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Synthesis and nitration of *N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines

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A Mannich reaction of 4-amino-3-R-furoxans with paraformaldehyde in 10% aqueous H_2SO_4 led to the high yields of *N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines, whose structure (using R = Me as an example) was confirmed by X-ray diffraction study. The *N*,*N*´-bis-(3-R-furoxan-4-yl)methylenediamines obtained were nitrated to *N*,*N*´-dinitro-*N*,*N*´-bis-(3-R-furoxan-4-yl)methylenediamines upon the action of 100% HNO_3 in acetic or trifluoroacetic anhydride.

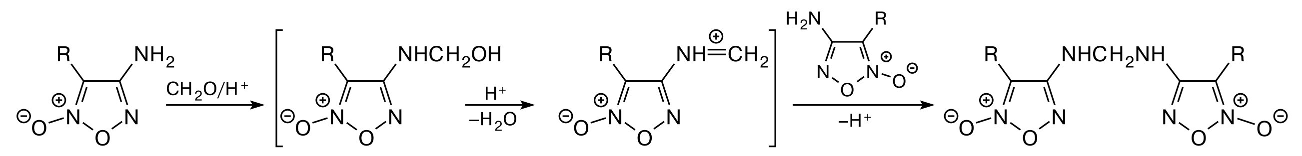
Key words: 4-amino-3-R-furoxans, paraformaldehyde, hydroxymethylation, the Mannich reaction, 4-hydroxymethylamino-3-R-furoxans, *N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines, N-nitration, *N*,*N*´-dinitro-*N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines.

Derivatives of methylenebisamines are widely used in synthetic organic chemistry, for example, as aminomethylating agents,[1] while methylenedinitramine fragments are a part of high-energy compounds, in particular, hexogene and octogene. The most common and convenient method for the synthesis of methylenediamine derivatives is condensation of 2 moles of amines with 1 mole of formaldehyde by the Mannich reaction. Conditions for this reaction vary within a wide range and depend, in particular, on the basicity of amines used.[2] This approach was used for the synthesis of derivatives of various heterocyclic amines and their *N*,*N*´-dinitro derivatives, including those derived from aminofurazans, *i.e.*, *N*,*N*´-bis(furazanyl)methylenediamines and *N*,*N*´-dinitro-*N*,*N*´-bis(furazanyl)methylenediamines.[3—7]

Though, compounds derived from *N*,*N*´-bis(furoxanyl)methylenedinitramines can be of interest for the preparation of potentially high-energy compounds,[8] the Mannich bases from aminofuroxans and their further transformations are not described in the literature by now, which is due, by all accounts, to the fact that aminofuroxans with suitable substituents at the second C atom are not easily available. 3-Aminofuroxans, except their 4-aryl derivatives,[9] are virtually unavailable. However, in the last years new fairly convenient methods for the preparation of functionally substituted 4-aminofuroxans were developed,[10—12] that allowed one to start an extensive study of their reactivity.

The present work is devoted to the study of behavior of isomeric 4- and 3-aminofuroxans in the Mannich reaction with formaldehyde in order to obtain *N*,*N*´-bis(furoxanyl)methylenediamines and their nitration to *N*,*N*´-dinitro derivatives. The study was started from 4-amino-3-R-furoxans **1a—f** with substituents of different types at the C(3) atom of the ring (Scheme 1). Initially, in the synthesis of target *N*,*N*´-bis(3-R-furoxan-4-yl)methylenedi-

Scheme 1



1a—f **3a—f** **4a—f** **2a—f**

R = Me (**a**), Ph (**b**), Ac (**c**), COOMe (**d**), $CONH_2$ (**e**), CON_3 (**f**)

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amines **2a—f** we used conditions for the preparation of similar furazan derivatives. According to the literature data,[4—7] *N,N'*-bis(4-R-furazan-3-yl)methylenediamines **5** were synthesized by the reaction of aminofurazans with formaldehyde, as a rule, in weakly acidic medium (HCOOH in MeCN, 0.5% aq. HCl or 1% aq. H_2SO_4). 3-Amino-4-nitrofurazan[4] was successfully involved into this reaction only in 80% aq. H_2SO_4, which, obviously, is due to the extremely low basicity of the compound under consideration because of strong electron-withdrawing effect of the nitrofurazanyl fragment.

