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

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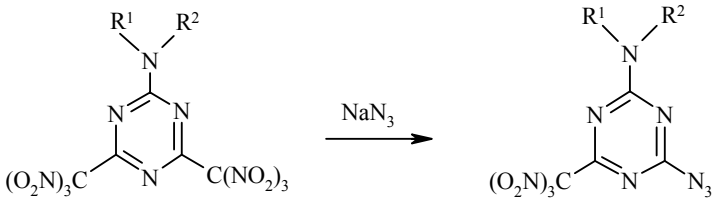
The aziridation of 2-R-4,6-bis(trinitromethyl)-1,3,5-triazines containing electron-donor substituents has been studied. It was found that the corresponding 4-azido-2-dialkylamino-6-trinitromethyl-1,3,5-triazines are formed when R = NMe_2, NEt_2. When R = $O^-NMe_4^+$ a novel reaction route was discovered leading to the tetramethylammonium salt of 5-polynitromethyltetrazolo[1,5-a]-1,3,5-triazin-7-one which is formed as a result of azido-tetrazole and lactim-lactam tautomeric conversion. Denitration of this salt at the trinitromethyl group occurs with retention of the tetrazolo-1,3,5-triazine structure. An X-ray analysis was carried out for the denitration product which was the dipotassium salt of 5-dinitromethyltetrazolo[1,5-a]-1,3,5-triazin-7-one.

Keywords: 2-substituted 4,6-bis(trinitromethyl)-1,3,5-triazines, condensed tetrazolo-1,3,5-triazines, 5-polynitromethyltetrazolo[1,5-*a*]-1,3,5-triazin-7-ones, aziridation, azido-tetrazole tautomerism.

Investigations of the synthesis and chemical properties of nitro- and polynitromethyl derivatives of 1,3,5-triazine have been actively carried out in recent years [1-9]. Our work is also based on a study of the reactivity of trinitromethyl derivatives of 1,3,5-triazine and concerns the potential synthesis of previously unreported polynitromethyltetrazolo-1,3,5-triazines in which a tetrazole ring is annelated to the 1,3,5-triazine ring.

The general method for preparing condensed tetrazoles is based on the annelation of tetrazole to the triazine ring *via* an azido-tetrazole tautomeric conversion of the azidoazomethine fragment in the molecule [10, 11]. For azido-1,3,5-triazines which contain electron-donor substitutents this question has been considered in [12, 13].



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

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

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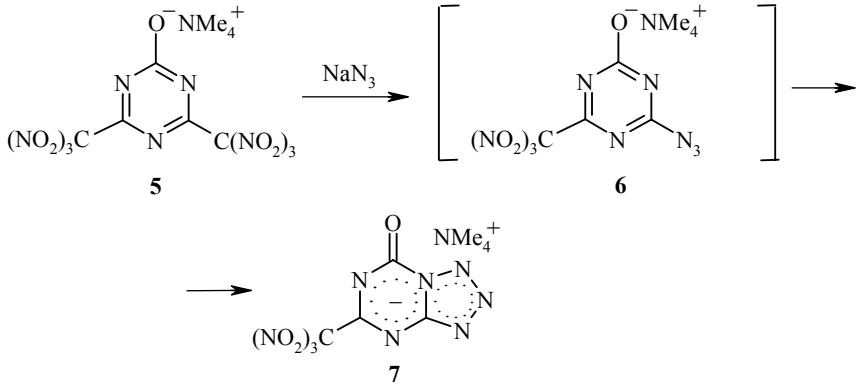
With the object of a preparative synthesis of condensed tetrazolo-1,3,5-triazines with polynitromethyl groups we have studied here the aziridation of 2-R-4,6-bis(trinitromethyl)-1,3,5-triazines containing the electron-donor substituents R = NMe_2, NEt_2, and $O^-NMe_4^+$.

Treatment of the 2-dialkylamino-4,6-bis(trinitromethyl)-1,3,5-triazines **3a,b** with sodium azide in acetonitrile occurs selectively and is accompanied by the substitution of one trinitromethyl group.

According to IR and ^1H and ^{13}C NMR spectroscopic data the synthesized compounds **4a,b** exist in the azide form both in the solid state and in deuterated solvent solutions. Hence, with the given combination of substituents, compounds **4a,b** do not undergo a potential azido-tetrazole tautomeric conversion.

