Synthesis of linear and cyclic compounds containing the 3,4-bis(furazan-3-yl)furoxan fragment

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Some chemical transformations of 3,4-bis(4-aminofurazan-3-yl)furoxan (**1**) and 3,4-bis-(4-nitrofurazan-3-yl)furoxan (**2**) were considered. Compounds **1** and **2** are valuable synthons for the preparation of linear and cyclic compounds containing the 3,4-bis(furazan-3-yl)furoxan fragment. The reaction of compound **2** with a series of N- and O-nucleophiles afforded novel heterocyclic systems: 7-R-7*H*-difurazano[3,4-*b*:3´,4´-*f*]furoxano[3″,4″-*d*]azepine and difurazano[3,4-*b*:3´,4´-*f*]furoxano[3″,4″-*d*]oxepin.

Key words: 3,4-bis(4-aminofurazan-3-yl)furoxan, 3,4-bis(4-nitrofurazan-3-yl)furoxan, 1,2,5-oxadiazole, electrophilic and nucleophilic substitution.

Heterocyclic systems containing the 1,2,5-oxadiazole ring in their structures are well known in the organic chemistry.[1] By analogy with furan, this system was called as "furazan".[2] The synthesis of 1,2,5-oxadiazole *N*-oxide originated from the work dedicated to the preparation of dibromofuroxan by the reaction of bromine with mercuric fulminate.[3] The beginning of the furoxan chemistry should be referred to 1880, when the first general procedures for the synthesis of furoxans were elaborated.[4] In 1908, the term "furoxan" was used for the modern formula of 1,2,5-oxadiazole-2-oxide.[5]

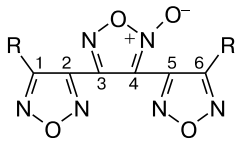
A rapid development of the heterocyclic chemistry being observed in recent decades also concerned this class of compounds, which attract attention due to a variety of chemical transformations and pronounced biological activity. There is a number of articles and reviews dedicated to the synthesis, chemical properties, and potential application of the 1,2,5-oxadiazole derivatives.[6—18] It should be noted that a positive experience in the use of the 3-nitrofurazan fragment for design of novel powerful energetic materials[19] gave rise to the chemistry of the heterocyclic systems under consideration. The aromatic system of the furazan (furoxan) ring not only provides a high energy compound with a certain thermal stability, but also increases its density due to planarity of the structure. In addition, in contrast to the most of other oxygen-containing heterocyclic systems furoxans and furazans contain "active oxygen", which does not bound to carbon or hydrogen atoms and, consequently, can oxidize these atoms to release energy.[20]

Although a number of linear chemical compounds[21] and macrocyclic systems[22,23] containing several 1,2,5-oxadiazole rings, which are linked through bridging groups, have been obtained, the synthesis of compounds consisting of two or more 1,2,5-oxadiazole rings linked directly to each other presents certain difficulties and relatively few examples of such compounds are known. Among the 3,3´-bifurazan derivatives, the best known is 4,4´-dinitro-3,3´-bifurazan (DNBF),[19] which was obtained in 1968 and is a powerful high explosive (HE) substance. Despite the successes achieved in the synthesis of its precursor, *viz.*, 4,4´-diamino-3,3´-difurazan,[24] the application of DNBF is limited due to its high sensitivity to a mechanical impact.[25]

The compounds containing three conjugated 1,2,5-oxadiazole rings in their structures are mainly exemplified by the 3,4-bis(furazan-3-yl)furoxan derivatives. In particular, 3,4-bis(4-aminofurazan-3-yl)furoxan[26] (**1**) is considered as a heat-resistant high explosive[27] and the preparation of its substituted analogs has been described.[28] 3,4-Bis(4-aminofurazan-3-yl)furazan was obtained by the reduction of the furoxan ring of compound **1** with $SnCl_2$.[29] The oxidation of diamine **1** with hydrogen peroxide in the acidic medium afforded the powerful melt-casting high-explosive substance, *viz.*, 3,4-bis(4-nitrofurazan-3-yl)-furoxan (**2**).[30—32] Also, 3,4-bis(4-azidofurazan-3-yl)-furoxan[26,33] (**3**) was proposed for application as energetic compound. It has been shown that a number of 3,4-bis(4-R-furazan-3-yl)furoxans,[34] as well as the furoxan trimers[35] **4a—g** possess a pronounced biological activity being efficient NO donors.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1019—1034, May, 2012.

1066-5285/12/6105-1024



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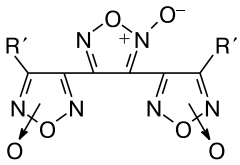


4a—g

R = NH_2 (**1**), NO_2 (**2**), N_3 (**3**)
4: R′ = Ph (**a**), Me (**b**), Pr (**c**), CH_2Cl (**d**), CH_2OH (**e**), EtO (**f**), PhO (**g**)

An efficient synthetic procedure for 3,4-bis(4-R-furazan-3-yl)furoxan derivatives **1** (R = NH_2) and **2** (R = NO_2) has been described,[36] which involves transformation of hydroxymoyl chloride **5** to nitrile oxide **6** followed by dimerization of the latter (Scheme 1). However, the chemical properties of compounds **1** and **2** obtained were studied scarcely. Meanwhile, the synthetic availability of diamine **1** and its dinitro derivative **2** allows one to consider them not only as high energy compounds, but also as intermediates in the synthesis of some novel 3,4-bis(4-R-furazan-3-yl)furoxan derivatives.

It is known that 3-nitro-4-R-furazans (furoxans) are highly reactive in nucleophilic substitution of the nitro group due to a strong electron-withdrawing effect of the 1,2,5-oxadiazole ring.[13,15,16] This reaction is an efficient tool for the preparation of 1,2,5-oxadiazole derivatives that are low-available or non-available by other methods.

The reactions of nitro furazans with O- and N- nucleophiles are the most studied. For example, the nitro group at the furazan ring is replaced with the alkoxy or phenoxy group under the action of excess alkoxide or phenoxide to afford the nucleophilic substitution products in high yields.[37—39] In the water-containing systems, the reactions of 3-nitro-4-R-furazans with weak bases[40,41] result in the replacement of the nitro group with the hydroxy group, while under anhydrous conditions symmetric difurazanyl ethers are produced. In the case where the molecular structure includes two terminal 4-nitrofurazan fragments, this reaction can proceed *via* intramolecular condensation to form macrocyclic ethers.[40] Various furazanyl ethers were also obtained in the reaction of sodium salts of hydroxyfurazans with nitrofurazans.[21]

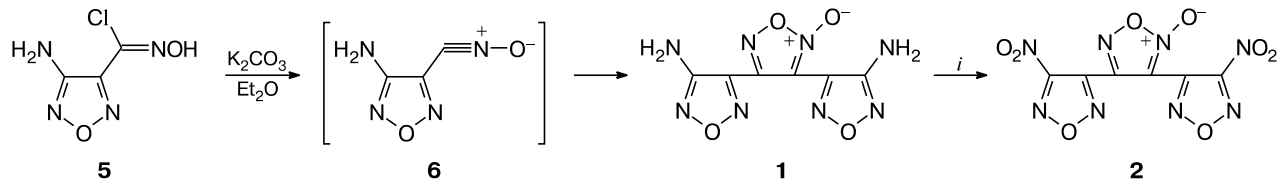
Our studies showed that 3,4-bis(4-nitrofurazan-3-yl)furoxan (**2**) is extremely sensitive to nucleophilic agents. The reaction of compound **2** with aqueous alkaline solutions is accompanied by not only saponification of both nitro groups, but also complete destruction of the molecule; a considerable heat effect and intense gas evolution were observed upon the hydrolysis. A solid product **2** can inflame upon the action of alkali solutions. In non-aqueous solvents, the reaction pathway of the dinitro derivative **2** with bases depends on a solvent. In particular, if the reaction is performed in methanol or ethanol with sodium hydroxide or, taking into account a low stability of compound **2** towards strong bases, with potassium carbonate as a base, the corresponding dialkoxy derivatives **7a—c** are produced in high yields (Scheme 2). Similarly to the reaction of 3-amino-4-nitrofurazan with 2-azidoethanol in aqueous acetonitrile in the presence of NaOH,[42] substitution of the 2-azidoethoxy groups for the nitro groups of compound **2** can occur to form 3,4-bis[4-(2-azidoethoxy)furazan-3-yl]furoxan (**7c**) in a moderate yield. Performing the reaction with potassium carbonate (as a base) in dichloromethane allowed us to increase the yield of compound **7c** to 70%.

The reaction of dinitro derivative **2** with potassium carbonate in anhydrous acetonitrile at 60—70 °C affords the cyclic difurazanyl ether, *viz.*, difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]oxepine (**8**), in 70% yield (see Scheme 2). In the latter case, the reaction is accompanied by evolution of nitrogen oxides whose formation can be explained by the fact that the reaction proceeds through the acetonitrile carbanion-initiated intramolecular rearrangement of the nitro group to nitrite.[41] The nitrite or its decomposition product, *viz*, the hydroxyfurazan anion, undergoes nucleophilic substitution of another nitro group of the substrate molecule to form the cyclic ether (see Scheme 2).

Oxepine **8** has a negative oxygen balance (−54.2%), but, according to the total explosive characteristics (Table 1), can be of a certain practical interest as a component in the formulations of meltcastable explosives and compositions processed by pressing.[43]

The cyclic ether **8** is insoluble in a cold aqueous solution of NaOH and reacts with base solutions at elevated temperatures to result in the oxepine ring opening followed by destruction of the starting compound. Alcoholysis of compound **8** in methanol in the presence of K_2CO_3 is accompanied by the oxepin ring opening and the formation of

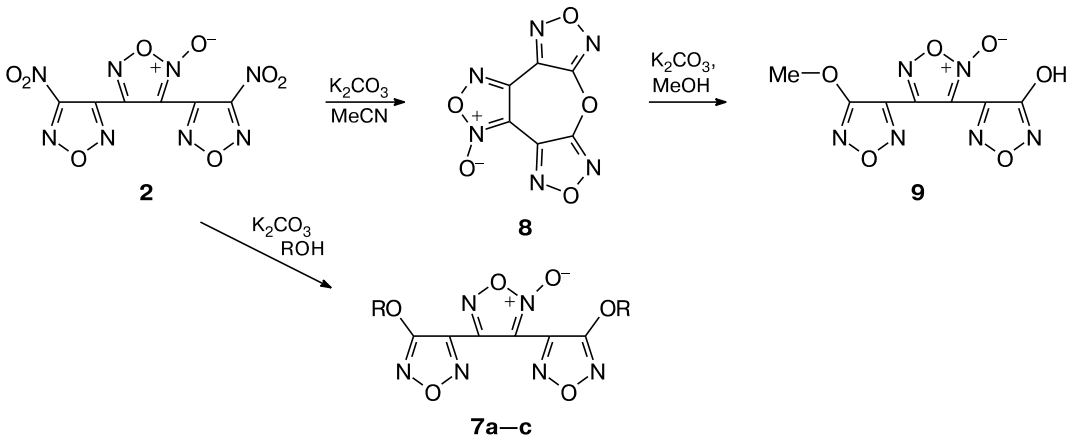
Scheme 1



5 **6** **1** **2**

i. H_2O_2, H_2SO_4, MeCN.

Scheme 2



7: R = Me (**a**), Et (**b**), $CH_2CH_2N_3$ (**c**)

3-(4-hydroxyfurazan-3-yl)-4-(4-methoxyfurazan-3-yl)-furoxan (**9**).

To confirm the structure of the compounds obtained, we used the ^1H and ^{13}C NMR and electron impact mass spectral data (Tables 2 and 3). It should be noted that the lack of hydrogen atoms in the starting compound **2** complicates the signal assignment to particular carbon atoms in the ^{13}C NMR spectra (Table 4). Only the signals of the terminal groups can be interpreted unambiguously: the most upfield chemical shift at ~104 (C(3)) was assigned to the carbon atoms at the N-oxide group of the furoxan ring[11] and two broadened signals with the most downfield chemical shift were assigned to the carbon atoms linked with the nitro group (C(1) and C(6)). A low signal intensity in the latter case is caused by quadrupolar broadening on the ^{14}N nuclei (see Refs 44–48). The analogous phenomenon has been observed in the spectra of 4,4′-dinitro-3,3-bifurazan[45] and other nitrofurazan derivatives[46] and is generally typical of the compounds containing the C—NO_2 fragment (see Ref. 47). Using two-dimensional ^{13}C NMR spectroscopy (see Ref. 36) to establish the bond order of the carbon atoms with different chemical shifts and using computational methods[48], the signals for dinitro derivative **2** were assigned as follows: 160.4 (C(1)); 137.3 (C(2)); 103.8 (C(3)); 143.2 (C(4)); 139.8 (C(5)); 160.4 (C(6))

Table 1. Comparison of the energy characteristics of some 3,4-bis(furazan-3-yl)furoxan derivatives

Compound	*d* /g cm^{-3}	*V* /m s^{-1}	*Q* /J g^{-1}	γ (10 kg, 25 cm)
1[31]	1.795	8100	—	24
2[32]	1.937	9250	6054	94
3[33]	1.743	8525	6162	86—100
8[43]	1.866	8256	6162	12
Octogene	1.903	9100	5799	100
Hexogene	1.816	8800	5315	80

Note: d is a density; *V* is a detonation velocity; *Q* is a heat of explosion; γ is an impact sensitivity.