Conditions for the preparation of *N,N'*-bis(3-R-furoxan-4-yl)methylenediamine derivatives **2** were optimized using 3-acetyl-4-aminofuroxan **1c** and 4-amino-3-azidocarbonylfuroxan **1f** as examples. The reaction progress was monitored by TLC and ^{1}H NMR spectroscopy analyzing samples of the reaction mixtures. When 1—3% aq. H_2SO_4 was used, the reaction mixture contained the starting aminofuroxans **1c,f** and small amount of intermediates, apparently, hydroxymethylaminofuroxans **3c,f**. When the concentration of H_2SO_4 was increased to 5—6%, the starting aminofuroxans completely disappeared and the reaction mixture contained comparable amounts of intermediates **3c,f** and target compounds **2c,f**. The R_f values for the intermediates were significantly lower than those for the final reaction products **2c,f**, while ^{1}H NMR spectra of the reaction mixture contained signals in the region δ 7.7—8.4 related to the intermediates and signals for the NH groups of the final products **2c,f** in the region δ 7.0—7.2. The optimum conditions for the preparation of compounds **2c,f** are the stirring a suspension of the starting components at room temperature in 10—12% aq. H_2SO_4 for 24 h. After the reaction reached completion, compounds **2a—f** were filtered off and isolated in virtually pure form in high yields (see Scheme 1).

From the mechanism of the Mannich reaction[2] and obtained results on the synthesis of compounds **2**, it follows that the first step of the process, *i.e.*, the formation of *N*-methylol derivatives **3**, proceeds in less acidic medium than subsequent steps, *i.e.*, formation of iminium cations **4** and their reaction with the second molecule of 4-aminofuroxan **1**.

The structure of synthesized *N,N'*-bis(3-R-furoxan-4-yl)methylenediamines **2a—f** was established based on the combination of elemental analysis data and spectral characteristics; the structure of *N,N'*-bis(3-methylfuroxan-4-yl)methylenediamine **2a** was confirmed by X-ray diffraction study. The mass spectra of all the compounds obtained are characterized by the presence of highly intensive peaks, which correspond to the fragments formed upon the CH_2—N bonds cleavage in their molecules. Only the mass spectra of compounds **1a** and **1c** contained peaks of low intensities corresponding to the molecular ions.

The X-ray diffraction data on monocrystals of compound **2a** (Fig. 1) show that the molecule of *N,N'*-bis(3-methylfuroxan-4-yl)methylenediamine is in particular position and is placed on the second order axis passing through the C(4) atom. Distribution of bond distances in the compound is expected for aminofuroxans, the bond between the furoxan ring and the amino group is shortened and its length approximates to that of a multiple bond, that is also common for this class of compounds (C(3)—N(3) 1.3618(12) Å, *cf.* with C—NH_2, 1.344 Å in 4-amino-3-methylfuroxan[13]). The N(3) nitrogen atom of the NH group comes out of the plane of the C(3), C(4), and H(3N) atoms by 0.175(7) Å. Such an arrangement of substituents on the nitrogen atom has been also found earlier for the symmetric methylenediamine derivatives containing aryl or heteroaryl substituents (see, for example, Ref. 14). The electron pair on the amine nitrogen atom is antiperiplanar to the C(4)—N(3A) bond, that allows one to suggest a possibility of stereoelectronic interaction between the lone pair of electrons mentioned and the antibonding orbital of the C(4)—N(3A) bond (n—σ*-interaction). Apparently, the very existence of the anomeric effect leads to the pyramidalization of the fragment involving the NH nitrogen atom, despite significant double-bond character of the C(3)—N(3) bond.

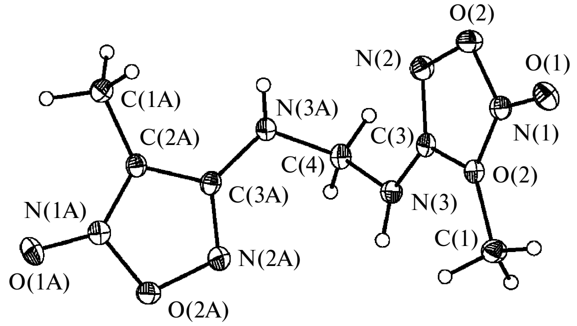


Fig. 1. General view of compound **2a**. Nonhydrogen atoms are given as probability ellipsoids of thermal vibrations (p = 50%).

