A study of the reaction mechanism of 3-nitro-4-R-furoxans formation by nitrosation of dipotassium salts of 1-hydroxyimino-2,2-dinitro-1-R-ethanes*

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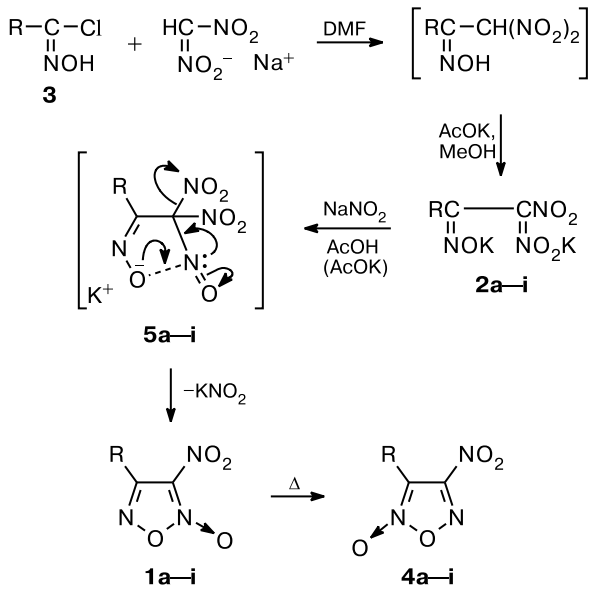
The mechanism proposed earlier for explanation of the furoxan ring formation in the nitrosation of dipotassium salts of 1-hydroxyimino-2,2-dinitro-1-R-ethanes with $NaNO_2$/AcOH was confirmed experimentally by determining the ionization constants of the dinitromethyl and oxime fragments in the starting dipotassium salt and by examining ^1H, ^{13}C, ^{14}N, and ^{15}N NMR and mass spectra of isomeric 3(4)-nitro-4(3)-R-furoxans with the $^{15}N(5)$ and $^{15}N(2)$ ring atoms, respectively, and 3,4-diarylfuroxan with both ^{15}N-labeled ring atoms. A comparative analysis of the IR and Raman spectra of the ^{15}N-labeled furoxan derivatives obtained and their unlabeled analogs allowed refinement of the literature data on interpretation of the vibrational spectra of furoxan derivatives.

Key words: mechanism, nitrosation, dipotassium salts of 1-hydroxyimino-2,2-dinitro-1-R-ethanes, ionization constants, isomeric ^{15}N-labeled 3(4)-nitro-4(3)-R-furoxans, ^{15}N-labeled 3,4-diarylfuroxan, ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra, IR spectroscopy, mass spectrometry, $^{13}C—^{15}N$ coupling constants.

Earlier,[1,2] a novel method for the synthesis of 3-nitro-4-R-furoxans **1** has been developed at the laboratory of nitrogen-containing compounds of the N. D. Zelinsky Institute of Organic Chemistry (Russian Academy of Sciences). The method involves nitrosation of dipotassium salts of 1-hydroxyimino-2,2-dinitro-1-R-ethanes **2** with $NaNO_2$/AcOH. The starting compounds **2** were prepared from hydroximoyl chlorides **3** and a sodium salt of dinitromethane. Thermodynamically more stable 4-nitro-3-R-furoxans **4** were obtained by thermal isomerization of 3-nitro isomers **1** in boiling toluene. The aforesaid synthesis of compounds **1** offers a novel method of furoxan ring formation. The mechanism proposed for this reaction involves (1) nitrosation of the anion of the dinitromethyl fragment in compounds **2**, (2) an intramolecular attack of the oxime anion in intermediate **5** on the N atom of the nitroso group, and (3) elimination of NO_2 anion, which leads to furoxan **1** (Scheme 1).

Here we present experimental data that confirm the earlier proposed mechanism. The data were obtained using two approaches: (1) determination of the ionization constants of the dinitromethyl and oxime fragments in dipotassium salts **2** and (2) synthesis of isomeric 3(4)-nitro-4(3)-R-furoxans **1′** and **4′** with the $^{15}N(5)$ and $^{15}N(2)$ ring atoms, respectively, and 3,4-R_2-furoxan **6′** with both ^{15}N-labeled ring atoms and examination of their ^1H, ^{13}C, ^{14}N, and ^{15}N NMR and mass spectra.