Reaction of the tetramethylammonium salt of 2-hydroxy-4,6-bis(trinitromethyl)-1,3,5-triazine (**5**) with sodium azide in aqueous acetone also leads to substitution of one trinitromethyl group for azide, however the azide **6** formed undergoes a further reaction to the previously unknown tetramethylammonium salt of 5-trinitromethyltetrazolo[1,5-*a*]-1,3,5-triazin-7-one (**7**):

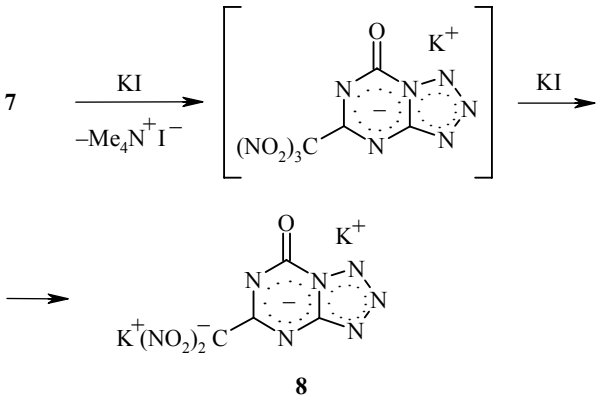


5 **6** **7**

We propose that the given reactions occur sequentially or together *via* lactim-lactam and azido-tetrazole tautomeric rearrangements which lead to compound **7**. Elemental analysis of compound **7**, the presence in its IR spectrum of stretching bands for the oxo group at 1720 cm^{-1}, and the absence of stretching bands for the azide group at 2100-2200 cm^{-1}, together with the ^1H and ^{13}C NMR spectroscopic data confirm the structure of the salt **7**.

The denitration of salt **7** using potassium iodide in methanol according to method [14] gives the dipotassium salt of 5-dinitromethyltetrazolo[1,5-*a*]-1,3,5-triazin-7-one (**8**). According to the IR and ^{13}C NMR spectra the tetrazolo-1,3,5-triazine structure is preserved.

It is proposed that in the course of the reaction there occurs an initially rapid cation exchange and then an immediate denitration of the trinitromethyl to a dinitromethyl group:



8

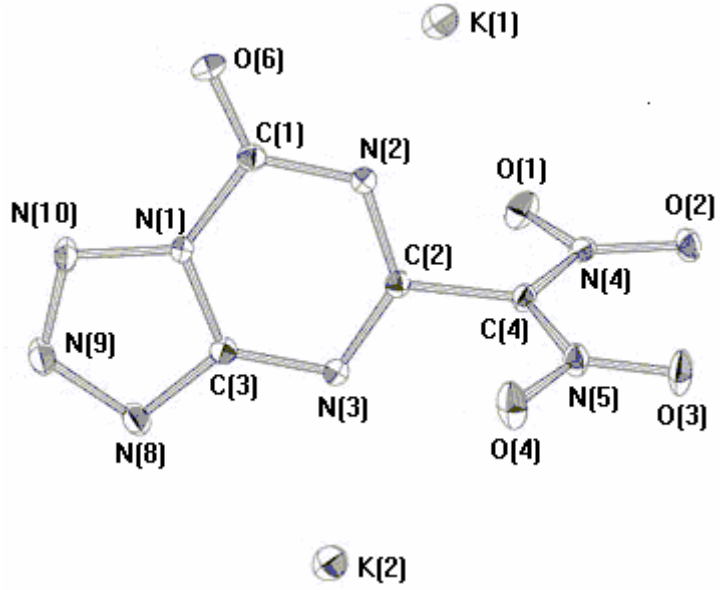


Fig. 1. The structure of the molecule of compound **8**.

Evidence for the structure of the synthesized salts **7** and **8** in this report came from an X-ray structural analysis of compound **8** (Figure 1 and Tables 1-3).