Analysis of crystal packing of **2a** (Fig. 2) showed that the oxygen atom of the N-oxide group is involved into the formation of both the weak intermolecular hydrogen bond with the NH fragment (H...O is 2.06 Å, N...O is 2.932(2) Å,

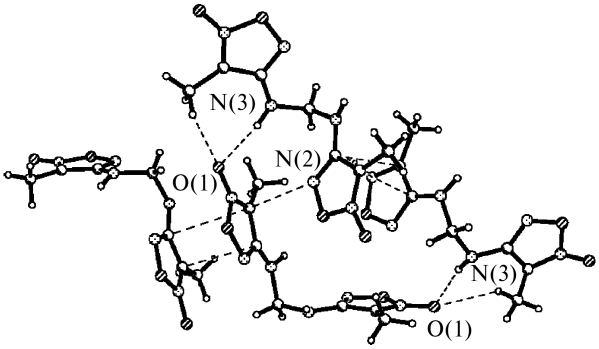
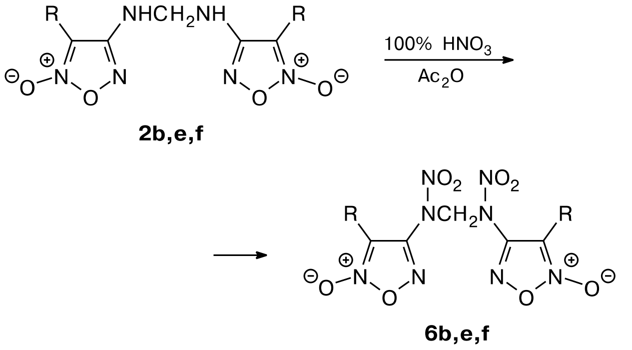


Fig. 2. Fragment of crystal packing of **2a**.

the N—H...O angle is 168°) and the CH...O contact with the methyl substituent of the furoxan ring (H...O is 2.66—2.70 Å, C...O is 3.10—3.68 Å). It is probable that the hydrogen bonds mentioned, together with stereoelectronic interactions, affect geometry of the amine nitrogen atom involved into the intermolecular bonding. Together with the H-bonds, the molecules in the crystal are involved into the strong enough stacking-interactions, which combine them in dimers (3.36 Å). In turn, such dimers are bound with each other by the N—π-interaction between the N(2) nitrogen atom and the π-system of the furoxan ring (N...C is 3.17 Å) (see Fig. 2).

The *N*,*N*′-bis(3-R-furoxan-4-yl)methylenediamines **2a—f** synthesized were studied in the nitration reaction in order to obtain *N*,*N*′-dinitro-*N*,*N*′-bis(3-R-furoxan-4-yl)methylenediamines **6**. The nitration of compounds **2a—f** with the mixture of 100% HNO_3—Ac_2O under conditions similar to those described in the works on the preparation of furazan derivatives[4,5,7] (in CCl_4 at 0 °C), allowed us to obtain only *N*,*N*′-dinitro derivatives **6b**,**e**,**f** (Scheme 2). These dinitro derivatives are poorly soluble in the HNO_3—Ac_2O mixture. They precipitated and were easily separated by filtration. Variation in the ratio $HNO_3 : Ac_2O$ virtually produces no change in the yield of the reaction products.

Scheme 2



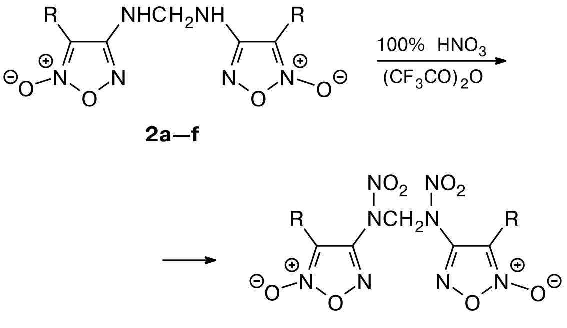
R = Ph (**b**), $CONH_2$ (**e**), CON_3 (**f**)