Scheme 1



R = 4-MeO-3,5-$(NO_2)_2C_6H_2$ (**a**), Ph (**b**), 2-$NO_2C_6H_4$ (**c**), 3-$NO_2C_6H_4$ (**d**), 4-$NO_2C_6H_4$ (**e**), 4-BrC_6H_4 (**f**), 3,4,5-$(NO_2)_3C_6H_2$ (**g**), COMe (**h**), CO_2Et (**i**)

* Dedicated to Academician V. N. Charushin on the occasion of his 60th birthday.

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Optimization of the conditions for this reaction has revealed[1,2] that addition of an equimolar amount of AcOK to the reaction mixture prior to the nitrosation of dipotassium salts **2** increases the yields of furoxans **1** from 50—55 to 68—80%. This fact is indirect evidence for the participation of the oxime anion in the cyclization. However, to verify this conjecture, as well as to estimate the participation of the anion of the dinitromethyl fragment in the first reaction step (nitrosation), we should experimentally determine the acidity constants of both the fragments. These constants were estimated spectrophotometrically on the example of dipotassium salt **2a** (R = 4-MeO-3,5-$(NO_2)_2C_6H_2$). The spectrum contains two absorption peaks with λ_{max} = 250 (weak) and 370 nm (intense). It is known[3a,b] that the intense band with λ_{max} = 350 nm corresponds to the π—π*-transition of the dinitromethyl group. Since the dinitromethyl group in salt **2a** is conjugated with the oxime group, the band with λ_{max} = 370 nm in its UV spectrum can most likely be attributed to the π—π*-transition of the oximino-dinitromethyl fragment, while the weak band with λ_{max} = 250 nm is probably due to the π—π*-transition of the benzene fragment.

Spectrophotometric determination of acidity constants is based on the dependence of the molar absorption coefficients on the relative contents of the fully protonated, half-protonated, and ionized forms in acid-base equilibrium. For salt **2a**, the UV spectra of its solutions in water and in 0.1 *M* NaOH are identical, indicating that this salt is fully ionized in water. As an aqueous solution of salt **2a** is gradually acidified with H_2SO_4, the molar absorption coefficient of the band with λ_{max} = 370 nm decreases to reach zero at *c* = 44% (*c* is the concentration of H_2SO_4 in solution); *i.e.*, salt **2a** is fully protonated (a nondissociated acid form) under these conditions. Note that at *c* = 0.50, 0.91, and 2.00%, the molar absorption coefficients of the band with λ_{max} = 370 nm are equal. Obviously, salt **2a** is monoprotonated in this pH range. Using the standard formula[4,5]

$$\lg\frac{\varepsilon_B - \varepsilon}{\varepsilon - \varepsilon_{BH^+}} = pK - H_X, \qquad (1)$$

where ε_B, ε, and ε_{BH+} are the molar absorption coefficients of the fully ionized, half-protonated, and fully protonated forms, respectively; H_X is the Hammett acidity function, we graphically determined the pK_a values of the oxime (pK_{a_1} = 4.45) and dinitromethyl fragments (pK_{a_2} = 2.23) (see Experimental).

The molar absorption coefficient of the band with λ_{max} = 250 nm changed only slightly during the experiment and did not reach zero upon the increase in *c*, which confirms the correct assignment of this band to the benzene fragment of the molecule.

The data obtained provide much evidence for the mechanism proposed. Indeed, the first reaction step should involve nitrosation of the anion of the dinitromethyl fragment. Insofar as the oxime fragment has a lower (though insignificantly) pK_{a_1} value (4.43) than the pK_a of AcOH (4.74), addition of AcOK actually increases the concentration of this fragment and, consequently, the yield of the final product 4-(4-methoxy-3,5-dinitrophenyl)-3-nitrofuroxan (**1a**).

As a second approach to proving the mechanism of the reaction discovered, we obtained isomeric 3(4)-nitro-4(3)-R-furoxans **1´** and **4´** containing ^{15}N-labeled atoms in the furoxan ring (N(5) and N(2), respectively, in compounds **1´f** and **4´f** as examples. For this purpose, we obtained from 4-bromobenzaldehyde and ^{15}N-labeled hydroxylamine (96.7%-enriched $^{15}NH_2OH \cdot HCl$) compound **3´f** (R = 4-BrC_6H_4) and then transformed it into furoxans **1´f** and **4´f** through intermediates **2´f** and **5´f**. In addition, dehydrochlorination of ^{15}N-labeled acid chloride **3´f** gave nitrile oxide **7**, which undergoes cyclodimerization into diarylfuroxan **6´** containing two ^{15}N ring atoms (Scheme 2). The ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra of all the ^{15}N-labeled furoxans obtained are given in Table 1.