Table 2. ^1H and ^{13}C NMR spectra of the products obtained upon the reaction of compound **2** with O-nucleophiles

Compound	^{13}C NMR, δ							^1H NMR, δ
	Oxadiazole atoms						Atoms of the side substituents R	
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)		
7a	164.6	134.2	104.2	144.2	136.8	164.4	60.91; 60.79	4.14 (s, 3 H, OCH_3); 4.04 (s, 3 H, OCH_3)
7c	164.34	134.0	103.7	143.7	136.5	163.18	72.27 (CH_2N_3); 49.21 (OCH_2)	4.40 (m, 4 H, OCH_2); 3.55 (m, 4 H, CH_2N_3)
8	160.5	135.5	105.0	144.3	137.7	159.9	—	—
9	164.5	134.7	104.7	144.4	137.0	163.0	60.78	4.14 (s, 3 H, OCH_3)
9 (K salt)	164.9	137.1	107.2	144.6	138.2	168.2	60.31	4.10 (s, 3 H, OCH_3)
10	164.4	137.2	142.9	142.9	137.2	164.4	60.8	4.18 (s, 6 H, 2 OCH_3)

Table 3. Mass and IR spectra of the compounds obtained upon the reaction of compound **2** with O nucleophiles

Compound	Yield (%)	M.p./°C	MS, *m/z*	IR spectrum, ν/cm^{-1}
1	—	169—171	252 $[M]^+$ (85); 222 $[M - NO]^+$ (75); 192 $[M - 2\ NO]^+$ (100); 58 $[NH_2 - C{=}N - O]^+$ (25); 30 $[NO]^+$ (30)	3464; 3421; 3335; 3259 (H—N—H); 1639 (N→O); 1609 (H_2N—C); 1578 (H—N—H, scissor.); 1561 (N=C—N, stretch.); 1540; 1463 (O—N→O); 1417; 1408; 1361 (C—N); 1147; 1010; 991 (N—O—N, symm.); 964, 883, 829 (N→O, stretch.); 696
2	—	109—110	312 $[M]^+$ (17); 282 $[M - NO]^+$ (20); 130 (10); 100 (21); 88 (9); 78 (20); 60 (100); 46 (87); 38 (11)	1640, 1584, 1564, 1516, 1448, 1356, 1316, 1284, 1176, 1000, 964, 912, 880
3	70	51—52	304 $[M^+]$ (7); 274 $[M - NO]^+$ (16); 102 (34); 88 (12); 76 (74); 62 (58); 50 (42); 38 $[C_2N]^+$ (100)	2178, 2150 (N_3), 1645; 1600, 1555, 1425, 1385 (furazan ring), 1630, 1532, 1463, 1230 (furazan ring)
7a	75	52—53	282 $[M]^+$ (6); 252 $[M - NO]^+$ (30); 222 $[M - 2\ NO]^+$ (12); 192 $[M - 3\ NO]^+$ (2); 135 (4); 107 (14); 91 (10); 76 (17); 62 (15); 54 (60); 43 (100)	3005; 2950; 1635; 1600; 1570; 1450; 1420; 1390; 1340; 1220; 1150; 990; 870; 810; 700; 690
7c	70	55—56	—	2540; 2300; 2160; 2120; 2100; 1630; 1610; 1590; 1580; 1550; 1480; 1440; 1435; 1410; 1380; 1350; 1330; 1300; 1260; 1220; 1160; 1060; 1045; 1035; 1030; 1010; 990
8	75	91—92 (Ref. 43: 92—93)	236 $[M]^+$ (15); 62 (7); 38 (6); 32 (26); 30 $[NO]^+$ (100)	1650; 1620; 1560; 1545; 1520; 1475; 1390; 1350; 1220; 1150; 1000; 975; 930; 830; 790; 600; 450
9	60	67	238 $[M - 30]^+$ (11); 211 $[M - NO]^+$ (12); 210 $[M - CO - NO]^+$ (100); 180 (11); 163 (20); 150 (32); 93 (11); 78 (14); 77 (29); 76 (15); 69 (13); 64 (11); 62 (20); 58 (14); 54 (58); 43 (72); 38 (29); 31 $[CH_3O]^+$ (99); 29 (64)	3610; 3590; 3010; 2950; 2920; 2850; 1630; 1610; 1590; 1575; 1560; 1450; 1315; 1215; 1150; 995; 960; 820; 700
10	45	19—21	266 $[M]^+$ (5); 236 $[M - NO]$ (5); 191 (7); 163 (6); 151 (5); 135 (6); 111 (44); 83 (100); 72 (13); 67 (13); 59 (10); 54 (74); 43 $[HCNO]^+$ (91)	3000 (ν_{as} CH_3); 2930 (ν_s CH_3); 1600; 1560; 1450 (δ_{as} CH_3); 1380 (δ_s CH_3); 1350; 1310; 1170 (ν_{as} C—O—C); 1050 (ν_s C—O—C); 1020; 990; 970; 900; 860

(see Table 4), which allowed interpretation of the ^{13}C NMR spectra of the 3,4-bis(3-R-furazan-3-yl)furoxans derivatives obtained (see Table 2).

The oxepine ring opening in compound **8** with the methoxide anion can result in the formation of two structures of type **9** differing in the position of the methoxy group relative to the furoxan ring. The conclusion in favor of the isomer proposed can be made on the basis of comparison of the ^{13}C NMR spectra of compound **9**, its potassium salt, and 3,4-bis(4-methoxyfurazan-3-yl)furazan (**10**), the latter being obtained by reduction of the furoxan ring of the dimethoxy derivative **7a** with stannous chloride under the conditions analogous to those used for the reduction of furoxan **1** (see Ref. 29). In addition, according to the rule of Mallory and Cammarata,[49] due to the shielding effect of the N-oxide group, the signals of the substituents adjacent to this group are in the more upfield region. Since in compound **9**, there remains the ^{13}C NMRmethoxy group with the chemical shift in the more downfield re-

Table 4. Signal assignment in the ^{13}C NMR spectrum of 3,4-bis-(4-nitrofurazan-3-yl)furoxan (**2**)

Atom	δ				
	Calculation[48]	Experiment			
C(1)	156.2	—[48]	—[31]	160.4[36]	160.4*
C(2)	137.9	140.4[48]	—[31]	137.3[36]	137.6*
C(3)	103.6	104.4[48]	104.4[31]	103.8[36]	103.9*
C(4)	146.1	138.1[48]	138.1[31]	143.2[36]	143.2*
C(5)	140.9	—[48]	—[31]	139.8[36]	139.9*
C(6)	156.1	143.7[48]	143.7[31]	160.4[36]	160.0*

* Our data.

gion, one can assume that this group is placed on the side opposite to the N-oxide atom.

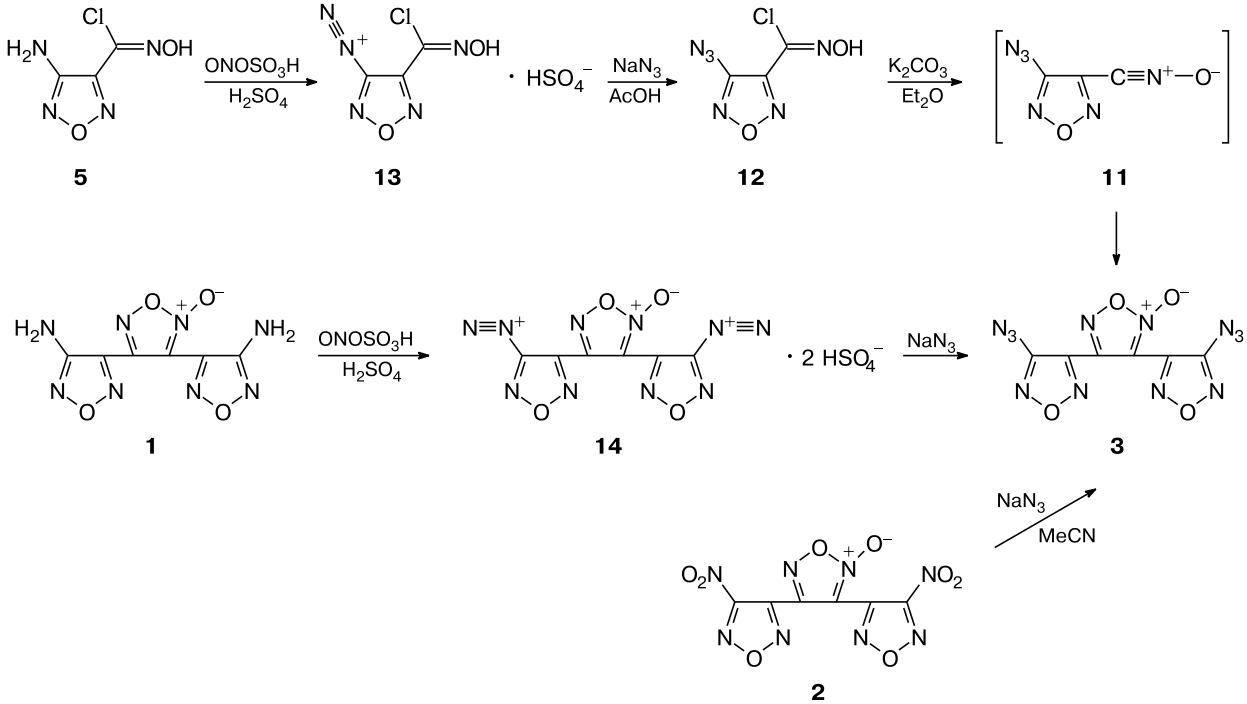
The mass spectrum of the dimethoxy derivative **7a** contains a low-intensity peak of the molecular ion $C_8H_6N_6O_6$, 282 $[M]^+$ (6). The mode of fragmentation is typical of 1,2,5-oxadiazoles[50], *i.e.*, successive elimination of NO molecules is observed: 252 $[M - NO]^+$ (30); 222 $[M - 2\ NO]^+$ (12); 192 $[M - 3\ NO]^+$ (2). The magnetic nonequivalence of the hydrogen and carbon nuclei of two methoxy groups in the ^1H and ^{13}C NMR spectra of compound **7a** is explained by asymmetry of the furoxan ring and can be indirect evidence of the substitution of both nitro groups for the methoxy groups in the starting compound **2** (in the case of the monosubsituted product, only one signal in the ^1H NMR spectrum would correspond to the methoxy group). The data from thin-layer chromatorgraphy support the individuality of compound **7a** obtained.

The mass spectrum of the cyclic ether **8** contains a low-intensity peak of the molecular ion $C_6N_6O_5$, 236 $[M]^+$ (15) and the peak of NO has the maximum intensity. The mass spectrum of compound **9** contains no peak of the molecular ion; the peak at *m/z* 238 (11) corresponds to elimination of NO from the molecule of the starting compound and the maximum intensities were observed for the peaks of the ions at *m/z* 211 $[M - CO - NO]^+$ and 31 $[CH_3O]^+$.

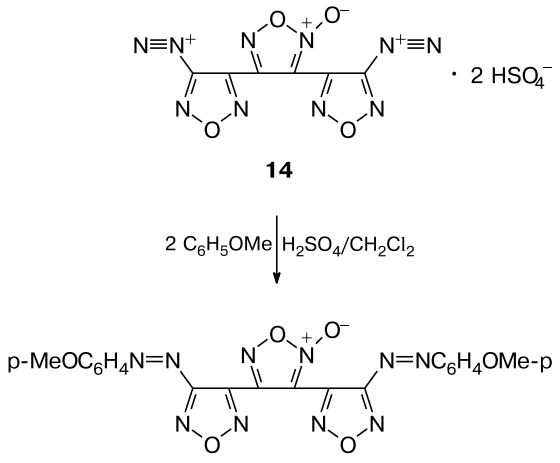
It is known that the nitro group of 3-nitro-4R-furazans can be replaced by the azido one in a high yield under the action of sodium azide in acetonitrile.[51] To perform successfully the analogous reaction with the dinitro derivative **2**, the selection of solvent is important: in the anion-solvating aprotic solvent (DMF), NaN_3 behaves like a base and single-electron reducing agent and the reaction proceeds to evolve nitrogen oxides and affords mainly the cyclic ether **8**; in less basic acetonitrile and acetone, the reaction proceeds in favor of nucleophilic substitution of the nitro group for azide to result in the high-yield formation of 3,4-bis(4-azidofurazan-3-yl)furoxan (**3**). The alternative procedures proposed earlier[26,33] for the synthesis of diazide **3** based on dimerization of 4-azidofurazan-3-carbonitrile oxide (**11**) generated *in situ* from oxime chloride **12** are less productive and practically less convenient, since the intermediate preparation of the corresponding diazonium salt **13** is required for introduction of the azido group to the molecule (Scheme 3).