The following can be noted from an analysis of the geometrical parameters of compound **8**. The formation of the tetrazole ring *via* an azidotetrazole tautomeric conversion occurs at atom $N_{(1)}$ in the 1,3,5-triazine ring in the direction of the exocyclic O(6) oxygen atom, i.e. towards the substituent causing the least steric hindrance. In compound **8** the cyclic system of the tetrazolo-1,3,5-triazine and the exocyclic bonds C(1)–O(6) and C(2)–C(4) lie virtually in one plane. The dinitromethyl fragment which bears one of the two negative charges (see below) turns around the C(2)–C(4) bond relative to the tetrazolo-1,3,5-triazine cyclic system by about 76°. The C(1)–O(6) bond is approximately 0.07 Å shorter than the analogous single bond in 2-hydroxy-4,6-bis(trinitromethyl)-1,3,5-triazine [1] and this infers an increase in the multiplicity of the C(1)–O(6) bond, i.e. to an increase in the double bond nature.

TABLE 1. Bond Lengths (*d*) in Structure **8**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O(1)–N(4)	1.2694(5)	K(2)–O(1)	2.8633	N(1)–C(3)	1.3564(5)
O(4)–N(5)	1.2545(5)	K(2)–N(8)	2.8460	N(8)–C(3)	1.3278(6)
N(4)–C(4)	1.3608(6)	K(2)–O(6)	2.7696	N(3)–C(2)	1.3186(6)
N(10)–N(9)	1.2936(6)	K(2)–O(3)	2.6390	C(2)–C(4)	1.4927(6)
N(2)–C(1)	1.3474(6)	O(6)–C(1)	1.2258(5)	K(1)–O(1)	2.7146
N(1)–C(1)	1.4088(6)	N(4)–O(2)	1.2476(5)	K(1)–N(8)	3.8597
N(8)–N(9)	1.3611(5)	N(10)–N(1)	1.3672(5)	K(1)–O(6)	2.9168
N(5)–C(4)	1.3713(5)	O(3)–N(5)	1.2409(4)	K(1)–O(3)	2.7865
N(3)–C(3)	1.3487(5)	N(2)–C(2)	1.3476(5)		

TABLE 2. Valence Angles (ω) in Structure **8**

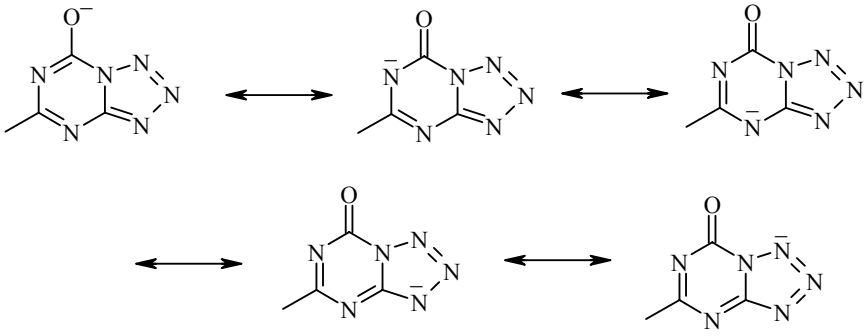
Angle	ω,deg	Angle	ω, deg
O(1)–N(4)–O(2)	119.9(1)	O(1)–N(4)–C(4)	115.6(1)
O(2)–N(4)–C(4)	124.5(1)	N(1)–N(10)–N(9)	104.8(1)
C(1)–N(2)–C(2)	119.3(1)	N(10)–N(1)–C(1)	127.7(1)
N(10)–N(1)–C(3)	108.9(1)	C(1)–N(1)–C(3)	123.4(1)
N(9)–N(8)–C(3)	105.2(1)	N(10)–N(9)–N(8)	112.9(1)
O(4)–N(5)–O(3)	120.3(1)	O(4)–N(5)–C(4)	116.7(1)
O(3)–N(5)–C(4)	123.0(1)	C(2)–N(3)–C(3)	112.2(1)
O(6)–C(1)–N(2)	126.2(1)	O(6)–C(1)–N(1)	120.3(1)
N(2)–C(1)–N(1)	113.4(1)	N(2)–C(2)–N(3)	129.5(1)
N(2)–C(2)–C(4)	113.5(1)	N(3)–C(2)–C(4)	117.0(1)
N(4)–C(4)–N(5)	122.7(1)	N(4)–C(4)–C(2)	117.9(1)
N(5)–C(4)–C(2)	119.3(1)	N(1)–C(3)–N(8)	108.2(1)
N(1)–C(3)–N(3)	122.2(1)	N(8)–C(3)–N(3)	129.6(1)