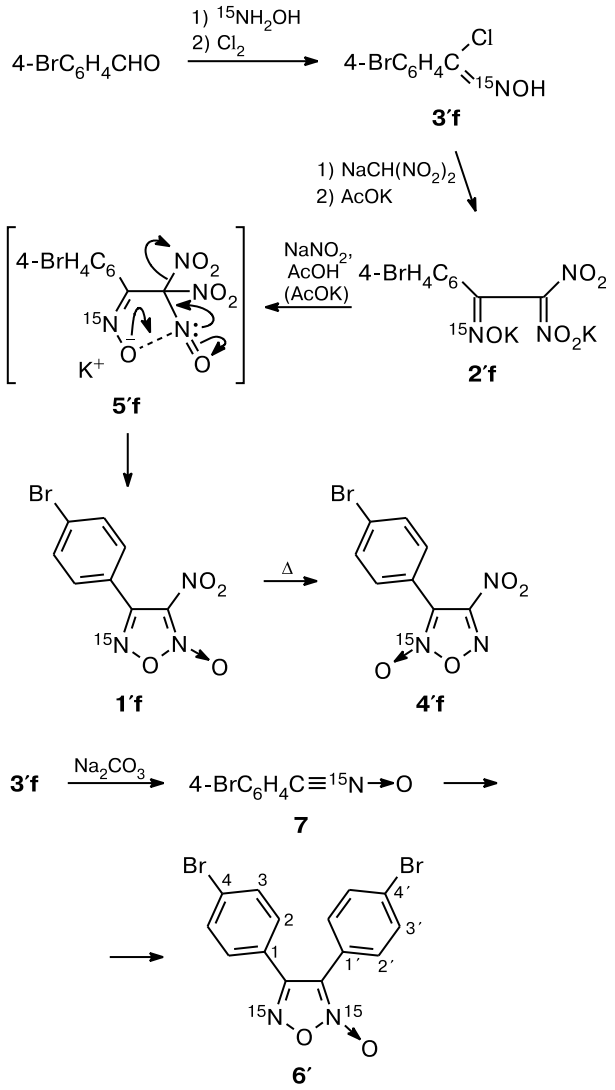
According to the data in Table 1, the labeled N atoms are included in the furoxan ring: the chemical shifts for the $^{15}N(5)$ atoms in compounds **1´f** and **6´** are identical and the chemical shifts for the $^{15}N(2)$ atoms in compounds **4´f** and **6´** have close values. The positions of the labeled ^{15}N atoms in the compounds studied are evident from the coupling constants $J_{^{13}C-^{15}N}$: the nearer the corresponding

Table 1. ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra of ^{15}N-labeled furoxans **1´f**, **4´f**, and **6´**

Furoxan	$\delta_{^1H}$	$\delta_{^{14}N}$ [$\delta_{^{14}N}$, $\Delta\nu_{1/2}$/Hz]	$\delta_{^{13}C}$, $J_{^{13}C-^{15}N}$/Hz
1´f	7.57, 7.70 (both d, ^3J = 8.2)	−12.0 (N(5)) [−39.0, NO_2, $\Delta\nu_{1/2}$ = 11]	122.4 (C(1), Ar, ^2J = 6.2); 126.1 (C(3), furoxan); 127.3 (C(4), Ar, ^5J = 0.6); 130.5 (C(2), Ar, ^3J = 2.0); 132.5 (C(3), Ar); 150.5 (C(4), furoxan, ^1J = 2.6)
4´f	7.47, 7.68 (both d, ^3J = 8.36)	−16.2, (N(2)) [−35.4, NO_2, $\Delta\nu_{1/2}$ = 36]	108.7 (C(3), furoxan, ^1J = 24.5); 118.4 (C(1), Ar, ^2J = 1.0); 126.7 (C(4), Ar, ^5J = 0.5); 130.3 (C(2), Ar, ^3J = 1.5); 132.6 (C(3), Ar); 157.7 (C(4), furoxan, ^2J = 1.0)
6´	7.38 (br.d, ^3J = 8.27); 7.57 (m)	−12.20 (N(5)), −25.38 (N(2))	113.3 (C(3), furoxan, ^1J = 24.56, ^2J = 1.33); 121.6 (C(1), Ar, ^2J = 1.19); 125.3 (C(4), Ar); 125.4 (C(1´), Ar, ^2J = 6.62, ^3J = 1.65); 126.0 (C(4´), Ar); 129.8 (C(2), Ar, ^3J = 1.98); 130.1 (C(2´), Ar, ^3J = 1.39); 132.5 (C(3´), Ar); 132.6 (C(3), Ar); 155.1 (C(4), furoxan, ^1J = 6.3, ^2J = 1.86)

C atom to the labeled ^{15}N atom, the higher the coupling constant. The coupling constants $J_{^{13}C-^{15}N}$ in the spectra of compounds **1′f** and **4′f** approximate to those in the spectrum of furoxan **6′**. Some differences in the chemical shifts of the corresponding C atoms, the labeled N atoms, and the coupling constants in the spectra of compounds **1′f**, **4′f**, and **6′** are due to the influence of the nitro group in the first two compounds.