Diazide **3** can also be synthesized by diazotization of diamine **1**. It should be taken into account that diazotization of the weakly basic amine groups of amino furazans proceeds generally in the strong acid medium[52] (sulfuric acid or its mixtures with orthophosphoric or acetic acid) using nitrososulfuric acid. Concentrated sulfuric acid was found to be the most suitable solvent for diazotization of 3,4-bis(4-aminofurazan-3-yl)furoxan (**1**). The treatment of the obtained solution of bis-diazonium salt **14** with an aqueous solution of sodium azide or anisole affords the diazido derivative **3** (Scheme 3) or the azocoupling product **15** (Scheme 4), respectively.

Scheme 3



Scheme 4

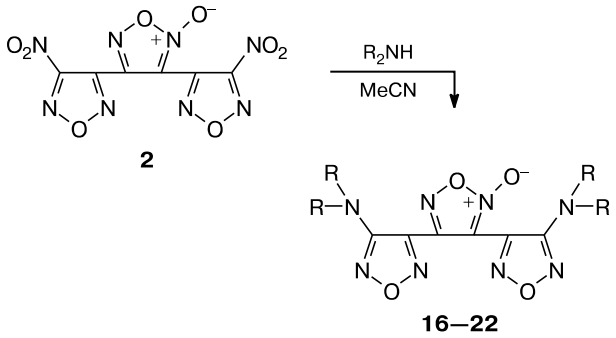


3,4-Bis(4-azidofurazan-3-yl)furoxan (**3**) possesses a high sensitivity to mechanical impact, which is typical of azides (see Table 1). Introduction of the azido groups results in a dramatic decrease in the packing densities of the molecules and, consequently, a decrease in the density of the single crystal and the detonation velocity. Nevertheless, due to a low melting point (51—52 °C) and high thermal stability, the compound can be of certain interest for formulation of fusible explosives.

Nitrofurazans react with aqueous ammonia to afford both the hydrolysis and ammonolysis products of the nitro group.[37] To avoid hydrolysis, this reaction is performed in anhydrous solutions of ammonia in organic solvents at low temperature. In the same manner, the nitro group can be replaced by other highly basic amines under mild conditions.[28] The reaction with arylamines is complicated by side formation of azo dyes due to diazotization of the starting amine with the produced nitrous acid followed by azo coupling with the excess of the amine.

The reaction of compound **2** with ammonia and highly basic amines proceeds fast even at low temperatures (0—10 °C) and is accompanied by a considerable exothermic effect. Depending on the structure of the amine used, we isolated two different types of products of substitution of the nitro group for other nucleophiles.[53] When performing the reaction with the excess of an amine (the stoichiometry requires using at least 4 moles of the amine per 1 mole of the starting compound), the products of substitution of nitro groups for both amino groups are produced (Scheme 5). In the lack of the amine, disubstituted amino derivatives are also produced, but the reaction is accompanied by side processes and we failed to isolate the monosubstitution products from the resulted mixture. Given that substitution of strong electron withdrawing nitro groups for mesomeric electron releasing group occurs in the course of the reaction, substitution of two nitro group for amine implies a considerable electron withdrawing effect of three conjugated 1,2,5-oxadiazole rings (for example, if only one nitro group in the 3,4-dinitrofurazan molecule is readily replaced by an amine, the reaction of 4,4′-dinitro-3,3′-bifurazan is difficult to stop at the step of monosubstitution[28]). It is convenient to perform the reaction of the dinitro derivative **2** with highly basic amines in acetonitrile; however, other organic solvents nonreacting with the starting amines can be used. It is known that many primary amines are available as salts. In this case, the pure base can be isolated from the reaction mixture by addition of the corresponding amount of sodium bicarbonate, which neutralizes the acid part of the ammonium salt. The yields of the reaction products are usually 70—85%.

Scheme 5



NR_2 = morpholino (**16**); NEt_2 (**17**); piperidino (**18**); 4-methylpiperidino (**19**); 4-methylpiperazin-1-yl (**20**); $N(Me)CH_2CH_2OH$ (**21**); $R = NHBu^t$ (**22**)

The NMR spectra of 3,4-bis(3-R-furazan-4-yl)furoxans **16**—**21** and compound **22** are given in Table 5.

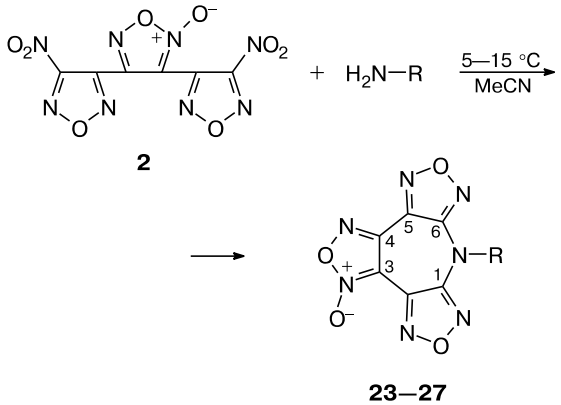
The nonequivalence of the carbon atoms of the furazan rings, as well as of the substituents in the NMR spectra of compounds **16**—**22** is caused by the molecular asymmetry due to the exocyclic NO group of the furoxan fragment. The chemical shifts of the signals in the ^{13}C NMR spectra of compounds **3** and **16**—**22** are close to those in 3,4-bis(4-aminofurazan-3-yl)furoxan (**1**). The mass spectra of the synthesized compounds (Table 6) contain low-intensity peaks of the ions whose mode of fragmentation is similar to those of the close analogs.[28]

The reaction of compound **2** with highly basic primary amines or ammonia proceeds readily even at low temperatures. But, contrary to the formation of disubstituted amino derivatives of 3,4-bis(furazan-3-yl)furoxan as in the case of the reaction with secondary amines, the reaction with ammonia and primary amines proceeds unusually, *i.e.*, the replacement of both nitro groups in one molecule takes place with one molecule of the starting primary amine resulting in the formation of a novel seven-membered heterocyclic structure, *viz.*, 7-R-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (**23**—**27**) (Scheme 6).

Table 5. ^{1}H and ^{13}C NMR spectra of 3,4-bis(4-RR´N-furazan-3-yl)furoxans

Compound	^{13}C NMR, δ							^{1}H NMR, δ
	Oxadiazole atoms						Atoms of the side substituents R	
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)		
1 (R = NH_2)	156.3	133.5	104.6	147.0	136.3	155.3	—	6.37 (s, 2 H, NH_2); 6.47 (s, 2 H, NH_2)
3 (R = N_3)	154.6	136.0	103.4	144.5	138.8	153.9	—	—
15 (R = N=NC_6H_4OMe)	165.98	135.8	105.9	145.4	139.1	165.87	162.53; 162.24; 146.4; 146.3; 127.03; 127.02; 115.8; 115.6; 56.65, 58.58 (2 OCH_3)	7.82; 7.80; 7.75; 7.73; 7.16; 7.14; 7.01; 6.98 (8 s, 1 H each, 2 C_6H_4); 3.95, 3.89 (2 s, 3 H each, 2 OCH_3)
16 (R_2N = morpholino)	159.6	134.3	105.5	145.1	138.0	159.5	65.61, 65.59; 49.41, 48.81	3.61, 3.53 (m, 8 H, 2 $O(CH_2)_2$); 3.23(m, 4 H, $C_1N(CH_2)_2$); 3.11 (m, 4 H, $C_6N(CH_2)_2$)
17 (R_2N = NEt_2)	157.7	136.5	107.4	146.7	137.4	157.6	44.76; 41.70; 12.48; 11.36	3.28 (q, 4 H, $C(1)N(CH_2)_2$, J = 6.5 Hz); 2.85 (q, 4 H, $C(6)N(CH_2)_2$, J = 6.5 Hz); 1.17—1.06 (q, 12 H, 2 CH_3)
18 (R_2N = pyperidino)	159.9	134.5	105.4	145.2	138.1	159.8	50.40; 49.90; 24.80; 24.74; 23.31	3.17 (m, 4 H, $C(1)N(CH_2)_2$); 3.04 (m, 4 H, $C(6)N(CH_2)_2$); 1.52 (m, 8 H); 1.45 (m, 4 H)
19 (R_2N = 4-methyl-pyperidino)	159.8	134.5	105.4	145.1	138.1	159.7	50.35; 49.26; 33.01; 29.92; 21.70	3.2, 3.05 (m, 8 H, 4 CH_2CH_2); 2.5 (m, 2 H, 2 CH); 2.3 (m,6 H, 2 CH_3)
20 (R_2N = -methyl-pyperazin-1-yl)	159.58	134.5	105.4	145.0	138.0	159.54	53.82; 53.75; 49.19; 48.76; 46.06	3.16 (m, 8 H, 4 CH_2); 3.10 (m, 3 H) and 2.35 (m, 3 H) (3 CH_2); 2.28, 2.25, 2.21 (m, overlap., 8 H, CH_2, 2 CH_3)
21 (R_2N = $NMeCH_2CH_2OH$)	164.8	136.3	106.3	144.5	138.0	159.8	77.21; 53.00; 38.17	4.58 (t, 4 H, CH_2, J = 5.5 Hz); 3.63 (t, 4 H, CH_2, J = 5.5 Hz); 3.10 (s, 6 H, 2 CH_3)
22 (R = $NHBu^t$)	159.9	135.4	105.0	144.3	137.7	159.8	51.18, 50.31; 27.82, 27.54	7.50 (s, 1 H, NH); 1.30 (s, 9 H, $C(CH_3)_3$); 1.29 (s, 9 H, $C(CH_3)_3$)

Scheme 6



23—27

R = H (**23**), Me (**24**), CH_2Ph (**25**), CH_2CH_2OH (**26**), *cyclo*-C_7H_{13} (**27**)

It should be noted that, in a series of 1,2,5-oxadiazole derivatives annulated with the seven-membered nitrogen-containing heterocycles, diazepine structures obtained by the reaciton of 3,4-diaminofurazan with β-dicarbonyl compounds are mainly studied.[54,55] Among possible four modes of 1,2,5-oxadiazole and azepine rings annulation, only few furazano[3,4-*c*]azepine derivatives have been obtained to date.[14,56]

The high yield of compounds **23**—**27**, as well as the absence of linear diamino derivatives among the reaction products can be explained by the certain preorganized nature of dinitro compound **2**, which favors the formation of cyclic products. For example, it was established by X-ray diffraction study that, in the crystalline state, the planes of two furazan rings in the molecule of compound **2** are turned to each other.[30,57] It seems that such spatial arrangement