TABLE 3. Torsional Angles ϕ (deg) in Structure **8**

Angle	ω, deg	Angle	ω, deg
O(1)–N(4)–C(4)–N(5)	169.3	O(1)–N(4)–C(4)–C(2)	-8.9
O(2)–N(4)–C(4)–N(5)	-9.3	O(2)–N(4)–C(4)–C(2)	172.5
N(1)–N(10)–N(9)–N(8)	0.1	N(9)–N(10)–N(1)–C(1)	-178.6
N(9)–N(10)–N(1)–C(3)	-0.6	C(2)–N(2)–C(1)–O(6)	179.8
C(2)–N(2)–C(1)–N(1)	0.4	C(1)–N(2)–C(2)–N(3)	0.4
C(1)–N(2)–C(2)–C(4)	-179.8	N(10)–N(1)–C(1)–O(6)	-2.6
N(10)–N(1)–C(1)–N(2)	176.8	N(10)–N(1)–C(3)–N(8)	0.9
N(10)–N(1)–C(3)–N(3)	-177.5	C(3)–N(1)–C(1)–O(6)	179.7
C(3)–N(1)–C(1)–N(2)	-0.9	C(1)–N(1)–C(3)–N(8)	179.0
C(1)–N(1)–C(3)–N(3)	0.6	C(3)–N(8)–N(9)–N(10)	0.5
N(9)–N(8)–C(3)–N(1)	-0.8	N(9)–N(8)–C(3)–N(3)	177.4
O(4)–N(5)–C(4)–N(4)	-175.9	O(4)–N(5)–C(4)–C(2)	2.3
O(3)–N(5)–C(4)–N(4)	3.8	O(3)–N(5)–C(4)–C(2)	-178.0
C(3)–N(3)–C(2)–N(2)	-0.7	C(2)–N(3)–C(3)–N(1)	0.2
C(2)–N(3)–C(3)–N(8)	-177.9	C(3)–N(3)–C(2)–C(4)	179.5
N(2)–C(2)–C(4)–N(4)	-76.7	N(2)–C(2)–C(4)–N(5)	105.0
N(3)–C(2)–C(4)–N(4)	103.1	N(3)–C(2)–C(4)–N(5)	-75.2

The structure of the 1,3,5-triazine ring in compound **8** is formed under the influence of two factors, *viz*. annelation of the tetrazole ligand and partial delocalization of the second negative charge in the molecule. The geometric parameters of compound **8** differ uniformly from those of the covalent polynitromethyl-1,3,5-triazines having a heteroaromatic ring [3]. The greatest differences are in the increase in the length of the C(3)–N(1) and C(1)–N(1) bonds by 0.04 to 0.08 Å and increase in the N(3)–C(3)–N(1) and C(3)–N(1)–C(1) valence angles by 6-10° with a simultaneous decrease in the N(1)–C(1)–N(2) angle by about 9°.

The geometric parameters for the tetrazole ring in compound **8** are intermediate in value between those of the covalent aminotetrazole [15] and the sodium salt of tetrazole [16], in which the tetrazole ring is ionized. This shows that the annelated tetrazole ring takes part in the delocalization of the second negative charge in compound **8**. Delocalization of the second negative charge in compound **8** can be represented by five resonance structures.



The geometric parameters of the dinitromethyl fragment in compound **8** are extremely close to those for the dinitromethyl groups in salts of the general formula $R(NO_2)_2^-K^+$ where R = CN, Ph, $CONH_2$ etc. [17, 18] in which the negative charge is delocalized across two conjugated nitro groups. The dinitromethyl anion in compound **8** is almost planar, the angle of rotation of the ionized nitro groups from the N(4)–C(4)–N(5) plane not exceeding 10°. The observed, slight nonequivalence of the nitro groups in the anion (small differences in valence angles and bond lengths) is likely due to the nature of the packing of compound **8** in the crystal lattice, as previously noted for $RC(NO_2)_2^-K^+$ salts [18].