Scheme 2



Fragmentation of all three compounds **1′f**, **4′f**, and **6′** in the mass spectra also agrees with the ^{15}N-labeled structures proposed. Because bromine exists as a mixture of the ^{79}Br and ^{81}Br isotopes in equal amounts, the fragmentation data for compounds **1′f** and **4′f** are given separately for either isotope (^{79}Br-**1′f**,^{81}Br-**1′f**, ^{79}Br-**4′f**, and ^{81}Br-**4′f**; Table 2). These four compounds undergo identical fragmentation with different relative peak intensities for the corresponding fragmentation ions (see Table 2). The fragmentation character fully agrees with known data on the fragmentation of diarylfuroxans and nitrofuroxans.[6a] EI-induced fragmentation of a furoxan ring is characterized by successive elimination of two NO fragments; nitrofuroxans lose the NO_2 group and the NO fragment of the ONO group into which the NO_2 group isomerizes under electron impact. A similar pattern was observed in the mass spectra of the compounds studied.

Thus, the determination of the ionization constants of the dinitromethyl and oxime fragments in the starting dipotassium salts **2** (with salt **2a** as an example), as well as the synthesis of ^{15}N-labeled furoxans (with compounds **1′f**, **4′f**, and **6′** as examples) and comparative analysis of their ^1H, ^{13}C, and ^{15}N NMR and mass spectra, provides experimental evidence that the mechanism proposed earlier for the novel synthesis of 3-nitro-4-R-furoxans is correct.

The synthesis of ^{15}N-labeled furoxans **1′f**, **4′f**, and **6′** allowed some refinements to the literature data on the IR and Raman spectra of the furoxan ring using the spectra of the unlabeled isomeric furoxans 4-(4-bromophenyl)-3-nitrofuroxan (**1f**), 3-(4-bromophenyl)-4-nitrofuroxan (**4f**), and 3,4-bis(4-bromophenyl)furoxan **6** and their ^{15}N-labeled analogs **1′f**, **4′f**, and **6′** (Tables 3—5).

As expected, ^{15}N-labeling of the furoxan ring causes noticeable shifts of the vibrational frequencies of the ring bonds to the lower frequencies (see Tables 3—5). In addition, analogous shifts are experienced by some of the absorption bands of the benzene ring. This makes it somewhat more difficult to interpret the spectral patterns, especially for compounds **6** and **6′**. The lower-frequency shifts in the spectra of compound **6′** (by 35 (IR) and 14 cm^{-1} (Raman)) and in the IR spectrum of compound **4′f** (by 19 cm^{-1}) compared to the corresponding spectra of their unlabeled analogs **6** and **4f** are observed for a band at 1600 cm^{-1} (stretching vibrations of the furoxan ring). Insofar as ^{15}N-labeling of the N(5) atom of the furoxan ring (compound **1′f**) does not change the frequency of these vibrations against those in compound **1f**, it is obvious that they are mainly contributed by the fragment C=N→O. This conclusion agrees with the literature data.[6b]

The small lower-frequency shifts (by 3—4 cm^{-1}) of the absorption bands at 1500—1550 cm^{-1} in the IR spectra of ^{15}N-labeled compounds **1′f**, **4′f**, and **6′** compared to their unlabeled analogs **1f**, **4f**, and **6** suggest that these vibrations are mainly contributed by the fragments containing no labeled atoms; for this reason, we assigned them to the C—C stretching vibrations in the furoxan ring. For compound **1′f**, the lower-frequency shift of the weak band at 1480 cm^{-1} (by 9 cm^{-1}) compared to compound **1f** (see Table 3) can be attributed to a substantial contribution of the N(5)-containing fragment of the furoxan ring (C=N—O) to these vibrations. In the Raman spectrum (compounds **6** and **6′**, Table 5), this vibration (1466 cm^{-1}) is of medium