Table 6. Mass and IR spectra of 3,4-bis(4-RR´N-furazan-3-yl)furoxans

Compound	Yield (%)	M.p./°C	MS, *m/z*	IR, ν/cm^{-1}
15	40	137	490 $[M]^+$ (0.3); 147 (11); 135 $[CH_3OC_6H_4N{=}N]^+$ (26); 107 $[CH_3OC_6H_4]^+$ (100); 92 $[C_6H_4O]^+$ (42); 78 (16); 77 (70); 64 (19); 30 $[NO]^+$ (22)	3100 (Ar—H); 2975 (as, CH_3); 2940 (s, CH_3); 1660; 1510; 1420; 1370; 1330; 1270; 1230; 1150; 1000; 990; 860; 560
16	70	119	392 $[M]^+$ (5); 375 $[M - OH]^+$ (22); 362 $[M - NO]^+$ (2); 328 (6); 86 $[O(CH_2CH_2)_2N]^+$ (39); 69 [86—OH] (33); 56 C_2H_2NO (92); 45 (100)	2980; 2960; 2860; 1625; 1590; 1545; 1530; 1470; 1450; 1370; 1260; 1210; 1160; 1120; 1070; 1020; 990; 965; 913; 890; 807; 720; 550
17	63	122	364 $[M]^+$ (0.1); 234 (6); 167 (84); 83 (7); 73 (8); 72 (5); 69 (7); 58 (39); 56 (31); 55 (16); 44 (7); 43 (8); 42 (17); 41 (7); 30 [NO] (100); 29 $[C_2H_5]^+$ (81)	2985; 2940; 2880; 2860; 2470; 2405; 1625; 1570; 1540; 1470; 1460; 1385; 1360; 1290; 1225; 1200; 1045; 990; 960; 860; 810
18	70	94	388 $[M]^+$ (0.2); 372 $[M - O]^+$ (2); 371 $[M - OH]^+$ (12); 177 (13); 125 (10); 109 (26); 84 $[(CH_2)_5N]^+$ (12); 83 (9); 82 (12); 69(34); 68 (12); 67 (12); 6 (12); 55 (85); 54 (15); 53 (10); 43 $[CH_2NH{=}CH_2]^+$ (11); 42 $[CH_2NH{=}CH_2]^+$ (60); 41 (100); 39 (17); 30 (27); 29 (33)	2940 (as, CH_2); 2860 (s, CH_2); 1630; 1590; 1445; 1385; 1280; 1260; 1220; 1160; 1140; 1110; 1010; 990; 965; 900; 810; 715; 600
20	63	117	418 $[M]^+$ (3); 124 (6); 123 (51); 99 (8); 98 (6); 97 (17); 86 (11); 83 (6); 72 (5); 71 (24); 70 (29); 58 (14); 57 (27); 56 (34); 55 (6); 54 (8); 44 (25); 43 $[CH_2NH{=}CH_2]^+$ (100); 42 $[CH_2NH{=}CH_2]^+$ (78); 41 (7); 40 (5); 32 (59); 30 $[NO]^+$ (16); 29 (8)	2970; 2940; 2852; 2800; 2770; 1620; 1540; 1530; 1450; 1375; 1300; 1290; 1280; 1210; 1145; 1080; 1005; 995; 970;910; 815; 785
21	60	120	293 [M – 75] (24); $[M - CH_3NCH_2CH_2OH - H]$; 205 (24); 137 (7); 130 (6); 69 (20); 68 (14); 67 (6); 57 (13); 55 (7); 44 (11); 43 (26); 42 (74); 30 (100)	2980; 2940; 2920; 1630; 1590; 1575; 1550; 1535; 1475; 1450; 1440; 1410; 1325; 1285; 1190; 1155; 1140; 1030; 995; 980; 965; 880; 805; 600; 535
22	64	*	364 $[M]^+$ (0.5); 349 $[M - CH_3]^+$ (1.5); 334 $[M - NO]^+$ (2.5); 309 $[M - C_4H_7]^+$ (1); 293 $[M - NO - CH_2{=}CH - CH_2]^+$ (18); 167 (23); 83 (28); 58 (99); 56 $[C_4H_8]^+$ (99); 41 (100); 40 (100)	3410; 3280; 2980; 2940; 2880; 1650; 1620; 1560; 1540; 1470; 1300; 1150; 1090; 1050; 1030; 990; 820; 780; 715

* Liquid.

of furazan rings in compound **2** is also preferred in solution. Consequently, the sterically favorable arragnement of substituents in the furazan rings favors the fact that, after the replacement of the first amino group with the amine, despite a dramatic decrease in its basicity, this substituent is still capable of nucleophilic substitution of the second nitro group to form the cyclic product. The importance of the steric factor is confirmed by the formation of the only linear diamino derivative **22** analogous to compounds **16**—**21** in the reaction of compound **2** with the sterically hindered *tert*-butylamine.

The order of reagent mixing upon the preparation of azepines **23**—**27** has no noticeable effect on the results of the reaction. Nevertheless, taking into account the potential explosion risk of dinitro derivative **2** and a considerable exothermal effect of the reaction, the addition of a solution of **2** to a solution of the corresponding amine taken in excess seems to be preferable from the viewpoint of safe conducting the reaction. Variation of the reaction conditions and the use of other solvents instead of acetonitrile, such as dichloromethane or dioxane, influence weakly the yield of cyclic products and do not result in the formation of linear diaminosubstituted 3,4-bis(4-R-furazan-3-yl)-furoxan derivatives. In any case, the replacement of nitro groups proceeds fast and the rate of addition of reactants is limited by the possibilities of cooling the reaction mass.

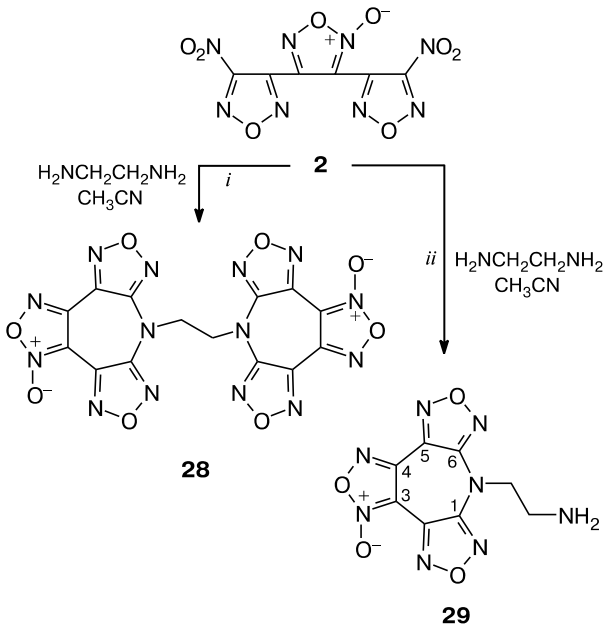
In contrast to the examples considered above, the reaction of compound **2** with ethylenediamine, depending

on the reaction conditions, can afford two different products (Scheme 7). If ethylenediamine is added slowly to a solution of compound **2** in acetonitrile, both amino groups are involved in the reaction which results in 1,2-bis-[7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepin-7-yl]ethane (**28**). Upon the reverse order of reagents mixing and addition of excess ethylenediamine, only one amino group of the substrate is involved in the reaction to furnish 7-(2-ethylamino)-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano-[3″,4″-*d*]azepine (**29**). Note that while product **28** is a thermally stable compound melting at 318 °C without decomposition upon heating in a capillary tube, amine **29** decomposes violently at 160 °C without melting. Such behavior of the latter is likely caused by the high-temperature reaction of the highly basic free amino group with the furoxan rings.

The formation of cyclic products was proved by instrumental analysis methods (Tables 7 and 8) and confirmed by the chemical properties of the compounds obtained.

The ^{1}H NMR spectra of compounds **24**—**28** contain no signals, which correspond to the NH group in the case of linear nucleophilic substitution product. In the ^{1}H NMR spectrum of compound **23** (R = H) obtained by the reaction of compound **2** with ammonia, the downfield shift of the proton signal for the N—H group (δ = 12.4) compared to the signals for the NH_2 groups of the linear diamino derivative **1** (δ = 6.37 and 6.47[58]) suggests the presence of strong electron-withdrawing substituents at the amino group under consideration. The IR spectrum of compound **23** slightly differ from that of compound **1**, the greatest differences are observed in the high-frequency region (the region of characteristic stretching frequencies of

Scheme 7



i. Lack of EDA; *ii*. Excess of EDA.

Table 7. ^{1}H and ^{13}C NMR spectra of the 7-R-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine derivatives **23**—**29**

Compound	R	^{13}C NMR, δ							^{1}H NMR, δ
		Oxadiazole atoms						Atoms of the side substituents R	
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)		
23	H	152.4	135.8	106.4	145.6	138.1	152.0	—	12.4 (s, 1 H, NH)
24	CH_3	154.4	135.4	106.6	145.3	137.5	154.1	38.47	3.72 (s, 3 H, CH_3)
25	CH_2Ph	154.0	135.6	106.2	145.6	137.7	153.7	Ar: 134.4 (C(1′)); 128.9 (C(3′)); 128.2 (C(4′)); 127.6 (C(2′)); 55.16 (CH_2)	5.41 (s, CH_2); 7.53—7.51, 7.38—7.27 (m, 2 H, m, 3 H, Ar)
26	CH_2CH_2OH	154.0	135.4	106.0	145.3	137.6	153.6	56.0; 53.8	4.29 (t, 2 H, J = 6 Hz); 3.79 (t, 2 H, J = 6 Hz); 5.0—4.7 (s, 1 H, OH)
27	*cyclo*-C_7H_{13}	153.46	136.05	105.91	145.3	138.2	153.03	66.82; 30.17; 27.74; 25.79	4.62 (m, 1 H, C—H); 2.38 (m, 2 H, CH_2); 1.87 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 1.69—1.59 (m, 6 H, $CH_2CH_2CH_2$)
28	—CH_2—CH_2—	153.95	135.4	105.7	145.0	137.6	153.55	47.20	4.65 (s, 4 H, CH_2CH_2)
29	$CH_2CH_2NH_2$	154.1	135.4	106.0	145.4	137.6	153.7	54.79; 37.60	4.22 (t, 2 H, CH_2-Het, J = 7 Hz); 3.00 (t, 2 H, $C\underline{H}_2$—NH_2, J = 7 Hz); 2.5—1.0 (NH_2 + D_2O)

Table 8. Mass and IR spectra of the 7-R-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine derivatives (**23**—**29**, **32**)

Compound	Yield (%)	M.p./°C	MS, *m/z*	IR spectrum, ν/cm^{-1}
23	68	226	235 $[M]^+$ (100); 205 $[M - NO]^+$ (26); 175 $[M - 2\,NO]^+$ (30); 145 $[M - NO]^+$ (11); 53 $[C_2HN_2]^+$ (63)	3570 (as, NH); 3500 (s, NH); 3000, 2850, 2760 (assoc. NH); 1620 (skeletal vibrations of furazan + planar C=N→O of furoxan); 1600, 1570, 1530 (furoxan); 1500; 1470; 1360; 1150; 1000; 970; 830
24	72	198	249 $[M]^+$ (92); 233 $[M - O]^+$ (1); 219 $[M - NO]^+$ (15); 189 $[M - 2\,NO]^+$ (100); 159 $[M - 3\,NO]^+$ (16); 105 (18); 83 (33); 67 (44)	3400, 1650 (furoxan), 1610, 1600, 1560, 1540, 1350, 1130, 1050, 990, 970, 850
25	78	174	325 $[M]^+$ (2.7); 309 $[M - O]^+$ (1); 91 $[PhCH_2]^+$ (100), 65 (16); 39 (56); 30 $[NO]^+$ (23)	3065; 3032; 2920; 1650; 1310; 1590; 1560; 1530; 1480; 1455; 1432; 1390; 1360;1230; 1160; 1020; 990; 900; 830
26	60	193	279 $[M]^+$ (19); 249 $[M - NO]^+$ (6.5); 248 $[M - CH_2 - OH]^+$ (13); 236 $[M - CH_2{=}CH - O]^+$ (65) or $[M - HNCO]^+$; 205 $[236 - NO - H]^+$ (8); 189 $[M - 3\,NO]^+$ (24); 176 $[236 - 2\,NO]^+$ (15); 45 $[CH_2CH_2OH]^+$ (100)	3550 (OH); 2980 ($\nu_{as}CH_2$); 2920 (ν_sCH_2); 1640; 1610; 1590; 1570; 1520; 1480; 1350; 1640; 1610; 1590; 1570; 1520; 1480; 1350; 1200; 1160; 1070 (ν_{as} C—C—O); 1020; 980; 970; 900; 840
27	60	219	331 $[M]^+$ (1.4); 98 $[C_7H_{14}]^+$ (82); 97 $[C_7H_{13}]^+$ (88); 96 (24); 81 (7); 69 (14); 67 (13); 56 (8); 55 (100); 54 (8); 53 (13); 43 (16); 42 (8); 41 (69); 40 (5); 39 (27); 30 (91); 29 (30)	2930; 2855; 1650; 1620; 1585; 1555; 1525; 1475; 1390; 1350; 1330; 1230; 1160; 1010; 990; 970; 890; 850; 825; 790; 720; 680; 590; 545
28	70	318	496 $[M]^+$ (4); 436 $[M - 2\,NO]^+$ (1); 262 (58); 248 $[M/2]^+$ (100); 232 $[M/2 - O]^+$ (20); 201 (88); 188 $[M/2 - 2\,NO]^+$ (90)	2980 ($\nu_{as}CH_2$); 2920 (ν_sCH_2); 1640; 1610; 1600; 1560; 1520; 1480;1360; 1210; 1160; 1020; 990; 970; 900; 840
29	70	160 (dec.)	278 $[M]^+$ (7); 248 $[M - NO]^+$ (2.5); 232 $[M - NO - O]^+$ (6); 188 $[M - 3\,NO]^+$ (11); 42 $[C_2H_4N]^+$ (100)	3370 ($\nu_{as}NH_2$); 3200 ($\nu_{as}NH_2$); 1650; 1610; 1600; 1550; 1520; 1480; 1440; 1360; 1200; 1140;1010; 980; 960; 900; 880; 830; 800; 720; 590

the N—H groups). In general, the comparision of the IR spectra of the annulated systems **23**—**29** with those of the linear products **16**—**21** shows a certain complication of the spectrum in the wavelength range of 1650—1500 cm^{-1} due to the emergence of a new ring.

The absence of signal splitting of the hydrogen atoms of the methyl group in the NMR spectra of compound **24** agrees with the cyclic form of the product; in the case of the formation of the linear substitution product of two nitro groups for methylamino groups, the chemical shifts of the signals for two methyl substituents must differ slightly in view of nonsymmetry of the furoxan ring being part of the molecule. The analogous pattern is observed in the NMR spectra of the other cyclic products.