However, only dinitro derivatives **6b**,**f** were successfully isolated in the analytically pure form and completely characterized. According to the TLC (R_f 0.36 ($CHCl_3$—EtOAc, 1 : 1)) and ^1H NMR spectroscopic data (acetone-d_6, δ: 6.42 (s, 2 H, CH_2), 7.64 (s, 2 H, NH_2), 7.95 (s, 2 H, NH_2)), the structure of compound **6e** agreed with the desired *N*,*N*′-bis(3-aminocarbonylfuroxan-4-yl)-*N*,*N*′-dinitromethylenediamine. However, it was impossible to obtain good ^{13}C and ^{14}N NMR spectra for this compound, since signals for the products of its decomposition rapidly appeared in the spectrum of **6e** on standing in acetone-d_6 and DMSO-d_6. The mass spectrum of this compound has also proved poorly informative, it exhibited only low-weight fragment ions corresponding to the deep disintegration of the starting molecule. Compounds **2a**,**c**,**d** were soluble in the nitrating HNO_3—Ac_2O mixture, but no any products were isolated from the solution after the reaction was completed.

N,*N*′-Dinitro derivatives with Me (**6a**), Ac (**6c**), and COOMe (**6d**) substituents were successfully obtained in high yields upon nitration of compounds **2a**,**c**,**d** with the 100% HNO_3—$(CF_3CO)_2O$ mixture. Dinitramines **6a**,**d** under these conditions precipitated from the reaction mixture and were isolated in high yield. Compound **6c** was soluble in the nitrating mixture and isolated from the reaction mixture after evaporation of HNO_3 and $(CF_3CO)_2O$ on a rotary evaporator at room temperature. Nitration of methylenebisamines with the aminocarbonyl (**2e**) and azidocarbonyl (**2f**) substituents with the HNO_3—$(CF_3CO)_2O$ mixture led to the isolation of the same products **6e**,**f**, which were formed in the HNO_3—Ac_2O mixture. In this case, their yield somewhat increased (by 3—4%), while the nitration time half decreased.

Nitration of *N*,*N*′-bis(3-phenylfuroxan-4-yl)methylenediamine **2b** with the mixture of HNO_3 and $(CF_3CO)_2O$ involves, besides the NH group, the phenyl fragment to form *N*,*N*′-dinitro-*N*,*N*′-bis[3-(4-nitrophenyl)furoxan-4-yl]methylenediamine (**6j**) (Scheme 3). Its structure was confirmed by a combination of elemental analysis data and spectral characteristics.

Scheme 3



2a—f

6a,c—j

R = Me (**a**), Ph (**b**), Ac (**c**), COOMe (**d**), $CONH_2$ (**e**), CON_3 (**f**), 4-$NO_2C_6H_4$ (**j**)

Behavior of 3-aminofuroxans in the Mannich reaction with formaldehyde was studied using 3-amino-4-phenylfuroxan **7** as an example. However, in aqueous H_2SO_4 of different concentrations (3.5, 10, 25, and 50%) for 24—150 h at 20 °C, in all the cases the starting furoxan **7** was isolated from the mixture. The same result was also obtained when H_2SO_4 was replaced by HCOOH in MeCN. When the reaction was carried out in weakly basic medium (pH = 8—9), decomposition of the starting furoxan **7** occurred after 48 h.

In conclusion, the study of behavior of aminofuroxans in the Mannich reaction with formaldehyde showed that only 4-aminofuroxans can be involved into this reac-

Table 1. Yields and some physicochemical characteristics of synthesized *N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines **2a—f** and *N*,*N*´-dinitro-*N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines **6a—d**,**f**,**j**