Table 2. Mass spectra of ^{15}N-labeled furoxans **1´f**, **4´f**, and **6´**

Compound	MS, m/z (I_{rel} (%))
^{79}Br-**1´f**	286 $[M]^+$ (28), 255 $[M - {}^{15}NO]^+$ (16), 240 $[M - NO_2]^+$ (23), 225 $[M - {}^{15}NO - {}^{14}NO]^+$ (44), 209 $[M - {}^{15}NO - NO_2]^+$ (98), 195 $[M - {}^{15}NO - 2\,{}^{14}NO]^+$ (6), 179 $[M - {}^{15}NO - {}^{14}NO - NO_2]^+$ (12), 167 $[Br + C_6H_4 + C]^+$ (29), 155 $[Br + C_6H_4]^+$ (9), 130 $[M - BrC_6H_4]^+$ (8), 114 $[M - BrC_6H_4 - O]^+$ (9), 99 $[M - BrC_6H_4 - {}^{15}NO]^+$ (32)
^{81}Br-**1´f**	288 $[M]^+$ (29), 257 $[M - {}^{15}NO]^+$ (16), 242 $[M - NO_2]^+$ (28), 227 $[M - {}^{15}NO - {}^{14}NO]^+$ (39), 211 $[M - {}^{15}NO - NO_2]^+$ (90), 197 $[M - {}^{15}NO - 2\,{}^{14}NO]^+$ (6), 181 $[M - {}^{15}NO - {}^{14}NO - NO_2]^+$ (13), 169 $[BrC_6H_4 + C]^+$ (23), 157 $[BrC_6H_4]^+$ (7), 131 $[M - BrC_6H_4 - 1]^+$ (7), 102 $[M - BrC_6H_4 - {}^{15}NO - 1]^+$ (100), 101 $[M - BrC_6H_4 - {}^{14}NO - 1]^+$ (9), 100 $[M - BrC_6H_4 - {}^{15}NO]^+$ (55)
^{79}Br-**4´f**	286 $[M]^+$ (28), 255 $[M - {}^{15}NO]^+$ (23), 240 $[M - NO_2]^+$ (17), 225 $[M - {}^{15}NO - {}^{14}NO]^+$ (69), 209 $[M - {}^{15}NO - NO_2]^+$ (55), 195 $[M - {}^{15}NO - 2\,{}^{14}NO]^+$ (7), 179 $[M - {}^{15}NO - {}^{14}NO - NO_2]^+$ (10), 167 $[BrC_6H_4 + C]^+$ (54), 155 $[BrC_6H_4]^+$ (9)], 130 $[M - BrC_6H_4]^+$ (5), 114 $[M - BrC_6H_4 - O]^+$ (22), 99 $[M - BrC_6H_4 - {}^{15}NO]^+$ (49)
^{81}Br-**4´f**	288 $[M]^+$ (27), 257 $[M - {}^{15}NO]$ (22), 242 $[M - NO_2]^+$ (16), 227 $[M - {}^{15}NO - {}^{14}NO]^+$ (72), 211 $[M - {}^{15}NO - NO_2]^+$ (54), 197 $[M - {}^{15}NO - 2\,{}^{14}NO]^+$ (6), 181 $[M - {}^{15}NO - {}^{14}NO - NO_2]^+$ (11), 169 $[BrC_6H_4 + C]^+$ (53), 157 $[BrC_6H_4]^+$ (7), 131 $[M - BrC_6H_4 - 1]^+$ (4), 102 $[M - BrC_6H_4 - {}^{15}NO - 1]^+$ (100), 101 $[M - BrC_6H_4 - {}^{14}NO - 1]^+$ (6), 100 $[M - BrC_6H_4 - {}^{15}NO]^+$ (57)
6´	396 $[M]^+$ (for two ^{79}Br) (6), 398 $[M]^+$ (for ^{79}Br and ^{81}Br) (12), 400 $[M]^+$ (for two ^{81}Br) (6), 334 (52), 336 (100), 338 $[M - 2\,{}^{15}NO]^+$ (50), 177 $[M - 2\,{}^{15}NO - 2\,{}^{81}Br]^+$ (13), 176 $[M - 2\,{}^{15}NO - 2\,{}^{81}Br - 1]^+$ (82), 175 $[M - 2\,{}^{15}NO - 2\,{}^{81}Br]^+$ (14), 174 $[M - 2\,{}^{15}NO - 2\,{}^{81}Br - 1]^+$ (10)

intensity and the corresponding band is shifted by 4 cm^{-1} to the lower frequencies.