It is interesting to note that despite the closeness between the chemical shifts of the corresponding carbon atoms of the heterocyclic system and its acyclic analogs (see Table 6), the signals for the C(1) and C(6) carbon atoms in the ^{13}C NMR spectra of products **23**—**29** are slightly shifted downfield (δ 3—6) compared to the acyclic analogs, which is likely due to involvement of lone pair electrons at the nitrogen atom of the azepine ring in the π-system of the molecule to result in the electron density redistribution.

The intensity of molecular ion peaks in the mass spectra of products **23**—**29** is usually higher than in the case of the linear diamino derivatives **17**—**22**. The mass numbers of molecular ion peaks correspond to the cyclic structure proposed. The relative intensities of the ion peaks with *m/z* [M + 1]/[M] and [M + 2]/[M] do not contradict the intensities calculated according to the natural content of the N and O isotopes in the structures proposed. The mode of molecular fragmentation of the compounds synthesized under the electron impact is typical of that for furazan and furoxan derivatives.[59]

Compared to the linear diamino derivatives, which are very soluble in the most of organic solvents (except CCl_4 and petroleum ether) and characterized by relatively low

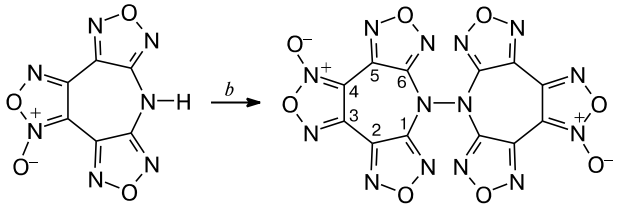
melting points, compounds **23**—**29** having annulated structure melt at a higher temperature and much less soluble in organic solvents.

Chemical properties of the synthesized annulated heterocyclic systems confirm their structures. In contrast to 3,4-bis(4-aminofurazan-3-yl)furoxan (**1**), which is readily acylated at the terminal amino groups to form mono-[34], di- (**30**), and even triacetyl (**31**) derivatives (see Experimental), compoudns **23**—**25**, **27**, and **28** were found to be indifferent toward acetic anhydride. In the case of compound **23** (R = H), the result can be explained by a decrease in the nucleophilicity of the amino group of the seven-membered ring due to a strong electron-withdrawing effect of two adjacent furazan substituents and, in other cases, suggests the absence of free N—H groups in the molecule and confirms indirectly the cyclic structure proposed, since in the case of the preparation of the linear diamino substituted product, the N—H groups must be acylated easily by analogy to the properties of compound **1**. In addition, compound **23** undergoes alkylation of the imino group with methyl iodide, dimethyl sulfate, and benzyl chloride to form the corresponding 7-alkyl substituted derivatives, which, according to IR spectra, are identical to compounds **24** and **25** obtained by the reaction of **1** with methylamine and benzylamine, respectively. Alkylation proceeds slowly, which is likely due to a steric effect of the adjacent furazan rings.

Inertness of compounds **24**, **27**, and **28** toward different nitrating mixtures (HNO_3, HNO_3/H_2SO_4, and HNO_3/Ac_2O) also evidences the absence of the free N—H group in the compound obtained.

The study of the behavior of azepine **23** in different nitrating systems showed an unusual result. The compound was inert toward concentrated nitric acid and a mixture of acetyc anhydride and ammonium nitrate (a); however, in such systems as HNO_3/Ac_2O, HNO_3/H_2SO_4, HNO_3/oleum, and $HNO_3/(CF_3CO)_2O$ (b), oxidative "dimerization" of the starting compound to form a new N(7)—N(7′) bond between two substrate molecules and precipitation of diazepinyl **32** was observed instead of the expected N-nitration (Scheme 8).

Scheme 8



23 **32**

In contrast to the starting azepine **23**, the resulting dimer **32** is insoluble in aqueous alkali; hardly soluble in nitric, trifluoroacetic, acetic acids, ethanol, and chlorobenzene even when heated; and readily soluble in diethyl carbonate and diethylformamide. Heating of solutions of the dimer in DMF above 100 °C is accompanied by N—N bond cleavage and the formation of the starting compound **23**. To a large extent, such unusual behavior of **23** in different nitrating systems is similar to the features of nitration of 4,8-dihydrofurazano[3,4-*b*,*e*]pyrazine (BFP)[17], as well as to those of oxidation of its 4,8-diamino derivative.[60] The failed attempts to prepare the *N*-nitro BFP derivative[61] are associated with the formation of a stable biradical stabilized due to the negative mesomeric effect of two furazan rings and the formation of the 14-electron aromatic system.[62] Apparently, dimerization of azepine **23** proceeds also through the intermediate formation of a radical stabilized by the system of three 1,2,5-oxadiazole rings.

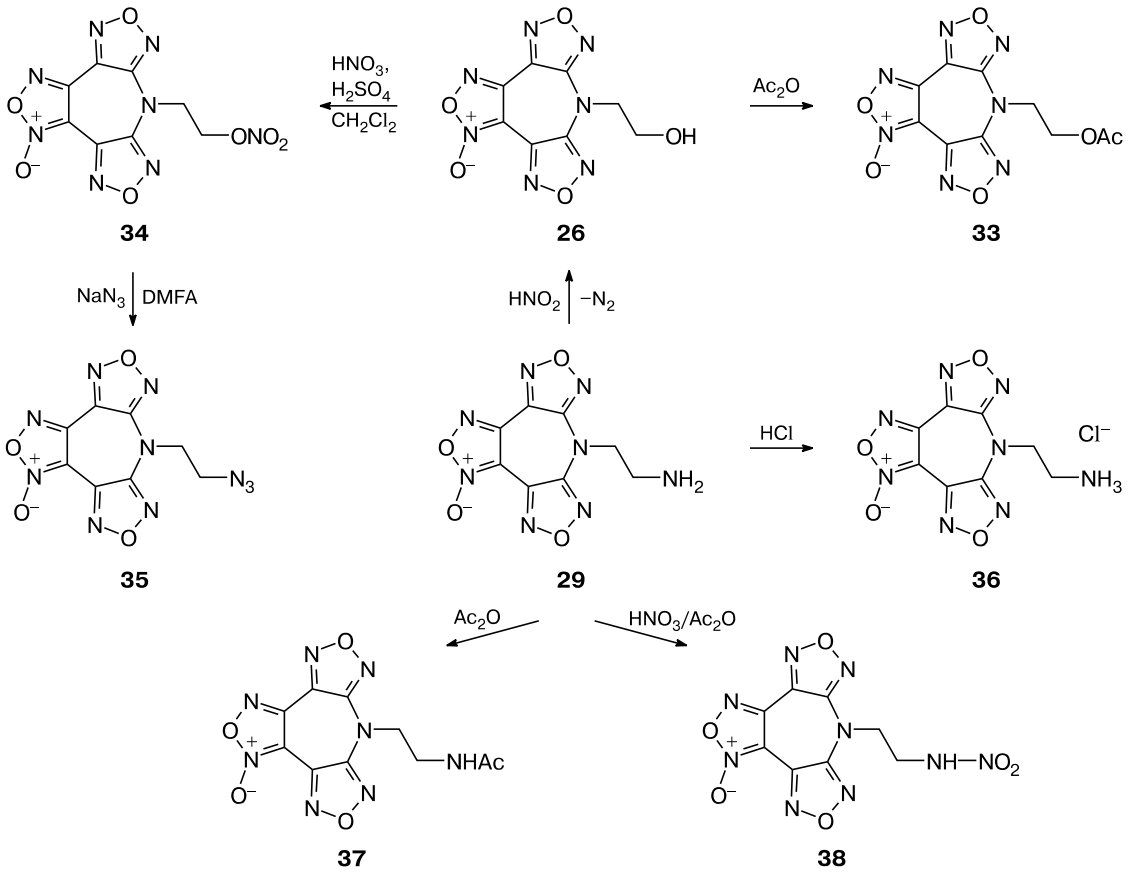
The side-chain substituents containing functional groups undergo reactions typical of the functional groups under consideration (Scheme 9). The presence of free hydroxyl group in compound **26** is confirmed by the formation of the corresponding acetate **33** and nitrate **34**. Under the action of sodium azide, the nitrate group is replaced by the azido group to form compound **35** (Table 9).

The presence of the primary amino group in compound **29** is confirmed by the salt formation, acylation, nitration, and diazotization of this group (see Table 9). The alcohol formed in the latter case had the

Table 9. Chemical shifts of the protons in the substituted 7-(2-X-ethyl) derivatives of 7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]-azepine (**33**—**38**)

Compound	R	δ		
		Het—C<u>H</u>$_2$	Terminal C<u>H</u>$_2$ group	Substituent X
33	CH_2CH_2OAc	4.25 (t, 2 H, J = 7.0 Hz)	3.47 (t, 2 H, J = 7.0 Hz)	1.73 (s, 3 H, $COCH_3$)
34	$CH_2CH_2ONO_2$	4.96 (br.s, 2 H)	4.61 (br.s, 2 H)	—
35	$CH_2CH_2N_3$	4.40 (br.s, 2 H)	3.81 (br.s, 2 H)	—
36	$CH_2CH_2NH_3^+Cl^-$	4.62 (t, J = 6.5 Hz)	4.25 (t, J = 6.5 Гц)	—
37	CH_2CH_2NHAc	4.25 (t, 2 H, J = 7.0 Hz)	3.46 (t, 2 H, J = 7.0 Hz)	7.9—7.8 (br.s, 1 H, NH); 1.73 (s, 3 H, $COCH_3$)
38	$CH_2CH_2NHNO_2$	4.62 (t, 2 H, J = 3.5 Hz)	4.98 (t, 2 H, J = 3.5 Hz)	9.50 (br.s, 1 H, NH)

Scheme 9



IR spectrum identical to that of compound **26** considered above.

Thus, a high synthetic potential shown for 3,4-bis-(4-nitrofurazan-3-yl)furoxan (**2**) allows one to consider this compound as a valuable building block for the design of a wide spectrum of novel 1,2,5-oxadiazole derivatives, including also complex polyheterocyclic annulated systems.

Experimental

Melting points were measured on a Kofler stage. IR spectra were recorded on a FSM-1201 IR spectrometer (KBr pellets). ^1H and ^{13}C NMR spectra (300.13 and 75.47 MHz) at the natural isotope content were recorded on a Bruker DRX-500 spectrometer in DMSO-d_6. The NMR spectral data are given in Tables 1—3, 5, 7, and 9. Mass spectra were recorded on Varian MAT CH-6 and Varian MAT CH-111 (electron impact, 70 eV) spectrometers. TLC were performed on Silufol 254UV plates in the benzene—dioxane—acetic acid—ethanol (90 : 24 : 4 : 4) solvent system (UV irradiation was used for visualization). Compoudns **1** and **2** were prepared according to the published procedures.[26,30—32,58]

*Attention! The starting dinitro derivative **2**, diazide **3**, as well as some compounds prepared are potentially explosive and require delicate handling.*

The spectral characteristics of the compounds obtained, which are not given in Experimental, are listed in Tables 2, 3, and 5—8.

3,4-Bis(4-methoxyfurazan-3-yl)furoxan (7a). To a solution of compound **1** (3 g, 0.0096 mmol) in anhydrous methanol (40 mL), anhydrous K_2CO_3 (4.14 g, 0.03 mmol) was added. The mixture was stirred for 8 h at 40 °C and diluted with water (150 mL). The separated oil slowly crystallized upon stirring. The precipitate was filtered off, washed with water, and recrystallized from CH_2Cl_2—CCl_4, 1 : 1 (v/v). The yield was 2.1 g (75%), m.p. 52 °C. Found (%): C, 33.87; H, 2.48; N, 25.75. $C_8H_6N_6O_6$. Calculated (%): C, 34.04; H, 2.13; N, 25.53.

3,4-Bis[3-(2-azidoethoxy)furazan-4-yl]furoxan (7c). ***A.*** A solution of compound **2** (1.2 g, 4 mmol) in acetonitrile (30 mL) was mixed with 2-azidoethanol (0.7 g) as a 27% solution in dichloromethane and a solution of NaOH (0.16 g, 10 mmol) in the minimum amount of water was added at ~20 °C. The reaction mass was left for 16 h, the precipitate was filtered off, the solvent was removed *in vacuo*, and the residue was recrystallized from CCl_4. The yield was 0.4 g (27%), m.p. 55—56 °C.