Hence we have, for the first time, prepared polynitromethyl derivatives of 1,3,5-triazine containing an annelated tetrazole ring and having the structure of 5-substituted tetrazolo[1,5-*a*]-1,3,5-triazin-7-ones.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer (300 and 75 MHz respectively) using DMSO-d_6 and with HMDS (for ^1H) or TMS (for ^{13}C) as internal standard. IR spectra were recorded on a Specord M-80 spectrometer for KBr tablets (for **4b** as a thin film).

X-ray analysis of **8** was performed on an Enraf-Nonius Kappa CCD diffractometer at 298°K (λ = 0.71073 Å, MoKα, graphite monochromator, $\theta/2\theta$ scanning, θ_{max} = 26°). The basic treatment of the diffraction pattern was carried out using the Denzo program and calculations performed using the MaXus program.

Crystals of compound **8** ($C_4H_8O_5K_2$, M = 396.49, grown from a mixture of MeOH and water) were monoclinic: a = 90.872(1), b = 8.679(1), c = 12.397(1) Å; β = 100.74(1)°; V = 1043.5(2) Å^3; d_{calc} = 2.026 g/cm^3, Z = 4, space group $P2_1/n$. The structure was solved by a direct method using least squares refinement in the anisotropic approximation for non-hydrogen atoms. The final difference factors were R = 0.033, R_w = 0.054 for 1921 independent reflections with $I > 3\sigma(I)$.

Standard Silufol UV-254 plates were used for TLC.

The synthesis of compound **3a** has been reported in [2].

Compound 3b was prepared according to the method reported in [2] using a solution of Et_2NH in chloroform. Yield 80%; mp 138-139°C (decomp.). IR spectrum, ν, cm^{-1}: 3000-2850, 1640-1580, 1450, 1280, 1215, 1175, 1100-1060, 975, 930, 845, 795. ^1H NMR spectrum, δ, ppm: 1.26 (6H, t, CH_3); 3.65 (4H, q, NCH_2). Found, %: C 23.89; H 2.37; N 31.08. $C_9H_{10}N_{10}O_{12}$. Calculated, %: C 24.00; H 2.22; N 31.11.

Compound 5 was prepared by the method reported in [6] using Me_4NOH for neutralization. Yield 45%; mp 178-179°C (decomp.). IR spectrum, ν, cm^{-1}: 2930, 2870,1655, 1640, 1625, 1590-1580, 1480, 1460, 1420, 1335, 1295, 1115, 1080, 950, 910, 860, 840, 810, 800, 780. ^1H NMR spectrum, δ, ppm: 3.37 (12H, s, CH_3). Found, %: C 23.11; H 2.42; N 29.82. $C_9H_{12}N_{10}O_{13}$. Calculated, %: C 23.08; H 2.56; N 29.91.

4-Azido-2-dimethylamino-6-trinitromethyl-1,3,5-triazine (4a). Sodium azide (0.36 g, 5.5 mmol) was added with stirring to a solution of compound **3a** (2.11 g, 5 mmol) in MeCN (20 ml) at 0-5°C and held for

1-1.5 h, the reaction being monitored using TLC. The reaction mixture was poured with stirring into water (100 ml) and the precipitated solid was filtered off, washed with water, and dried in air to give the azidotriazine **4a** (1.41 g, 90%); mp 75-76°C. IR spectrum, ν, cm^{-1}; 2944, 2216, 2152, 1624, 1592, 1504, 1432, 1396, 1372, 1336, 1296, 1280, 1220, 1104, 1048, 984, 856, 792. ^{1}H NMR spectrum, δ, ppm: 3.11 and 3.20 (6H, d, NMe). ^{13}C NMR spectrum, δ, ppm: 169.08 (C–N_3); 163.41(C–$C(NO_2)_3$); 161.21 (C–NMe_2); 36.49 and 36.08 (CH_3). Found, %: C 23.01; H 2.05; N 44.47. $C_6H_6N_{10}O_6$. Calculated, %: C 22.93; H 1.91; N 44.59.