Compound	Yield (%)	M.p. /°C	R_f (eluent)	Found / Calculated (%) C	H	N	Molecular formula
2a	74	178—179	0.33	34.55	4.30	34.90	$C_7H_{10}N_6O_4$
			($CHCl_3$—EtOAc, 1 : 1)	34.71	4.16	34.70	
2b	75	190—191	0.76	55.47	3.81	23.07	$C_{17}H_{14}N_6O_4$
			($CHCl_3$—EtOAc, 1 : 1)	55.74	3.85	22.94	
2c	93	162—162.5	0.64	36.12	3.57	28.30	$C_9H_{10}N_6O_6$
			($CHCl_3$—EtOAc, 3 : 1)	36.25	3.38	28.18	
2d	91	215—216	0.70	32.44	3.22	25.61	$C_9H_{10}N_6O_8$
			($CHCl_3$—EtOAc, 1 : 1)	32.74	3.05	25.45	
2e	95	252—253	0.36	33.29	2.39	34.60	$C_9H_8N_8O_6$
			($CHCl_3$—EtOAc, 1 : 1)	33.34	2.49	34.56	
2f	87	140	0.57	—	—	—	$C_7H_4N_{12}O_6$
		(decomp. with sparkling)	($CHCl_3$—EtOAc, 4 : 1)				
6a	86*	129—130	0.31	25.42	2.29	34.00	$C_7H_8N_8O_8$
			($CHCl_3$—EtOAc, 3 : 1)	25.31	2.43	33.73	
6b	72**	136—137	0.53	44.68	2.80	24.80	$C_{17}H_{12}N_8O_8$
			($CHCl_3$—EtOAc, 8 : 1)	44.75	2.65	24.56	
6c	89*	Caramel	0.40	28.12	2.00	29.08	$C_9H_8N_8O_{10}$
			($CHCl_3$—EtOAc, 4 : 1)	27.85	2.08	28.86	
6d	84*	124—125	0.38	25.68	1.78	26.63	$C_9H_8N_8O_{12}$
			($CHCl_3$—EtOAc, 3 : 1)	25.73	1.92	26.67	
6f	91*, 88**	131	0.77	—	—	—	$C_7H_2N_{14}O_{10}$
		(decomp. with sparkling)	($CHCl_3$—EtOAc, 3 : 1)				
6j	82*	96—97	0.77	37.50	1.76	25.49	$C_{17}H_{10}N_{10}O_{12}$
			($CHCl_3$—EtOAc, 8 : 1)	37.37	1.84	25.64	

* Nitrating mixture: 100% HNO_3—$(CF_3CO)_2O$.

** Nitrating mixture: 100% HNO_3—Ac_2O.

tion. 3-Amino-4-phenylfuroxan does not give the Mannich reaction products. Based on 4-aminofuroxans, the earlier unknown *N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines **2a—f** were synthesized in high yields, conditions for their nitration at the nitrogen atoms were found and the earlier unknown *N*,*N*´-dinitro-*N*,*N*´-bis(3-R-furoxan-4-yl)-methylenediamines **6a—j** were also obtained.

*Attention! Compounds **2f** and **6f** containing each two azidocarbonyl groups in the molecule and two N—NO_2 fragments (compound **6f**) are sensible to impact and require careful handling.*

The reaction conditions, yields, spectral and physicochemical characteristics of the synthesized compounds **2a—f** and **6a—d**,**f—j** are given in Tables 1 and 2.

Table 2. The IR and ^{1}H, ^{13}C, ^{14}N NMR spectroscopic and mass spectrometric data for the synthesized *N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines **2a—f** and *N*,*N*´-dinitro-*N*,*N*´-bis(3-R-furoxan-4-yl)methylenediamines **6a—d**,**f**,**j**

Compound	IR spectrum, ν/cm^{-1}	^{1}H NMR, δ, *J*/Hz [MS, *m/z* (I_{rel} (%))]	^{13}C NMR, δ, [^{14}N NMR, δ, $\Delta\nu_{1/2}$/Hz]
2a	3272, 3152, 3048, 2964, 2924, 1688, 1624, 1568, 1524, 1436, 1380, 1292, 1264, 1116, 1032, 864, 716, 696	2.05 (s, 3 H, Me); 4.67 (s, 2 H, CH_2); 7.48 (br.s, 2 H, 2 NH) [242 $[M]^+$ (2), 160 (9), 128 (100), 115 (70), 98 (62)]	7.08 (Me); 49.61 (CH_2); 107.43 (C(3) in furoxan ring); 156.86 (C(4) in furoxan ring)
2b	3352, 3060, 2928, 1624, 1576, 1512, 1424, 1376, 1184, 1076, 1000, 956, 848, 780, 712, 692	4.77 (t, 2 H, CH_2, ^3J = 8.0); 7.17 (t, 2 H, 2 NH, ^3J = 8.0); 7.55 (m, 6 H, Ar); 7.73 (m, 4 H, Ar) [262 (5), 188 (11), 177 (19), 129 (100), 117 (62), 103 (72)]	50.74 (CH_2); 109.02 (C(3) in furoxan ring); 122.33, 127.90 (C(1), C(4), Ar); 128.98, 130.41 (C(3), C(2), Ar); 155.61 (C(4) in furoxan ring)