B. To a solution of compound **2** (6 g, 0.02 mol) in anhydrous dichloromethane (50 mL), anhydrous K_2CO_3 (10 g, 0.02 mol), 2-azidoethanol (2.5 g, 0.029 mol) as a 30% solution in CH_2Cl_2, and triethylbenzylammonium chloride (50—100 mg) were added. The mixture was stirred for 8 h at 35—40 °C and diluted with water (150 mL). The organic layer was separated and washed

with aqueous alkali. The solvent was removed *in vacuo* and the residue was recrystallized from CCl_4. The yield was 6.0 g (70%), m.p. 55—56 °C. Found (%): C, 30.20; H, 2.50; N, 42.40. $C_{10}H_8N_{12}O_6$. Calculated (%): C, 30.62; H, 2.06; N, 42.86.

Difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]oxepine (8). To a solution of compound **2** (15.6 g, 0.05 mol) in anhydrous acetonitrile (100 mL), anhydrous K_2CO_3 (5 g, 0.036 mol) was added with stirring. The reaction mass was stirred at 60 °C until the evolution of nitrogen oxides was terminated (3—5 h) and then was filtered from inorganic salts. The filtrate was poured into cold water (500 mL), stirred at room temperature until crystallization of the intially formed oil was complete. The precipitate was filtered off and washed with water until pH of the washing waters became neutral. The residue was crystallized from methanol. The yield was 8.8 g (75%), m.p. 91—92 °C (*cf.* Ref. 43: 92—94 °C). Found (%): C, 30.67; H, 0.03; N, 35.46. $C_6N_6O_5$. Calculated (%): C, 30.51; H, 0.00; N, 35.59.

3-(4-Hydroxyfurazan-3-yl)-4-(4-methoxyfurazan-3-yl)furoxan (9). The cyclic ester **8** (2.3 g, 0.01 mol) was dissolved in methanol (10 mL) and K_2CO_3 (2 g, 0.014 mol) was added. The resulted mixture was stirred for 3 h at 65 °C, cooled to room temperature, and filtered off from inorganic salts. The filtrate was evaporated to dryness *in vacuo*, the residue was dissolved in the minimum amount of water and acidified with conc. HCl to pH 2. The precipitate that formed was filtered off and recrystallized from methanol. The yield was 1.6 g (60%), m.p. 67 °C. Found (%): C, 26.71; H, 1.61; N, 31.17. $C_7H_4N_6O_6$. Calculated (%): C, 26.86; H, 1.49; N, 31.34.

3,4-Bis(4-methoxyfurazan-3-yl)furazan (10). To a solution of compound **7a** (2.8 g, 0.01 mol) in methanol (50 ml), conc. hydrochloric acid (20 mL) and stannous chloride dihydrate (9 g, 0.04 mol) were added. The reaction mass was heated with stirring for 4 h at 60 °C. The mixture was cooled to room temperature, diluted with water (150 mL), and extracted with dichloromethane (2×25 mL). The organic layer was separated and stirred for 20 min with a 1% aqueous solution of NaOH (50 mL) at room temperature. The organic layer was separated, washed with water, and dried over K_2CO_3. The solvent was removed *in vacuo* and the resulted oil was dissolved in CCl_4 (40 mL) and cooled fast to −20 °C (dry ice—dichloromethane bath). The oily precipitate that formed was separated by decantation and recrystallization was repeated once more. The yield was 1.2 g (45%), m.p. 19—21 °C. Found (%): C, 36.34; H, 2.44; N, 31.32. $C_8H_6N_6O_5$. Calculated (%): C, 36.09; H, 2.25; N, 31.58.

Diazotization of 3,4-bis-(4-aminofurazan-3-yl)furoxan (1), preparation of a solution of diazonium salt (14). Compound **1** (10 g, 0.040 mol) was added portionwise with stirring to conc. H_2SO_4 (50 mL). If necessary, the mixture was heated to 40—50 °C until the complete dissolution of compound **1**. A solution of nitrososulfuric acid prepared preliminary according to a known procedure[63] from $NaNO_2$ (6.9 g, 0.1 mol) and conc. H_2SO_4 (80 mL) was added to the resulted solution at the temperature below 5 °C. After the dosage was complete, the mixture was stirred for 3 h at 0—5 °C and the resulted solution of diazonium salt was used for subsequent reactions (~140 mL, 0.3 mmol mL^{-1}).

3,4-Bis(3-azidofurazan-4-yl)furoxan (3). ***A.*** Synthesis of **3** from compound **2**. To a suspension of NaN_3 (2 g, 0.029 mol) in acetonitrile (30 mL), compound **2** (3 g, 9.6 mmol) was added portionwise with vigorous stirring at 20 °C. The mixture was stirred for additional 4 h at 40 °C and poured into cold water (150 mL). The separated oil was extracted with dichloromethane (2×20 mL). The organic layer was separated, washed with water, and stirred vigorously with a 1% aqueous solution of NaOH (100 mL) at 50 °C. After the complete evaporation of CH_2Cl_2, the resulted emulsion was stirred for 2 h at 50 °C and cooled with stirring to 5—10 °C. The precipitate that formed was filtered off and recrystallized from methanol. The yield was 2.1 g (70%), m.p. 51—52 °C (*cf.* Refs 26 and 33: 51—52 °C). Found (%): C, 23.45; H, 0.08; N, 55.61. $C_6N_{12}O_4$. Calculated (%): C, 23.68; H, 0.00; N, 55.26.

B. Synthesis of **3** from bis-diazonium salt **14**. To a cooled to −10 °C (dry ice—dichloromethane bath) solution of diazonium salt **14** (50 mL, 0.015 mol) in sulfuric acid, a solution of NaN_3 (4 g, 0.058 mol) in the minimum amount of water was added dropwise with vigorous stirring using external cooling to maintain the reaction temperature within −10÷−5 °C. After the dosage was complete, the reaction mass was stirred for 2 h at room temperature and poured to ice-water mixture (200 g). The product separated as an oil, which slowly crystallized. The precipitate was separated by filtration, washed several times with water, and recrystallized from CH_2Cl_2—CCl_4, 1 : 2 (v/v). The yield was 2.5 g (55%), m.p. 51—52 °C.

3,4-Bis[3-(*p*-methoxyphenyl)azofurazan-4-yl]furoxan (15). To a solution (50 mL) of diazonium salt **14** in sulfuric aicd, CH_2Cl_2 (50 mL) was added with vigorous stirring. A solution of anisole (3.24 g, 0.03 mol) in dichloromethane (10 mL) was added to the resulted emulsion at the temperature below 5 °C (dry ice—dichloromethane bath). The reaction mass was stirred for 2 h at this temperature and diluted slowly with water (200 mL) while maintaining the reaction temperature in the range of 5—10 °C. The yellow precipitate was filtered off, washed with ethanol and water from residual CH_2Cl_2, and recrystallized from AcOH—EtOH, 1 : 5 (v/v). The yield was 5.7 g (40%), yellow crystalls, m.p. 137 °C. Found (%): C, 49.06; H, 2.99; N, 28.46. $C_{20}H_{14}N_{10}O_6$. Calculated (%): C, 48.98; H, 2.86; N, 28.57.

Reactions of 3,4-bis(4-nitrofurazan-3-yl)furoxan (2) with secondary amines and *tert*-butylamine: preparation of compounds 16—22 (general procedure). Compound **2** (0.01 mol, 3.12 g) was dissolved in acetonitrile (20 mL). The resulted solution was cooled to 5—10 °C and a solution of the corresponding secondary amine (0.04 mol) in acetonitrile (10 mL) was added dropwise with stirring at this temperature. After dosage of amine was completed, the mixture was heated to 30—40 °C and stirred for 2—3 h. The resulted solution was poured to cold water (150 mL) and extracted with dichloromethane (2×25 mL). The organic layer was separated, washed several times with water, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was recrystallized from CCl_4.

3,4-Bis(4-morpholinofurazan-3-yl)furoxan (16). The yield was 2.7 g (70%), m.p. 118—119 °C (*cf.* Ref 28: 118—120 °C). Found (%): C, 42.73; H, 4.23; N, 28.35. $C_{14}H_{16}N_8O_6$. Calculated (%): C, 42.86; H, 4.08; N, 28.5.

3,4-Bis(4-diethylaminofurazan-3-yl)furoxan (17). The yield was 2.3 g (63%), m.p. 122 °C. Found (%): C, 45.91; H, 5.62; N, 30.42. $C_{14}H_{20}N_8O_4$. Calculated (%): C, 46.15; H, 5.49; N, 30.77.

3,4-Bis(4-piperidinofurazan-3-yl)furoxan (18). The yield was 2.7 g (70%), m.p. 94 °C (*cf.* Ref. 28: 82—84 °C). Found (%): C, 49.67; H, 5.50; N, 28.24. $C_{16}H_{22}N_{10}O_4$. Calculated (%): C, 49.48; H, 5.15; N, 28.86.

3,4-Bis[4-(4-methylpiperidinofurazan-3-yl)]furoxan (19). The yield was 1.9 g (45%), m.p. 58—60 °C. Found (%): C, 49.89; H, 5.49; N, 29.29. $C_{16}H_{22}N_{10}O_4$. Calculated (%): C, 49.48;

H, 5.19; N, 28.85. IR, ν/cm^{-1}: 2950; 2930; 2870; 2850; 1630; 1580; 1540; 1465; 1460; 1440; 1385; 1315; 1260; 1155; 990.

3,4-Bis(4-methylpiperazinofurazan-3-yl)furoxan (20). The yield was 2.3 g (63%), m.p. 117 °C. Found (%): C, 45.56; H, 5.60; N, 33.24. $C_{16}H_{22}N_{10}O_4$. Calculated (%): C, 45.93; H, 5.26; N, 33.49.

3,4-Bis{4-[*N*-methyl-*N*-(2-hydroxyethyl)amino]furazan-4-yl}furoxan (21). The yield was 2.3 g (63%), m.p. 117 °C. Found (%): C, 39.65; H, 4.68; N, 30.04. $C_{16}H_{22}N_{10}O_4$. Calculated (%): C, 39.13; H, 4.35; N, 30.43.

3,4-Bis(3-*tert*-butylfurazan-4-yl)furoxan (22) was obtained analogously to compounds **16—21**. The second component was *tert*-butylamine (0.04 mol). The reaction product was purified by passing through SiO_2 column using CH_2Cl_2—hexane (1 : 5 v/v) as the eluent. The yield was 2.35 g (64%), viscous oil.

Reactions of 3,4-bis(4-nitrofurazan-3-yl)furoxan (2) with ammonia and primary amines: preparation of compounds 24—27 and 32 (general procedure). Compound **2** (3.12 g, 0.01 mol) (first component) was dissolved in acetonitrile (20 mL). The resulted solution was cooled to 5—10 °C and a solution of the corresponding primary amine (second component) (0.03 mol) in acetonitrile (10 mL) was added with stirring at this temperature (in the case of ammonia and methylamine, their aqueous solutions were used). During the addition of the amine, the red color of the solution was observed, which disappeared in several minutes. At the end of addition, pH of the resulted solution should be at least 8. After the dosage was complete, the mixture was heated to 30—40 °C and stirred for 2—3 h. The resulted solution was diluted with 2-3 volumes of water and the most of acetonitrile was removed under reduced pressure. The precipitate was filtered off and recrystallized from a suitable solvent.

7*H*-Difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (23). The second component was 25% aqueous ammonia. The yield was 1.6 g (68%), m.p. 226 °C (H_2O). Found (%): C, 41.54; H, 0.60; N, 41.36. $C_6H_1N_7O_4$. Calculated (%): C, 41.70; H, 0.43; N, 41.70.

7-Methyl-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (24). The second reactant was 25% aqueous methylamine. The yield was 1.8 g (72%), m.p. 198 °C (EtOH—DMF, 5 : 1 v/v). Found (%): C, 33.55; H, 1.54; N, 39.18. $C_7H_3N_7O_4$. Calculated (%): C, 33.73; H, 1.20; N, 39.36.

7-Benzyl-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (25). The second reactant was benzylamine. The yield was 2.5 g (78%), m.p. 174 °C (EtOH—DMF, 5 : 1 v/v). Found (%): C, 47.85; H, 2.42; N, 29.87. $C_{13}H_7N_7O_4$. Calculated (%): C, 48.00; H, 2.15; N, 30.15.

7-(2-Hydroxyethyl)-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (26). The yield was 1.65 g (60%), m.p. 193 °C (EtOH—AcOH, 10 : 1 v/v). Found (%): C, 34.09; H, 1.97; N, 34.86. $C_8H_5N_7O_5$. Calculated (%): C, 34.41; H, 1.79; N, 34.86.

7-Cycloheptyl-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (27). The second reactant was cycloheptylamine. The yield was 2.0 g (60%), m.p. 219 °C (EtOH—AcOH, 5 : 1 v/v). Found (%): C, 47.03; H, 4.05; N, 29.46. $C_{13}H_{13}N_7O_4$. Calculated (%): C, 47.13; H, 3.93; N, 29.61.