Two absorption bands in the 1300—1450 cm^{-1} range (the lower-frequency band at 1300—1360 cm^{-1} and the higher-frequency band at 1380—1450 cm^{-1}) in the spectra of all the compounds studied (**1f**, **4f**, and **6** and their ^{15}N-labeled analogs **1´f**, **4´f**, and **6´**) were assigned to the O—N→O stretching vibrations in the furoxan ring; for the isomeric arylnitrofuroxans, the lower-frequency band (1300—1360 cm^{-1}) is masked by the band $\nu_s(NO_2)$. The in-plane bending vibrations in the furoxan ring absorb at 800—1150 cm^{-1}.

On the whole, the band assignments for the furoxan ring we made from our experimental data agree with the results[6b] obtained by solving vibrational problems and interpreting the IR spectra of various furoxan derivatives. However, the comprehensive set of our experimental data allow some refinements to the previous interpretation of the vibrational spectra of furoxans. For instance, the bands at 1500—1550 cm^{-1}, which have been assigned[6b] to the C=N—O vibrations, we assigned to the C—C stretching vibrations in the ring and the C=N—O fragment probably absorbs at 1410—1475 cm^{-1}. The stretching vibrations of the fragment O—N→O, which is an "embedded" nitro group, seem to be manifested at 1300—1450 cm^{-1} rather than at 1410—1475 cm^{-1} as has been reported earlier;[6b] in addition, the fragment O—N→O absorbs at two frequencies: 1380—1450 (ν_s(O—N→O)) and 1300—1360 cm^{-1} (ν_{as}(O—N→O)).

To sum up, we obtained experimental data in favor of the earlier proposed mechanism of formation of the furoxan ring in the synthesis of 3-nitro-4-R-furoxans **1** by nitrosation of dipotassium salts of 1-hydroxyimino-2,2-

Table 3. IR spectra of compounds **1f** and **1´f**

ν/cm^{-1}		$\Delta\nu/cm^{-1}$	Assignment
1f	**1´f**		
716	712	4	ρ_{Ph}; β_{fur}; ν_{C-Br}
732	729	3	—«—
757	753	4	—«—
793	789	4	—«—
828	828	0	σ_{NO_2}
855	845	10	σ_{fur}
988	982	6	—«—
1012	1008	4	—«—
1020	1020	0	σ_{Ph}
1077	1075	2	—«—
1198	1196	2	—«—
1261	1257	4	σ_{fur}
1281	1280	1	σ_{Ph}
1338	1332	6	$\nu^s_{NO_2}$; ν_{fur}
1480	1471	9	ν_{fur}
1518	1514	4	—«—
1549	1548	1	$\nu^{as}_{NO_2}$
1578	1578	0	ν_{Ph}
1598	1598	0	—«—
1620	1620	0	ν_{fur}
1630	1630	0	—«—

Note. Here and in Tables 4 and 5, the symbols ν, σ, and β denote stretching, in-plane bending, and bending vibrations, respectively; the superscripts s and as refer to symmetric and antisymmetric vibrational modes, respectively.

Table 4. IR spectra of compounds **4f** and **4´f**

ν/cm^{-1}		Δν/cm^{-1}	Assignment
4f	**4´f**		
710	709	1	β_{Ph}
749	740	9	β_{fur}
760	758	2	β_{Ph}; β_{fur}; ν_{C-Br}
802	799	3	—«—
831	828	3	—«—
940	955	—	
955	965	—	
990	990	0	σ_{Ph}
1019	1019	0	—«—
1075	1072	3	σ_{fur}; σ_{Ph}
1126	1119	7	—«—
1190	1190	0	σ_{Ph}
1228	1230	—	σ_{Ph}
1271	1270	1	σ_{Ph}; σ_{fur}
1290	1289	1	—«—
1309	1309	0	
1367	1362	5	$\nu^{s}_{NO_2}$; ν_{fur}
1400	1400	0	ν_{Ph}
1442	1435	7	ν_{fur}
1488	1488	0	ν_{Ph}
1512	1509	3	ν_{fur}; ν_{Ph}
1579	1570	9	$\nu^{as}_{NO_2}$; ν_{fur}
1620	1601	19	ν_{fur}

