMENTAL

IR spectra of KBr disks (thin films for compounds **4b** and **5b**) were recorded with an Avatar spectrophotometer. ^{1}H NMR spectra were recorded with a Bruker AM-300 (300 MHz) machine with HMDS as internal standard.

X-ray crystallography of a crystal of compound **2a** is carried out at 20°C (T = 293 K) with an Enraf-Nonius CAD-4 automatic four-circle diffractometer (CuKα radiation [λ 1.5418 A], graphite monochromator, ω-scanning). No decrease in the intensity of three control reflexions was observed during the experiment. The structure was solved by direct methods using the SIR program [8] and refined initially in the isotropic and finally in the anisotropic approximation using the SHELX 97 program [9]. Coordinates of the hydrogen atoms bonded to carbon atoms were calculated on the basis of stereochemical criteria and refined using the "riding" model. All calculations were carried out using WinGX suite of programs [10]. Cell parameters and experimental data were obtained using the MoIEN programs [11] on a DEC Alpha Station 200. All figures and analysis of the intermolecular interactions were obtained using the PLATON program [12].

Crystals of compound **2a**: colorless, translucent prisms, triclinic: $C_5H_6N_7$–O^-·Na·$4H_2O$; M = 275.22; a = 6.981(4), b = 9.485(9), c = 9.80(1) Å; α = 111.69(8), β = 91.74(6), γ = 97.42(6)°; V = 596(1) Å^3; d_c = 1.53 g/cm^3; Z = 2; space group P-1. Scanning angle 4.87° < θ < 74.20°. 1906 independent reflexions were measured of which 1619 had $I \geq 2\sigma$. The calculated empirical absorption μ(Cu) = 14.53 cm^{-1}. The hydrogen

atoms of the water molecules (attached to O(14), O(15), O(16), and O(17)) were resolved from electron density difference syntheses and their contribution to the structure amplitudes was calculated with fixed and thermal parameters in the final stage of the refinement. The final residual factors were $R = 0.0767$ and $R_w = 0.2090$ for 1619 reflexions with $F > 2\sigma(F^2)$. The structure has been deposited in the Cambridge Crystal Structure Date Bank (CCDC 297197).

Compounds 4a-b were synthesized by a known method [3].

4-Azido-2-dimethylamino-1,3,5-triazin-6(1H)-one (1a) and 4-Azido-2-dimethylamino-6-methoxy-1,3,5-triazine (5a). Compound **4a** (3.14 g, 1 mmol) was added over 1 h with stirring at 20-25° to a solution of sodium nitrite (5 mmol) in a mixture of methanol (30 ml) and water (5 ml). The stirred reaction mixture was kept at 20-25° until complete disappearance of the trinitromethyl derivative (4-4.5 h, TLC). Methanol was then removed and the residue treated with water (50 ml). Sodium carbonate (0.83 g, 1 mol) was added with stirring to the suspension at 20-25°. The insoluble 4-azido-2-dimethylamino-6-methoxy-1,3,5-triazine **5a** was filtered off, washed with water, and air dried. Yield of **5a** 0.195 g (10%); mp 110-112°C. IR spectrum, ν, cm^{-1}: 2964, 2944, 2164, 2124, 1598, 1542, 1528, 1496, 1426, 1360, 1244, 1212, 1120, 1092, 1064, 968, 800. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 3.10 (6H, s, NCH_3); 3.84 (3H, s, OCH_3). Found, %: C 43.36; H 5.12; N 43.33. $C_7H_{10}N_6O$. Calculated, %: C 43.39; H 5.19; N 46.65.

After removal of compound **5a**, the remaining aqueous filtrate was acidified with 1N hydrochloric acid to pH 2-3, the precipitate of compound **1a** was filtered off, washed with water, and air dried. Yield of compound **1a** 1.18g (65%); mp 195-196°C (dec.). IR spectrum, ν, cm^{-1}: 3096, 2996, 2902, 2152, 1704, 1632, 1552, 1544, 1508, 1432, 1402, 1348, 1268, 1186, 1078, 1036, 956, 880, 816, 784. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.06 (6H, d, $J = 9.0$, NCH_3); 4.60 (br. s, H_3O^+). Found, %: C 40.04; H 4.42; N 46.56. $C_6H_8N_6O$. Calculated, %: C 40.00; H 4.48; N 46.65.