1,2-Bis[7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine-7-yl]ethane (28). To a solution of compound **2** (3 g, 0.01 mol) in acetonitrile (40 mL), a solution of ethylenediamine (2 g, 0.033 mol) in acetonitrile (25 mL) was added dropwise with stirring while maintaining temperature in the range of 5—10 °C. When the dosage was complete, the mixture was stirred for 2 h at this temperature, the excess of solvent was removed *in vacuo*, and the residue was diluted with water. The precipitate that formed was filtered off, washed with 10% HCl and water, and recrystallized from a DMF—AcOH (1 : 1 v/v) mixture. The yield was 1.7 g (70%), m.p. 318 °C. Found (%): C, 34.01; H, 1.01; N, 39.74. $C_{14}H_4N_{14}O_8$. Calculated (%): C, 33.88; H, 0.81; N, 39.52.

7-(2-Aminoethyl)-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (29). To a solution of ethylenediamine (15 g, 0.25 mol) in acetonitrile (100 mL), compound **2** (15.6 g, 0.05 mol) was added portionwise (per 1 g) with stirring while maintaining temperature in the range of 15—20 °C. When the dosage was complete, the mixture was stirred for 2 h at this temperature, the excess of solvent was removed *in vacuo*, and the residue was diluted with water. The precipitate that formed was filtered off, washed with water, and dissolved in 10% HCl (100 mL). The resulted solution was filtered through a paper filter to separate a slight amount of the the disubstituted product **28**. To the filtrate 10% aqueous NaOH was added carefully to adjust pH to 10, the mixture was cooled to room temperature, and the precipitate was filtered off on a glass filter. The product was recrystallized from an ethanol—DMF (10 : 1 v/v) mixture. The yield was 9.7 g (70%), m.p. 160 °C (dec.). Found (%): C, 34.65; H, 2.30; N, 39.98. $C_8H_6N_8O_4$. Calculated (%): C, 34.53; H, 2.16; N, 40.29.

Alkylation of 7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (23) (general procedure). Compound **23** (0.01 mol) was dissolved in DMF (25 mL), anhydrous K_2CO_3 (2 g, 0.015 mol) and the corresponding alkylating agent (0.01 mol) were added, and the mixture was stirred for 24 h at 50 °C. The reaction mass was poured with stirring into cold water (100 mL). The precipitate was filtered off, washed with water, and recrystallized from an ethanol—acetic acid (2 : 1 v/v) mixture.

7-Methyl-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (24). The alkylating agent was dimethyl sulfate or methyl iodide (in the case of methyl iodide, the reaction was performed in a flask equipped with a reflux condenser). The yield was 2.0 g (80%), m.p. 198 °C.

7-Benzyl-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (25). The alkylating agent was benzyl chloride. The yield was 2.6 g (80%), m.p. 174 °C.

Acylation of 3,4-bis(4-aminofurazan-3-yl)furoxan (1). *A*. Preparation of 3,4-bis(4-*N*-acetylaminofurazan-3-yl)furoxan (30). To a solution of diamine **1** (5 g, 0.02 mmol) in Ac_2O (30 mL), conc. H_2SO_4 (two droplets) was added with stirring. Precipitation began after 5 min. The reaction mass was kept for 15 min at room temperature and filtered. The precipitate was washed with water, dried, and recrystallized from dichloroethane. The yield was 4.4 g (66%), m.p. 173—174 °C. Found (%): C, 36.19; H, 2.79; N, 33.46. $C_{10}H_8N_8O_6$. Calculated (%): C, 35.70; H, 2.38; N, 33.30. ^{1}H NMR, δ: 11.6, 11.3 (s, 2 H, 2 NH); 2.06, 2.05 (s, 6 H, 2 CH_3CO). ^{13}C NMR, δ: 1,2,5-oxadiazole atoms — 150.56 (C(1)); 133.8 (C(2)); 107.1 (C(3)); 145.8 (C(4)); 136.6 (C(5)); 150.36 (C(6)); substituents — 169.86, 169.81 (2 $\underline{C}OCH_3$); 23.00, 22.66 (2 $CO\underline{C}H_3$). IR, ν/cm^{-1}: 3620 (N—H, as); 3430 (N—H, s); 3300—3100 (m, N—H assoc.); 2990 (Me); 1680 (C=O, amide 1); 1630; 1590 (stretch. heterocycle); 1560, 1530 (N—H_{def} + C—$N_{stretch}$, amide 2); 1500; 1390; 1260 (C—$N_{stretch}$ + + N—H_{def}, amide 3); 1000; 970; 950; 820; 800; 795; 600.

***B*. Preparation of 3-(4-*N*-acetylaminofurazan-3-yl)-4-(4-*N*,*N*-diacetylaminofurazan-3-yl)furoxan (31).** Acylation was performed analogously to the previous procedure, but the reaction temperature was maintained within 100—110 °C and the reac-

tion time was 2 h. After the separation of the precipitate of the diacetyl derivative **30**, the mother solution was poured into water (100 mL). The precipitate formed was filtered off and extracted with hot chloroform. Diacetyl derivative **30** (3.2 g) was isolated from the precipitate. The chloroform extract was evaporated to dryness and the residue was recrystallized from a CCl_4—$CHCl_3$ (1 : 1 v/v) mixture to yield triacetyl derivative **31** (1.25 g, 17%), m.p. 150—151 °C. Found (%): C, 38.25; H, 3.05; N, 29.93. $C_{12}H_{10}N_8O_7$. Calculated (%): C, 38.10; H, 2.64; N, 29.93. ^{1}H NMR, δ: 2.35 (s, 6 H, 2 CH_3); 2.10 (s, 3 H, CH_3); 11.7 (s, 1 H, NH).

Nitration of 7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]-azepine (23), preparation of 7,7′-bis(7*H*-difurazano[3,4-*b*:3′,4′-*f*]-furoxano[3″,4″-*d*]azepine) (32). To a vigorously stirred nitrating mixture (HNO_3—Ac_2O 1 : 1; HNO_3—H_2SO_4 1 : 2; HNO_3—20%-oleum 1 : 2, or HNO_3—$(CF_3CO)_2O$) 1 : 1 v/v) (30—40 mL), amine **23** (4.7 g, 0.02 mol) was added portionwize at the temperature no higher than 5—10 °C. (In the case of nitration in sulfuric acid-nitric acid or oleum-nitric acid mixtures, to avoid the formation of clots, the starting amine was dissolved first in nitric acid and then the resulted solution was added to sulfuric acid). After the addition of the amine was completed, the mixture was stirred for additional 3 h at 5—10 °C and poured into ice-water mixture (150 g). The precipitate was filtered off on a Buchner funnel and washed successively with HNO_3 (*d* 1.5, 10 mL) and water until neutral pH of the washing waters, and finally ethanol (20 mL). The precipitate was dried and placed to boiling ethanol (50 mL). The mixture was boiled with stirring for several minutes and filtered while it was hot. The precipitate was washed with boiling ethanol (3×20 mL) and dried at 50—60 °C. The yield was 3.7—4.2 g (80—90%), m.p. 280 °C (dec.). Found (%): C, 30.59; H, 0.08; N, 41.61. $C_{12}H_0N_{14}O_8$. Calculated (%): C, 30.77; H, 0.00; N, 41.88. ^{13}C NMR, δ: 150.8 (C(1)); 135.3 (C(2)); 106.0 (C(3)); 144.6 (C(4)); 137.2 (C(5)); 150.7 (C(6)). IR, ν/cm^{-1}: 1650; 1610; 1600; 1560; 1510; 1460; 1380; 1210; 1000; 980; 860; 800. MS, *m/z* (I_{rel} (%)): 468 [M] (2.5); 436 [M − 2 O] (0.4); 234 [M/2] (100); 88 (32); 62 (70); 53 (60); 38 (57).

7-(2-Acetoxyethyl)-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano-[3″,4″-*d*]azepine (33). Alcohol **26** (0.5 g, 1.8 mmol) was mixed with acetic anhydride (3 mL) and conc. H_2SO_4 (one droplet) was added. The mixture was kept for 30 min at 40 °C and poured into water (20 mL). After 1 day, the precipitate was filtered off and recrystallized from methanol The yield was 0.4 g (80%), m.p. 107 °C. Found (%): C, 37.49; H, 2.25; N, 30.19. $C_{10}H_7N_7O_6$. Calculated (%): C, 37.38; H, 2.18; N, 30.53. IR, ν/cm^{-1}: 2905; 1730; 1650; 1610; 1600; 1550; 1520; 1480; 1440; 1350; 1250; 1210; 1140; 1010; 980; 960; 900; 880; 830; 800; 720; 590.

7-(2-Nitroxyethyl)-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano-[3″,4″-*d*]azepine (34). CH_2Cl_2 (20 mL) was added to a nitrating mixture composed of HNO_3 (*d* 1.5, 10 mL) and conc. sulfuric acid (20 mL); after that alcohol **26** (3 g, 0.011 mol) was added in small portions with stirring at the reaction temperature below 20 °C. After the dosage was complete, the mixture was stirred for 2 h at 20 °C and poured to ice-water mixture (100 g). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (30 mL). The combined organic layers were washed with water, 1% $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was recrystallized from ethanol. The yield was 2.6 g (75%), m.p. 135 °C. Found (%): C, 29.44; H, 1.43; N, 34.61. $C_8H_4N_8O_7$. Calculated (%): C, 29.63; H, 1.23; N, 34.57. IR, ν/cm^{-1}: 2910; 1650; 1600; 1590; 1560; 1520; 1480; 1360; 1290 (ν_s NO_2); 1220; 1000; 980; 970; 900; 840 (N—O); 760 (δ NO_2). ^{13}C NMR, δ: 154.1; 153.7; 145.2; 137.7; 135.5; 105.9; 69.4 (CH_2ONO_2); 49.3 (CH_2-Het).

7-(2-Azidoethyl)-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano-[3″,4″-*d*]azepine (35). To a solution of nitrate **34** (1 g, 3 mmol) in DMF (15 mL), NaN_3 (0.5 g, 7.7 mmol) was added. The reaction mixture was stirred for 5 h at 50 °C and poured into water (100 mL). The precipitate that formed was filtered off and recrystallized from methanol. The yield was 0.6 g (65%), m.p. 115 °C. Found (%): C, 31.46; H, 1.41; N, 45.92. $C_8H_4N_{10}O_4$. Calculated (%): C, 31.58; H, 1.32; N, 46.05. IR, ν/cm^{-1}: 2950; 2920; 2110 (N_3); 1650; 1610; 1590; 1545; 1500; 1460; 1420; 1370; 1300; 1270; 1230; 1190; 1030; 1000; 985; 930; 900; 870; 840; 640; 590. ^{13}C NMR (DMSO-d_6), δ: 154.1; 153.7; 145.2; 137.7; 135.5; 105.9; 50.8 (CH_2N_3); 46.9 (CH_2-Het).

7-[2-(*N*-Acetylamino)ethyl]-7*H*-difurazano[3,4-*b*:3′,4′-*f*]-furoxano[3″,4″-d]azepine (37). Amine **26** (0.5 g, 2 mmol) was mixed with acetic anhydride (4 ml) and sodium acetate (100 mg) was added. The resulted suspension was refluxed for 2 h and then poured into water (50 mL). After 1 day, the precipitate was filtered off, washed with water, and recrystallized from propan-2-ol. The yield was 0.4 g (70%), m.p. 144 °C. Found (%): C, 37.64; H, 2.31; N, 35.16. $C_{10}H_8N_8O_5$. Calculated (%): C, 37.50; H, 2.50; N, 35.00. IR, ν/cm^{-1}: 3600 (ν_{as}NH); 3530 (ν_{as}NH); 3230, 3080 (NH assoc.); 1650; 1600; 1590; 1550; 1520; 1460; 1370; 1300; 1270; 1220; 1000; 960; 890; 840; 790; 600; 590. MS, *m/z*: 320 $[M]^+$ (4); 291 (0.5); 261 [291 — NO] (2.5); 248 (2.5); 201 (3); 188 (4); 84 (13); 72 (50); 43 $[COCH_3]^+$ (100).

7-[2-(*N*-Nitramino)ethyl]-7*H*-difurazano[3,4-*b*:3′,4′-*f*]furoxano[3″,4″-*d*]azepine (38). Amine **26** (0.5 g, 2 mmol) was added with stirring and cooling to a 1 : 1 (v/v) mixture (10 mL) of acetic anhydride and HNO_3 (*d* 1.5) at 0—5 °C. Precipitation began after 0.5 h. The reaction mixture was stirred for additional 0.5 h at 10 °C and poured into ice-water mixture (50 g). After 1 day, the precipitate that formed was filtered off, washed with water, and recrystallized from methanol. The yield was 0.48 g (75%), m.p. 129 °C. Found (%): C, 29.25; H, 1.65; N, 38.13. $C_8H_5N_9O_6$. Calculated (%): C, 29.18; H, 1.52; N, 38.30. IR, ν/cm^{-1}: 2950; 2921 (ν_{as}, ν_s CH_2); 1707; 1655; 1645; 1610; 1590 (ν_{as} NO_2); 1570; 1540; 1480; 1430; 1390; 1370; 1330; 1310; 1290; 1220 (ν_s NO_2); 1180; 1140; 1070; 1040; 990; 970; 850. MS, *m/z*: 43 (100); 42 (6); 30 $[NO]^+$ (28).