Table 5. IR and Raman spectra* of compounds **6** and **6´**

ν/cm^{-1}		Δν/cm^{-1}	Assignment
6	**6´**		
725 [726]	722 [722]	3 [4]	β_{Ph}; ν_{C-Br}
738	731	7	ρ_{fur}
752 [746]	746 [742]	6 [4]	—«—
830 [826]	820 [820]	10 [6]	σ_{fur}, σ_{Ph}
840	832	8	—«—
968	958	10	σ_{fur}
995 [990]	991 [986]	4 [4]	—«—
1018 [1012]	1018 [1008]	0 [4]	σ_{Ph}
1072 [1070]	1072 [1070]	0 [0]	—«—
1112 [1114]	1102 [1102]	10 [12]	σ_{fur}
	1118		
1180 [1174]	1180 [1174]	0 [0]	σ_{Ph}
1189	1187	2	—«—
1280	1280	0	—«—
1305 [1300]	1301 [1298]	4 [2]	ν_{fur}
1333 [1326]	1322 [1320]	11 [6]	—«—
1398 [1394]	1398 [1392]	0 [2]	ν_{fur}; ν_{Ph}
1448 [1466]	1448 [1462]	0 [4]	—«—
1505 [1500]	1502	3	—«—
1574 [1514]	1582 [1514]	— [0]	ν_{Ph}
1596 [1570]	1561 [1556]	35 [14]	ν_{fur}
1602 [1594]	1602 [1594]	0 [0]	ν_{Ph}

* The Raman spectra are given in square brackets.

dinitro-1-R-ethanes **2** with $NaNO_2$ in acetic acid. In addition, our comparative analysis of the IR and Raman spectra of three ^{15}N-labeled furoxans and their unlabeled analogs allowed some refinements to the known assignments of the absorption bands in the vibrational spectra of furoxans.

Experimental

Dipotassium salt **2a**, 4(3)-(4-bromophenyl)-3(4)-nitrofuroxans **1f** and **4f**, and ^{15}N-labeled samples **1´f** and **4´f** were prepared according to known procedures.[2] The melting point of compound **1f** (**1´f**) is 80.5—81 °C (*cf.* Ref. 2: m.p. 80—81 °C); the melting point of compound **4f** (**4´f**) is 57—58 °C (*cf.* Ref. 2: m.p. 56—57 °C). The synthesis of 3,4-bis(4-bromophenyl)-furoxan **6** and its ^{15}N-labeled analog **6´** was carried out as described earlier.[7] The melting point of compound **6** (**6´**) is 163—164 °C (*cf.* Ref. 7: m.p. 164 °C).

NMR spectra were recorded on Bruker WM-250 (^1H, 250 MHz) and Bruker AM-300 spectrometers (^{13}C, 75.5 MHz; ^{14}N and ^{15}N, 21.5 MHz) in DMSO-d_6. Chemical shifts δ are referenced to Me_4Si (^1H, ^{13}C) as the internal standard and to $MeNO_2$ (^{14}N and ^{15}N) as the external standard. Mass spectra were measured on a Varian MAT CH 6 instrument (EI, 70 eV).

The UV spectra of solutions of dipotassium salt **2a** were recorded on a Specord UV-VIS instrument for pH = 13.0—3.0 and on a Specord UV-VIS M40 instrument for moderately acidic media (C_{H2SO4} = 0.2—45%). In both cases, quartz 10-mm-thick cells were used.

IR spectra were recorded on an IFS 113 v FTIR spectrometer (KBr pellets). Raman spectra were recorded on Ramanor HG-2S, Ramalos, and U 1000 spectrometers with an argon laser as an excitation source.

Determination of the ionization constants of the dipotassium salt of 1-hydroxyimino-1-(4-methoxy-3,5-dinitrophenyl)-2,2-dinitroethane (2a). Dipotassium salt **2a** was dissolved in distilled water to produce a solution with the concentration $C = 0.82 \cdot 10^{-3}$ mol L^{-1}. Its aliquots (1 mL) were placed in volumetric flasks (50 mL) and working solutions were prepared by adding water, 0.1 *M* NaOH, buffer solutions (Table 6), or sulfuric acid solutions with precise concentrations (Table 7) to a total

Table 6. Processing of the UV spectroscopic data for determination of pK_{a1} of compound **2a**

Entry	pH	Optical density, *D*	$\log\frac{\varepsilon_B - \varepsilon}{\varepsilon - \varepsilon_{BH^+}}$
1	6.0	0.65	—
2	13.0	0.65	—
3	5.0	0.65	—
4	2.5	0.18	0.90
5	3.0	0.23	0.64
6	4.0	0.32	0.20
7	4.5	0.38	0.02
8	4.25	0.34	0.15
9	4.75	0.44	0.18

* $C_{\mathbf{2a}} = 0.04 \cdot 10^{-6}$ mol L^{-1}.