4-Azido-2-diethylamino-6-trinitromethyl-1,3,5-triazine (4b). Sodium azide (0.36 g, 5.5 mmol) was added with stirring to a solution of compound **3b** (2.25 g, 5 mmol) in MeCN (20 ml) at 0-5°C and held for 1-1.5 h, the reaction being monitored by TLC. The reaction mixture was poured with stirring into water (100 ml) and the oily compound formed was extracted with dichloroethane (20 ml). The extract was washed with water, dried over sodium sulphate, the dichloroethane was distilled off in vacuo (30-40 mm Hg), and the residue was evacuated (1-2 mm Hg, 20-25°C). Yield of compound **4b** 1.59 g (93%) as an oily, viscous liquid. IR spectrum, ν, cm^{-1}: 2992, 2944, 2888, 2216, 2144, 1632, 1592, 1504, 1472, 1452, 1400, 1368, 1324, 1296, 1264, 1248, 1224, 1200, 1088, 1056, 984, 848, 796. ^{1}H NMR spectrum, δ, ppm: 1.09 and 1.17 (6H, 2 t, CH_3); 3.52 and 3.65 (4H, 2 q, NCH_2). ^{13}C NMR spectrum, δ, ppm: 169.04 (C–N_3); 162.51 (C–$C(NO_2)_3$); 161.06 (C–$N(CH_3)_2$); 42.55 and 42.33 (NCH_2); 11.86 and 11.68 (CH_3). Found, %: C 28.19; H 3.21; N 40.82. $C_8H_{10}N_{10}O_6$. Calculated, %: C 28.08; H 2.92; N 40.94.

Tetramethylammonium Salt of 5-Trinitromethyltetrazolo[1,5-*a*]-1,3,5-triazin-7-one (7). Sodium azide (0.36 g, 5.5 mmol) was added with stirring to a solution of compound **5** (2.34 g, 5 mmol) in acetone (7.2 ml) and water (0.4 ml) at 20-25°C and held for 2.5-3 h, monitoring the reaction by TLC. The reaction mixture was poured with stirring into water (70 ml), and the precipitated solid was filtered off, washed with water, and dried in air to give **7** (1.17 g, 65%); mp 166°C (decomp.). IR spectrum, ν, cm^{-1}: 3048, 2936, 1720, 1634, 1604, 1598, 1556, 1534, 1490, 1426, 1370, 1332, 1300, 1168, 1118, 1072, 988, 950, 926, 844, 802, 782, 690. ^{1}H NMR spectrum, δ, ppm: 3.37 (12H, s, $(CH_3)_4N^+$). ^{13}C NMR spectrum, δ, ppm: 158.20 (C–$C(NO_2)_3$); 156.02 (N–C=N); 147.65 (C=O); 54.47, 54.42, and 54.37 ($(CH_3)_4N^+$). Found, %: C 26.62; H 3.41; N 39.03. $C_8H_{12}N_{10}O_7$. Calculated, %: C 26.67; H 3.36; N 38.89.

Dipotassium Salt of 5-Dinitromethyltetrazolo[1,5-*a*]-1,3,5-triazin-7-one (8). Potassium iodide (0.83 g, 5 mmol) was added with stirring to a solution of **7** (1.80 g, 6 mmol) in MeOH (15 ml) at 20-25°C, held for 5 min, and the precipitated tetramethylammonium iodide was filtered off. Potassium iodide (2.49 g, 15 mmol) was then added with stirring to the filtrate at 20-25°C and then held under these conditions for 48 h, the reaction being monitored by TLC. The precipitated salt **8** was filtered off, washed on the filter with MeOH (5 ml), and recrystallized from aqueous MeOH (50% by volume). Yield of compound **8** 1.19 g (60%); mp 238°C (decomp.). IR spectrum, ν, cm^{-1}: 1680, 1558, 1512, 1496, 1480, 1446, 1394, 1362, 1292, 1284, 1276, 1208, 1168, 1152, 1140, 1132, 1088, 1008, 940, 832, 800, 776, 764, 748, 732, 696, 680. ^{13}C NMR Spectrum, δ, ppm: 164.44 (C–$C(NO_2)_2^-$); 160.00 (N–C=N); 150.35 (C=O); 134.25 ($C(NO_2)_2$). Found, %: C 15.16; N 35.03. $C_4N_8O_5K_2$. Calculated, %: C 15.09; N 35.22.

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