4-Azido-2-diethylamino-1,3,5-triazin-6(1H)-one (1b) and 4-Azido-diethylamino-5-methoxy-1,3,5-triazine (5b) were prepared analogously to compound **1a** from sodium nitrite (3.25 g, 5 mmol) and compound **4b** (3.42 g, 1 mmol). After treatment of the aqueous suspension with sodium carbonate, compound **5b** was extracted with methylene chloride (2 × 10 ml), the methylene chloride solution was washed with water (3 × 10 ml), dried over sodium sulfate, the solvent was evaporated, and the residue was evacuated at 20-30 mm Hg at 20-25°C to give compound **5b** as a viscous light-yellow oil (0.334 g, 15%). IR spectrum, ν, cm^{-1}: 2977, 2935, 2873, 2129, 1581, 1517, 1471, 1459, 1442, 1363, 1317, 1257, 1226, 1178, 1099, 1060, 956, 811, 784, 752. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.04 and 1.19 (6H, two t, $J = 7.2$, $J = 7.0$, CH_3); 3.40 and 3.62 (4H, 2 q, $J = 7.2$, $J = 7.0$, NCH_2); 3.83 (3H, s, OCH_3). Found, %: C 48.57; H 6.41; N 37.74. $C_9H_{14}N_6O$. Calculated, %: C 48.64; H 6.35; N 37.81.

After removal of compound **5b,** the remaining aqueous filtrate was acidified with 1N hydrochloric acid to pH 2-3, the precipitate of compound **1a** was filtered off, washed with water, and air dried. Yield of compound **1b** 1.25 g (60%); mp 189-190°C (dec.). IR spectrum, ν, cm^{-1}: 3106, 2975, 2933, 2134, 1668, 1600, 1538, 1502, 1442, 1405, 1359, 1340, 1317, 1294, 1232, 1205, 1162, 1089, 1025, 991, 954, 840, 792. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J* Hz): 0.96 (6H, t, $J = 7.0$, CH_3); 3.34 (4H, q, $J = 7.0$, NCH_2). Found, %: C 46.20; H 5.92; N 40.34. $C_8H_{12}N_9O$. Calculated, %: C 46.15; H 5.81; N 40.36.

2-Dimethylamino-4-trinitromethyl-1,3,5-triazin-6(1H)-one (6a) and 2-Dimethylamino-6-methoxy-4-trinitromethyl-1,3,5-triazine (7a). Sodium nitrite (0.76 g, 1.1 mmol) was added by portions with stirring to a solution of 2-dimethylamino-4,6-bis(trinitromethyl)-1,3,5-triazine **3a** (4.22 g, 1 mmol) in methanol (35 ml) at 20-25°C. The mixture was stirred at 20-25°C until the trinitromethyl starting material had disappeared (TLC, 1-1.5 h). The methanol was then removed and the residue was treated with water (50 ml). Sodium carbonate (0.83 g, 1 mmol) was added by portions to the stirred suspension at 20-25°C. The insoluble precipitate of compound **7a** was filtered off, washed with water, and air dried. Yield of compound **7a** 0.76 g (25%); mp 79-81°C. IR spectrum, ν, cm^{-1}: 2926, 2882, 1616, 1592, 1502, 1476, 1448, 1382, 1312, 1294, 1200, 1164, 1048, 988, 962, 854, 792. ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 3.18 (6H, d, $J = 9.4$, NCH_3); 3.96 (3H, s, OCH_3). Found, %: C 31.85; H 3.41; N 27.73. $C_8H_{10}N_6O_7$. Calculated, %: C 31.80; H 3.34; N 27.81.

After removal of compound **7a**, the residual aqueous filtrate was acidified with 1 N hydrochloric acid to pH 2-3, the precipitate of compound **6a** was filtered off, washed with water, and air dried. Yield of compound **6a** 1.88 g (65%); mp 178-180°C. IR spectrum, ν, cm^{-1}: 3100, 3024, 2982, 1702, 1640, 1596, 1568, 1516, 1446, 1404, 1332, 1296, 1240, 1188, 1120, 1080, 992, 856, 800, 790. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.21 (6H, d, *J* = 9.2, NCH_3). Found, %: C 29.22; H 2.85; N 29.24. $C_7H_8N_6O_7$. Calculated, %: C 29.17; H 2.80; N 29.16.

2-Diethylamino-4-trinitromethyl-1,3,5-triazin-6(1H)-one (6b) and 2-Diethylamino-6-methoxy-4-trinitromethyl-1,3,5-triazine (7b) were prepared analogously to compound **6a** from compound **3b** (4.50 g, 1 mmol) and sodium nitrite (0.76 g, 1.1 mmol).