Table 7. Processing of the experimental data for determination of pK_{a_2} of compound **2a**

Entry	$C_{H_2SO_4}$ (%)	Optical density, *D*	Acidity function		$\log\frac{\varepsilon_{BH^+}-\varepsilon}{\varepsilon-\varepsilon_{BH^{2+}}}$
			H_0	H_A	
1	0.20	0.1233	—	—	—
2	0.60	0.1245	—	—	—
3	8.30	0.1177	−0.697	−0.996	−1.353
4	24.50	0.0645	−1.324	−1.807	−0.480
5	30.25	0.0302	−1.737	−2.577	0.480
6	35.13	0.0166	−2.069	−2.894	0.804
7	44.67	—	—	—	—

* $C_{\mathbf{2a}} = 0.04 \cdot 10^{-6}$ mol L^{-1}.

volume of 50 mL. The concentrations of the H_2SO_4 solutions were taken from tables relating concentration to specific gravity. The ionization constants of the oxime and dinitromethyl fragments were determined graphically according to standard formulas.[4,5]

The pK_{a_1} value of the oxime fragment was determined from the slope of a straight line governed by Eq. (1) (see Table 6). The *X*-intercept corresponds to $pK_{a_1} = 4.43$ (Fig. 1).

Since the dinitromethyl group in salts **2** is protonated at much lower pH values than the oxime group, its pK_{a_2} was determined by titrating the working solutions of salt **2a** with sulfuric acid solutions of moderate concentrations ($C_{H_2SO_4} < 45\%$; Table 7).

In Fig. 2, $\log[(\varepsilon_{BH^+} - \varepsilon)/(\varepsilon - \varepsilon_{BH_2^+})]$ is plotted versus H_x. The tangent of the slope of the straight line for H_0 (see Fig. 2, line *1*) largely differs from unity; $\log[(\varepsilon_{BH^+} - \varepsilon)/(\varepsilon - \varepsilon_{BH_2^+})] = -1.58 + 1.74H_0$). Therefore, the acidity function of the dinitromethyl fragment is not H_0. For H_A, the equation is

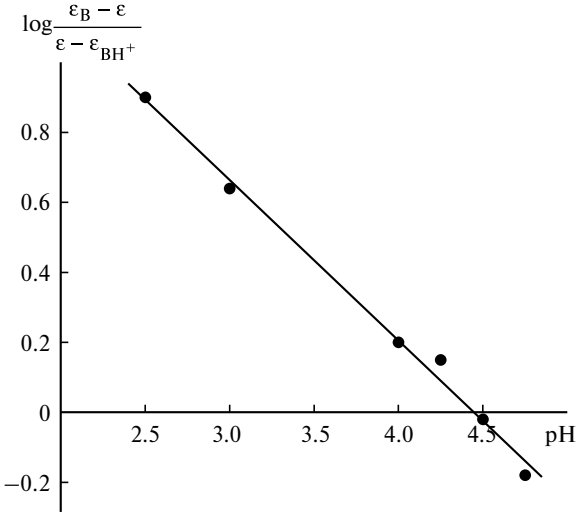


Fig. 1. Determination of the ionization constant pK_{a_1} of the oxime fragment in compound **2a**.

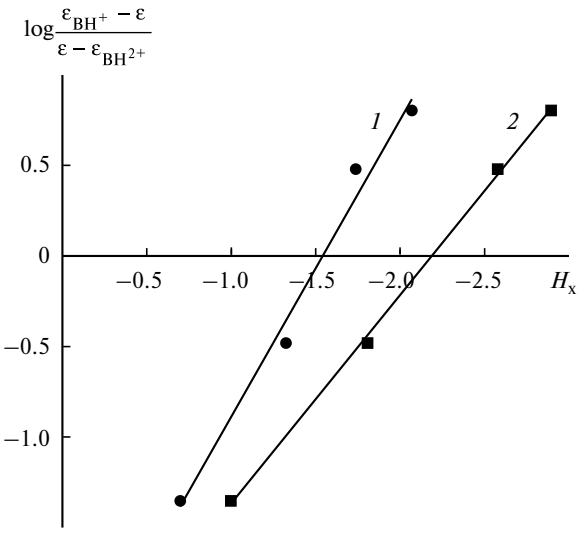


Fig. 2. Determination of the ionization constant pK_{a_2} of the dinitromethyl fragment in compound **2a**.

$\log[(\varepsilon_{BH^+} - \varepsilon)/(\varepsilon - \varepsilon_{BH_2^+})] = -2.23 + 1.10H_A$ and hence pKa_2 is 2.23 (see Fig. 2, line *2*).

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