(*to be continued*)

Table 2 (*continued*)

Compound	IR spectrum, ν/cm^{-1}	^{1}H NMR, δ, J/Hz [MS, m/z ($I_{\rm rel}$ (%))]	^{13}C NMR, δ, [^{14}N NMR, δ, $\Delta\nu_{1/2}$/Hz]
2c	3408, 3384, 2976, 1684, 1600, 1524, 1376, 1350, 1272, 1112, 988, 948, 840, 720, 608	2.48 (s, 3 H, Me); 4.82 (t, 2 H, CH$_2$, ^3J = 8.2); 7.13 (t, 2 H, 2 NH, ^3J = 8.2) [298 [M]$^+$ (2), 267 (1), 237 (1), 155 (87), 143 (94), 127 (16), 126 (48), 113 (100)]	28.21 (Me); 49.49 (CH$_2$); 108.84 (C(3) in furoxan ring); 155.07 (C(4) in furoxan ring); 188.92 (CO)
2d	3444, 2964, 2880, 1736, 1696, 1580, 1532, 1432, 1384, 1328, 1224, 1124, 1008, 808, 772, 732, 680	3.88 (s, 6 H, Me); 4.83 (t, 2 H, CH$_2$, ^3J = 8.2); 6.98 (t, 2 H, 2 NH, ^3J = 8.2) [172 (37), 159 (73), 142 (100), 129 (63), 112 (92), 101 (65)]	49.79 (CH$_2$); 53.02 (Me); 103.03 (C(3) in furoxan ring); 154.88 (C(4) in furoxan ring); 157.00 (CO)
2e	3360, 3188, 2880, 1680, 1628, 1580, 1532, 1392, 1340, 1256, 1168, 1116, 1028, 988, 852, 728, 644	4.81 (t, 2 H, CH$_2$,^3J = 8.0); 7.12 (t, 2 H, 2 NH, ^3J = 8.0); 7.71 (s, 2 H, NH$_2$); 8.50 (s, 2 H, NH$_2$) [265 (4), 241 (4), 231 (4), 156 (100), 144 (7), 127 (34), 114 (46)]	49.50 (CH$_2$); 104.25 (C(3) in furoxan ring); 155.94 (C(4) in furoxan ring); 157.26 (CO)
2f	3420, 3376, 2176, 1712, 1600, 1568, 1520, 1372, 1324, 1216, 1120, 1080, 960, 872, 820, 748, 732, 676	4.83 (t, 2 H, CH$_2$, ^3J = 8.8); 7.02 (t, 2 H, NH, ^3J = 8.8) [193 (3), 183 (12), 170 (24), 154 (25), 140 (24), 126 (7), 111 (32)]	49.83 (CH$_2$); 104.53 (C(3) in furoxan ring); 154.61 (C(4) in furoxan ring); 161.80 (CO)
6a	3420, 3012, 2932, 2852, 1640, 1592, 1488, 1426, 1408, 1388, 1280, 1248, 1108, 1076, 1036, 968, 908, 856, 768, 748, 724, 688, 640, 632	2.45 (s, 6 H, Me); 6.74 (s, 2 H, CH$_2$) [173 (13), 128 (12), 127 (100), 101 (20), 97(44), 84 (33)]	7.52 (Me); 64.85 (CH$_2$); 111.51 (C(3) in furoxan ring); 152.09 (C(4) in furoxan ring) [–40.3 (NO$_2$), $\Delta\nu_{1/2}$ = 260]