Yield of compound **7b** 0.99 g (30%); mp 42-43°C. IR spectrum, ν, cm^{-1}: 2991, 2941, 2877, 1631, 1585, 1504, 1483, 1459, 1446, 1386, 1365, 1324, 1290, 1251, 1216, 1193, 1091, 1018, 991, 966, 848, 800. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.10 and 1.19 (6H, two t, *J* = 6.8, CH_3); 3.50 and 3.64 (4H, two q, *J* = 6.8, NCH_2); 3.95 (3H, s, OCH_3). Found, %: C 36.31; H 4.20; N 25.56. $C_{10}H_{14}N_6O_7$. Calculated, %: C 36.37; H 4.27; N 25.45.

Yield of compound **6b** 1.90 g (60%); mp 157-158°C (dec.). IR spectrum, ν, cm^{-1}: 3160, 3088, 2992, 2904, 1700, 1632, 1588, 1564, 1504, 1472, 1456, 1424, 1392, 1368, 1336, 1296, 1192, 1176, 1096, 1072, 1008, 984, 848, 800. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.08 and 1.28 (6H, two t, *J* = 6.8, CH_3); 3.42 and 3.65 (4H, two q, *J* = 6.8, NCH_2); 5.09 (1H, br. s, NH). Found, %: C 34.19; H 3.75; N 26.49. $C_9H_{12}N_6O_7$. Calculated, %: C 34.18; H 3.82; N 26.58.

4-Azido-2-dimethylamino-1,3,5-triazin-6(1H)-one (1a). Sodium azide (0.69 g, 1.05 mmol) was added in portions with stirring to a solution of compound **6a** (2.89 g, 1 mmol) in 95% aqueous acetone (acetonitrile) (30 ml) at 20-25°C. The stirred reaction mixture was kept at 20-25°C until the trinitromethyl starting material had disappeared (TLC, 1.5-2 h). The precipitate of **1a** was filtered off, washed with acetone and air dried. Yield 1.54 g (85%).

4-Azido-2-diethylamino-1,3,5-triazin-6(1H)-one (1b) was prepared analogously from compound **6b** (3.17 g, 1 mmol) and sodium azide (0.069 g, 1.05 mmol). Yield 1.67 g (80%).

Sodium Salt of 5-Dimethylaminotetrazolo[1,5-*a*]-1,3,5-triazin-7-one (2a). Compound **1a** (1.81 g, 1 mmol) was suspended in water (15 ml). Sodium hydroxide solution (10 ml, 1 N) was added dropwise with stirring to the suspension at 20-25°C. The starting material dissolved by degrees (0.5-1 h). The solution was cooled with stirring to 0-5°C and kept for 3 h. The precipitate of compound **2a** was filtered off, washed with ice water (3-4 ml), and air dried. Yield 1.62 g (80%); mp 264-265°C (dec.). IR spectrum, ν, cm^{-1}: 3224, 3000, 2960, 1692, 1590, 1560, 1462, 1420, 1384, 1300, 1192, 1158, 1110, 1074, 1046, 1010, 776, 732. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.06 (6H, s, NCH_3).

4-Azido-2-dimethylamino-1,3,5-triazin-6(1H)-one (1a) from Compound 2a. A stirred solution of compound **2a** (0.508 g, 0.25 mmol) in water (30 ml) at 20-25°C was acidified with 1 N hydrochloric acid to pH 2-3, the precipitate of compound **1a** was filtered off, washed with water, and air dried. Yield 0.43 g (95%).

Sodium Salt of 5-Diethylaminotetrazolo[1,5-*a*]-1,3,5-triazin-7-one (2b) was prepared analogously to compound **2a** from compound **1b** (2.09 g, 1 mmol). Yield of compound **2b** 1.39 g (60%); mp 240-241°C. IR spectrum, ν, cm^{-1}: 2975, 2935, 2873, 1683, 1579, 1533, 1440, 1384, 1322, 1290, 1234, 1174, 1151, 1103, 1051, 991, 933, 783. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.10 (6H, t, *J* = 7.0, CH_3); 3.54 (4H, q, *J* = 7.0, NCH_2).

2-Azido-2-diethylamino-1,3,5-triazin-6(1H)-one (1b) from compound 2b. A stirred solution of compound **2b** (0.578 g, 0.25 mmol) in water (30 ml) was acidified with 1 N hydrochloric acid to pH 2-3, the precipitate of compound **1b** was filtered off, washed with water, and air dried. Yield 0.47 g (90%).

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