References

1. H. Goldschmidt, *Chem. Ber.*, 1883, **16**, 2176.
2. L. Wolf, *Liebigs Ann.*, 1890, **260**, 79.
3. A. Kekulé, *Liebigs Ann.*, 1858, **105**, 279.
4. P. Toennies, *Chem. Ber.*, 1880, **13**, 1845.
5. H. Wieland, L. Semper, *Liebigs Ann.*, 1908, **358**, 36.
6. V. G. Andrianov, A. V. Eremeev, *Khim. Geterotsikl. Soedin.*, 1984, 1155 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1984, **20**, 937].
7. R. M. Paton, in *Comprehensive Heterocyclic Chemistry*, Eds A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Pergamon Press, Oxford, 1984, **6**, 393.
8. V. G. Andrianov, A. V. Eremeev, *Khim. Geterotsikl. Soedin.*, 1990, 1443 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1990, **26**, 1199].

9. R. M. Paton, in *Comprehensive Heterocyclic Chemistry-II*, Eds A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Pergamon Press, Oxford, 1996, **4**, p. 229.
10. A. B. Sheremetev, *J. Heterocycl. Chem*., 1995, **32**, 371.
11. L. I. Khmel´nitskii, S. S. Novikov, T. I. Godovikova, *Khimiya furoksanov: stroenie i sintez* [*Chemistry of Furoxans: Structure and Synthesis*] (2nd Ed., revised), Nauka, Moscow, 1996, 383 pp. (in Russian).
12. L. I. Kmel´nitskii, S. S. Novikova, T. I. Godovikova, *Khimiya furoksanov: reaktsii i primenenie* [*Chemistry of Furoxans: Reactions and Application*] (2nd Ed., revised), Nauka, Moscow, 1996, 430 pp. (in Russia)
13. A. B. Sheremetev, *Ross. Khim. Zh.*, 1997, **41**, 43 [*Mendeleev. Chem. J.* (*Engl. Transl.*), 1997, **41**, 62].
14. A. B. Sheremetev, *Usp. Khim.*, 1999, **68**, 154 [*Russ. Chem. Rev*. (*Engl. Transl.*), 1999, **68**, 137].
15. A. B. Sheremetev, in *Energeticheskie kondensirovannye sistemy. Kratkii entsiklopedicheskii slovar´* [*Energetic Condensed Systems. Concise Encyclopedic Dictionary*], Ed. by B. P. Zhukov (2nd Ed., revised), Yanus-K, Moscow, 2000, p. 318.
16. A. B. Sheremetev, N. N. Makhova, W. Friedrichsen, *Adv. Heterocycl. Chem*., 2001, **78**, 65.
17. A. B. Sheremetev, I. L. Yudin, *Usp. Khim.*, 2003, **72**, 93 [*Russ. Chem. Rev*. (*Engl. Transl.*), 2003, **72**, 87].
18. G. Nikonov, S. Bobrov, in *Comprehensive Heterocyclic Chemistry III*, Eds A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor, Elsevier Science, Amsterdam—London, 2008, v. **5**, p. 315.
19. M. D. Coburn, *J. Heterocycl. Chem*., 1968, **5**, 83.
20. A. B. Sheremetev, T. S. Pivina, *Proc. 27th Int. Ann. Conf. ICT* (*Karlsruhe*, *Germany, June 24—28, 1996*), pp. 30/1.
21. A. B. Sheremetev, V. O. Kulagina, N. S. Aleksandrova, D. E. Dmitriev, Y. A. Strelenko, *Propellants, Explos., Pyrotech.*, 1998, **23**, 142.
22. A. B. Sheremetev, E. A. Ivanova, D. E. Dmitriev, V. O. Kulagina, B. B. Averkiev, M. Yu. Antipin, *J. Heterocycl. Chem*., 2005, **42**, 803.
23. M. A. Epishina, A. S. Kulikov, N. N. Makhova, *Izv. Akad. Nauk*, *Ser. Khim.,* 2008, 631 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 644].
24. A. B. Sheremetev, E. V. Mantseva, *Mendeleev Commun.*, 1996, **6**, 246.
25. P. Ravi, D. M. Badgujar, G. M. Gore, S. P. Tewari, A. K. Sikder, *Propellants, Explos., Pyrotech.*, 2011, **36**, 393.
26. I. V. Tselinskii, S. F. Mel´nikova, T. V. Romanova, N. P. Spiridonova, E. A. Dundukova, *Zh. Org. Khim.*, 2001, **37**, 1419 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2001, **37**, 1355].
27. J. Wang, J. Li, Q. Liang, Y.Huang, H. Dong, *Propellants, Explos., Pyrotech.*, 2008, **33**, 347.
28. A. B. Sheremetev, V. G. Andrianov, E. V. Mantseva, E. V. Shatunova, N. S. Aleksandrova, I. L. Yudin, D. E. Dmitriev, B. B. Averkiev, M. Yu. Antipin, *Izv. Akad. Nauk*, *Ser. Khim*., 2004, 569 [*Russ. Chem. Bull., Int. Ed*., 2004, **53**, 596].
29. P. V. Anokina, T. V. Romanova, S. F. Mel´nikova, I. V. Tselinskii, *Zh. Org. Khim.*, 2011, **47**, 1575 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2011, **47**, 1606].
30. A. B. Sheremetev, E. A. Ivanova, N. P. Spiridonova, S. F. Melnikova, I. V. Tselinsky, K. Y. Suponitsky, M. Yu. Antipin, *J. Heterocycl. Chem*., 2005, **42**, 1237.
31. Z. Feng-qi, C. Pei, H. Rong-zu, L. Yang, Z. Zhi-zhong, Z. Yan-shui, Y. Xu-wu, G. Yin, G. Sheng-li, S. Qi-zhen, *J. Hazard. Mat*., 2004, **A113**, 67.
32. W. Jun, D. Haishan, H. Y. Gang, L. J. Shan, *Proc. 11 Seminar: New Trends in Research of Energetic Materials* (*Czech Republic, Pardubice, April 09—11, 2008*), 182.
33. Z. Yanshui, W. Bozhou, Z. Cheng, L. Jiankang, C. Zhiqun, L. Peng, Z. Zhizhong, *Chin. J. Org. Chem*., 2010, **30**, 1044.
34. S. V. Pirogov, S. F. Mel´nikova, I. V. Tselinskii, T. V. Romanova, N. P. Spiridonova, V. L. Betin, A. B. Postnikov, A. Ya. Kots, Yu. V. Khropov, S. A. Gavrilova, M. A. Graphov, N. A. Medvedeva, N. V. Pyatakova, I. S. Severina, T. V. Bulargina, *RF Pat. RU 2240321*, 2004, *Byull. izobret.*, 2004, **32**; *Chem. Abstr.*, 141, p. 395564.
35. A. M. Gasco, C. Cena, A. D. Stilo, G. Ermondi, C. Medana, A. Gasco, *Helv. Chim. Acta*, 1996, **79**, 1803.
36. Z. Yan-shui, W. Boz-hou, L. Jian-kang, Z. Cheng, H. Lan, C. Zhi-qun, Z. Zhiz-hong, *Acta Chim. Sinica*, 2011, **69**, 1673.
37. A. B. Sheremetev, O. V. Kharitonova, E. V. Mantseva, V. O. Kulagina, E. V. Shatunova, N. S. Aleksandrova, T. M. Mel´nikova, E. A. Ivanova, D. E. Dmitriev, V. A. Eman, I. L. Yudin, V. S. Kuz´min, Yu. A. Strelenko, T. S. Novikova, O. V. Lebedev, L. I. Khmel´nitskii, *Zh. Org. Khim.*, 1999, **35**, 1555 [*Russ. J. Org. Chem* (*Engl. Tranl.*), 1999, **35**].
38. A. B. Sheremetev, O. V. Kharitonova, *Mendeleev Commun.*, 1992, **2**, 157.
39. A. B. Sheremetev, E. V. Shatunova, B. B. Averkiev, D. E. Dmitriev, V. A. Petukhov, M. Yu. Antipin, *Heteroatom Chem*., 2004, **15**, 131.
40. A. B. Sheremetev, V. O. Kulagina, *J. Org. Chem*., 1996, **61**, 1510.
41. A. B. Sheremetev, O. V. Kharitonova, T. M. Mel´nikova, T. S. Novikova, V. S. Kuz´min, L. I. Khmel´nitskii, *Mendeleev Commun*., 1996, **6**, 141.
42. S. F. Mel´nikova, S. V. Pirogov, S. N. Vergizov, I. V. Tselinskii, *Zh. Org. Khim*., 1999, **35**, 143 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1999, **35**, 137].
43. Y. Zhou, B. Wang X. Wang, C. Zhou, H. Huo, Y. Zhang, *Chin. J. Energ. Mater.*, 2012, **20**, 137.
44. N. N. Makhova, I. V. Ovchinnikov, B. N. Khasapov, L. I. Khmel´nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1982, **31**, 646 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1982, **31**, 573].
45. M. D. Coburn, *J. Labell. Comp. Radiopharm*., 1985, **22**, 183.
46. M. D. Coburn, *J. Heterocycl. Chem*., 1986, **23**, 421.
47. M. D. Coburn, C. B. Storm, D. W. Moore, T. G. Archibald, *Magnetic Res. Chem*., 1990, **28**, 16.
48. H. Ma, J. Song, H. Xiao, R. Hu, F. Zhao, *Chin. J. Expl. Prop*., 2006, **3**, 43.
49. F. B. Mallory, A. Cammarata, *J. Am. Chem. Soc*., 1966, **88**, 61.
50. M. R. Arshadi, *Org. Mass Spectrom*., 1978, **13**, 379.
51. V. Yu. Rozhkov, L. V. Batog, M. I. Struchkova, *Izv. Akad. Nauk, Ser. Khim*., 2005, 1866 [*Russ. Chem. Bull.*, *Int. Ed.*, 2005, **54**, 1923].
52. O. A. Rakitin, O. A. Zalezova, A. S. Kulikov, N. N. Makhova, T. I. Godovikova, L. I. Khmel´nitskii, *Izv. Akad. Nauk*, *Ser. Khim*., 1993, 1949 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1993, **42**, 1865].
53. A. A. Astrat´ev, D. V. Dashko, A. I. Stepanov, *Centr. Eur. J. Chem*., 2012, DOI 10.2478/s11532-012-0020-7.

54. A. Gasco, G. Ruá, E. Menziani, G. M. Nano, G. Tappi, *J. Heterocycl. Chem.*, 1970, **7**, 131.
55. A. V. Eremeev, V. G. Andrianov, I. P. Piskunova, *Khim. Geterotsikl. Soedin.*, 1978, 1196 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1978, **14**, 963].
56. E. I. Ivanov, I. P. Konup, L. A. Konup, D. E. Stepanov, L. V. Grischuk, V. V. Vysotskaya, *Khim.-Farm. Zh.*, 1993, **27**, No. 7, 37 [*Pharm. Chem. J.* (*Engl. Transl.*), 1993, **27**, 501].
57. Z. Yan-shui, Z. Zhi-zhong, L. Jain-kang, G. Xi-ren, H. Xin-Ping, Z. Cheng, *Chin. J. Expl. Propellants*, 2005, **28**, 43.
58. C. H. Lim, T. K. Kim, K. H. Kim, K. H. Chung, *Bull. Korean. Chem. Soc.*, 2010, **31**, 1400.
59. H. Cerecettoa, M. González, G. Seoanea, C. Stankoa, O. E. Pirob, E. Castellanoc, *J. Braz. Chem. Soc.*, 2004, **15**, 232.
60. A. B. Sheremetev, I. L. Yudin, *Mendeleev. Commun.*, 2002, **12**, 66.
61. I. V. Tselintskii, S. F. Mel´nikova, T. V. Romanova, S. V. Pirogov, G. K. Khisamutdinov, T. A. Mratkuzina, V. L. Korolev, I. Z. Kondukov, I. Sh. Abrakhamov, S. P. Smirnov, *Zh. Org. Khim.*, 1997, **33**, 1739 [*Russ. J. Org. Chem.*, 1997, **33**, 1656].
62. I. V. Starchenkov, V. G. Andrianov, A. F. Mishnev, *Khim. Geterotsikl. Soedin.*, 1997, 250 [*Chem. Heterocycl. Compd.*, 1997, **33**, 216].
63. H. E. Fierz-David, L. Blangey, *Grundlegende Operationen der Farbenchemie, Siebente Univeränderte Auflage*, Springer-Verlag, Wien, 1947.

Received December 12, 2011;
in revised form April 16, 2012