6b	3420, 3012, 2924, 2852, 1624, 1576, 1508, 1464, 1424, 1408, 1364, 1316, 1280, 1208, 1120, 1092, 1040, 1004, 988, 976, 924, 904, 840, 792, 772, 744, 720, 700, 664, 640	6.96 (s, 2 H, CH$_2$); 7.61 (m, 6 H, Ar); 7.75 (m, 4 H, Ar) [204 (3), 201 (8), 189 (20), 178 (7), 173 (10), 172 (10), 132 (41), 129 (100), 119 (5), 116 (36), 102 (76)]	65.23 (CH$_2$); 110.13 (C(3) in furoxan ring); 120.73, 126.45 (C(1), C(4), Ar); 129.57, 131.67 (C(3), C(2), Ar); 150.36 (C(4) in furoxan ring) [–39.7 (NO$_2$), $\Delta\nu_{1/2}$ = 231]
6c	3112, 2932, 1708, 1604, 1552, 1532, 1460, 1424, 1348, 1312, 1280, 1224, 1176, 1040, 1016, 984, 876, 856, 800, 720, 624	2.61 (s, 6 H, Me); 6.23 (s, 2 H, CH$_2$) [179 (48), 167 (100), 148 (31), 137 (34), 120 (59), 112 (28), 101 (76), 95 (94)]	28.12 (Me); 66.34 (CH$_2$); 109.64 (C(3) in furoxan ring); 149.22 (C(4) in furoxan ring); 186.96 (CO) [–38.3 (NO$_2$), $\Delta\nu_{1/2}$ = 227]
6d	3784, 3036, 2964, 1756, 1716, 1664, 1584, 1492, 1324, 1280, 1216, 1100, 1044, 1020, 900, 752, 712, 684	3.91 (s, 6 H, 2 Me); 6.50 (s, 2 H, CH$_2$) [217 (37), 183 (58), 171 (80), 111 (100)]	54.05 (Me); 65.71 (CH$_2$); 104.52 (C(3) in furoxan ring); 148.81 (C(4) in furoxan ring); 155.31 (CO) [–36.7 (NO$_2$), $\Delta\nu_{1/2}$ = 243]
6f	3044, 2992, 2858, 2248, 2176, 1832, 1688, 1648, 1592, 1492, 1404, 1352, 1284, 1180, 1072, 1040, 988, 876, 776, 728, 704, 684, 628	6.65* (s, 2 H, CH$_2$) [264 (1), 228 (11), 194 (12), 182 (10), 154 (5), 111 (12), 101 (17), 54 (100)]	66.61* (CH$_2$); 106.14 (C(3) in furoxan ring); 149.21 (C(4) in furoxan ring); 161.20 (CO) [–43.0* (NO$_2$), $\Delta\nu_{1/2}$ = 78]
6j	3420, 2962, 2924, 2840, 1596, 1528, 1508, 1464, 1348, 1280, 1216, 1168, 1116, 1092, 980, 880, 856, 760, 708, 624	7.14* (s, 2 H, CH$_2$); 8.14 (d, 2 H, Ar, ^3J = 10.2); 8.46. (d, 2 H, Ar, ^3J = 10.2) [234 (7), 218 (19), 188 (22), 176 (41), 174 (89), 164 (28), 149 (48), 147 (86), 134 (24), 129 (62), 118 (37), 104 (59), 102 (100)]	65.72* (CH$_2$); 111.53 (C(3) in furoxan ring); 116.79 (C(1), Ar); 124.96, 128.71 (C(2), C(3), Ar); 149.73 (C(4), Ar); 151.06 (C(4) in furoxan ring) [–42.4* (NO$_2$), $\Delta\nu_{1/2}$ = 134]

* NMR spectra were recorded in (CD$_3$)$_2$CO.

Experimental

IR spectra were recorded on a UR-20 spectrometer in KBr pellets. NMR spectra were recorded on a Bruker WM-250 (^{1}H, 250 MHz) and Bruker AM-300 spectrometers (^{13}C, 75.5 MHz; ^{14}N, 21.5 MHz) in DMSO-d$_6$. Chemical shifts in the ^{1}H and ^{13}C NMR spectra were measured relatively to Me_4Si as an internal standard, the ^{14}N NMR spectra, relatively to $MeNO_2$ as an external standard. Mass spectra were obtained on a Varian MAT CH 6 instrument (70 eV). Thin-layer chromatography was performed on Silufol UV-254 with visualization under the UV light. 4-Amino-3-methylfuroxan **1a**,[15] 4-amino-3-phenylfuroxan **1b**,[9] 3-acetyl-4-aminofuroxan **1c**,[10] 4-amino-3-methoxycarbonylfuroxan **1d**,[12] 4-amino-3-aminocarbonylfuroxan (**1e**),[12] and 4-amino-3-azidocarbonylfuroxan (**1f**)[12] were obtained according to the known procedures.

Crystals of **2a** are tetragonal (100 K), the space group is *I*-42*d*, $a = b = 12.240(6)$ Å, $c = 13.608(7)$ Å, $V = 2038.8(17)$ Å^3, $Z = 8$ ($Z' = 0.5$), $M = 242.21$ g mol^{-1}, $d_{\text{calc}} = 1.578$ g cm^{-3}, μ(Mo-Kα) = 1.70 cm^{-1}, $F(000) = 1008$. Intensities of 10837 reflections were measured on a Smart Apex II CCD diffractometer (λ(Mo-Kα) = 0.71072 Å, ω-scanning, $2\theta < 60°$), 1499 of them were independent reflections ($R_{\text{int}} = 0.0234$), which were used in the further refinement. The structure was solved by the direct method and refined by the least squares method in anisotropic full-matrix approximation on F^2_{hkl}. Positions of the hydrogen atoms of the NH group were found from differential Fourier-syntheses, positions of the rest of hydrogen atoms were calculated starting from the geometrical assumptions and refined with the fixed thermal parameters $U_{\text{iso}} = 1.2C_{\text{iso}}$ in isotropic approximation. The final value of the reliability factors for **2a**: $R_1 = 0.0251$ (calculated on F_{hkl} for 1463 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0686$ (calculated on F^2_{hkl} for all the 1499 reflections), GOF = 1.051. The calculations were performed using the SHELXTL 5.10 program package.[16]

Synthesis of *N*,*N*′-bis(3-R-furoxan-4-yl)methylenediamines 2a—f (general procedure). Aminofuroxan **1a—f** (4.0 mmol) was added to a suspension of paraformaldehyde (60 mg, 2.0 mmol) in 10% aq. H_2SO_4 (10 mL) at ~20 °C with stirring. The reaction mixture was stirred for 20—30 h until the starting amine disappeared (TLC monitoring). A precipitate was filtered off, washed with some water to neutrality, and dried in air.

Synthesis of *N*,*N*′-dinitro-*N*,*N*′-bis(3-R-furoxan-4-yl)-methylenediamines 6b,e,f by nitration of compounds 2b,e,f with 100% HNO_3 in Ac_2O (general procedure). Concentrated HNO_3 (1.0 mL, 24 mmol) and CCl_4 (4 mL) were added to acetic anhydride (2.5 mL, 26.5 mmol) at –2—0 °C over 5—10 min. After 15 min, finely triturated *N*,*N*′-bis(3-R-furoxan-4-yl)diaminomethane **2b,e,f** (1 mmol) was added in portions at this temperature. The reaction mixture was stirred for 6 h at 0—5 °C. A precipitate was filtered off, washed with CCl_4 (2×2 mL) and dried in a vacuum desiccator over KOH.

Synthesis of *N*,*N*′-dinitro-*N*,*N*′-bis(3-R-furoxan-4-yl)-methylenediamines 6a—f by nitration of compounds 2a—f with 100% HNO_3 in $(CF_3CO)_2O$ (general procedure). Concentrated HNO_3 (1.0 mL, 24 mmol) was added to trifluoroacetic anhydride (4.0 mL, 28.8 mmol) at –2—0 °C over 5—10 min. After 15 min, finely triturated *N*,*N*′-bis(3-R-furoxan-4-yl)diaminomethane **2a—f** (1 mmol) was added in portions at this temperature. The reaction mixture was stirred for 2 h at 0—5 °C. A precipitate was filtered off, washed with CCl_4 (2×2 mL), and dried in a vacuum desiccator over KOH.

Upon nitration of *N*,*N*′-bis(3-methylfuroxan-4-yl)diaminomethane (**2a**), a product fairly well soluble in the reaction mixture is formed. The yield of product **6a** after filtration of a precipitate was 61%. After the mother liquor was concentrated on a rotary evaporator at room temperature, 25% of compound **6a** was additionally isolated.

Upon nitration of *N*,*N*′-bis(3-acetylfuroxan-4-yl)methylenediamine (**2c**), the final product **6c** forms no precipitate. It was isolated by concentration of the reaction mixture on a rotary evaporator at room temperature.

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