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Synthesis of 1,3- and 1,4-bis(3-nitrofurazan-4-yl)benzenes and isomeric 1,3- and 1,4-bis[3(4)-nitrofuroxan-4(3)-yl]benzenes

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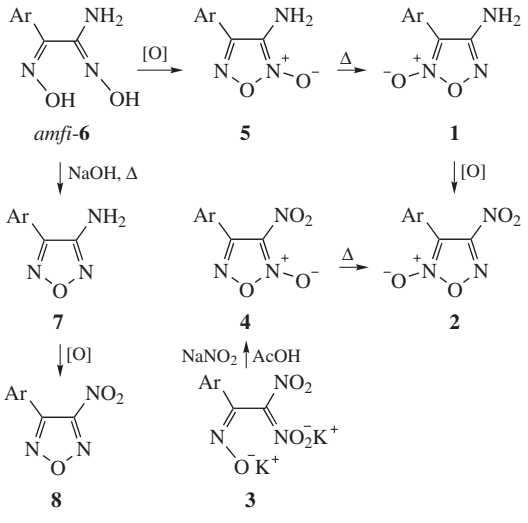
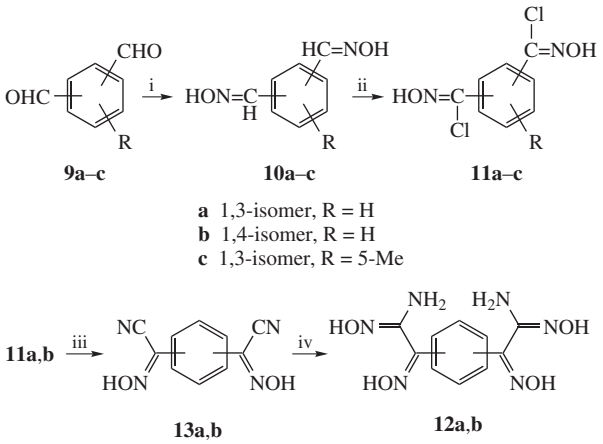
The 1,3- and 1,4-bis(3-nitrofurazan-4-yl)benzenes have been synthesized by dehydration of 1,3- and 1,4-bis(2-aminoglyoximo-1-yl)benzenes followed by oxidation of amino groups. The 1,3- and 1,4-bis(3-nitrofuroxan-4-yl)benzenes have been prepared by nitrozylation of tetrapotassium salts of 1,3- and 1,4-bis(2,2-dinitro-1-oximinoethyl)benzenes and thermally isomerized to 1,3- and 1,4-bis(4-nitrofuroxan-3-yl)benzenes.

There are two main approaches to the preparation of arylnitrofuroxans, namely, oxidation of 4-amino-3-arylfuroxans **1** into 3-aryl-4-nitrofuroxans[1] **2** and nitrosylation of 1-aryl-2,2-dinitro-1-oximinoethane dipotassium salts **3** with the formation of 4-aryl-3-nitrofuroxans[2] **4**. The latter can be thermally isomerized to 3-aryl-4-nitofuroxans[2] **2** being more preferential in terms of thermodynamics. Initial 4-amino-3-arylfuroxans **1** are synthesized by thermal isomerization of 3-amino-4-arylfuroxans **5** formed, in turn, through oxidation of 1-amino-2-arylglyoximes *amfi*-form **6**.[3,4] Dehydration of compounds **6** (*amfi*- and *anti*- or *syn*-forms) under the action of inorganic bases is practiced to prepare 3-amino-4-arylfurazans[5] **7**, which can be oxidized into 4-aryl-3-nitrofurazans[5] **8** (Scheme 1).

In this paper, all these approaches were investigated to prepare isomeric 1,3- and 1,4-bis[3(4)-nitrofuroxan-4(3)-yl]-benzenes and their nitrofurazanyl analogues – potential high-energy compounds. Benzene-1,3(**9a**)- and 1,4(**9b**)-dicarboxaldehydes, as well as 5-methylbenzene-1,3-dicarboxaldehyde (**9c**), were selected as initial compounds. Using known methods,[6,7] we transformed dicarboxaldehydes **9a–c** to corresponding oximes **10a–c** under the action of hydroxylamine, and compounds **10a–c** were treated with gaseous Cl_2 in aqueous HCl to obtain 1,3- and 1,4-bis(hydroximoyl) chlorides **11a–c**. To synthesize 1,3- and 1,4-bis(2-aminoglyoximo-1-yl)benzenes **12a**,**b**,



Scheme 1



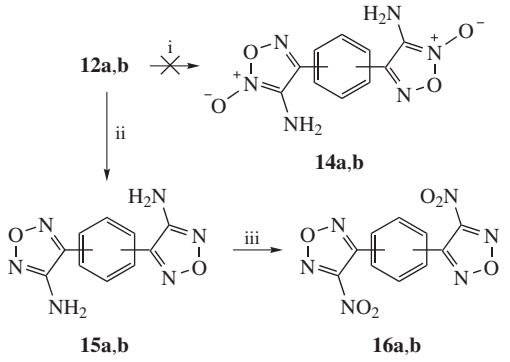
Scheme 2 *Reagents and conditions*: i, $NH_2OH{\cdot}HCl$ (2 mol), NaOH, MeOH, 40–50 °C, 30 min; ii, Cl_2 (2 mol), conc. HCl/MeOH, 0–10 °C, 1 h; iii, KCN (2 mol), H_2O, 20 °C, 1 h; iv, $NH_4OH{\cdot}HCl$ (2 mol)/$NaHCO_3$ (2 mol), H_2O, 100 °C, 4 h.

precursors of 1,3- and 1,4-bis[aminofuroxanyl(furazanyl)]-benzenes, compounds **11a**,**b** were first transformed to 1,3- and 1,4-bis(cyanooximinomethyl) derivatives **13a**,**b** and then treated with hydroxylamine (Scheme 2).† It could be expected that compounds **12a**,**b** will mainly have *amfi*-configuration because the similar transformation of arylhydroximoyl chlorides results in a mixture of *amfi*- and *syn*-isomers of 1-amino-2-arylglyoximes with preferential formation of *amfi*-form.[3]

The most preferable oxidizers for oxidizing *amfi*-form of 1-amino-2-arylglyoximes **6** to 3-amino-4-arylfuroxans **5** are Br_2 in hydrochloric acid[3] or $K_3Fe(CN)_6$ in the presence of bases (ammonia or aqueous NaOH solution).[4(a),(b)] Other oxidizers either badly oxidize (Cl_2, CrO_3, $KMnO_4$) or do not oxidize (N_2O_4, NaOCl, HNO_3) 1-amino-2-arylglyoximes into 3-amino-4-arylfuroxans.[8(a),(b)] Unfortunately, all our attempts to oxidize 1,3- and 1,4-bis(2-aminoglyoximo-1-yl)benzenes **12a**,**b** to 1,3- and 1,4-bis(3-aminofuroxan-4-yl)benzenes **14a**,**b** with Br_2 in hydrochloric acid resulted in a complex mixture of the compounds (TLC data), in which the aminofuroxan ring was absent [signals of C(3) furoxan carbon atoms at 108–110 ppm were absent from the ^{13}C NMR spectra]. A major part of initial aminoglyoximes **12a**,**b** decomposed when using $K_3Fe(CN)_6$ in the presence of different bases. It is likely that compounds

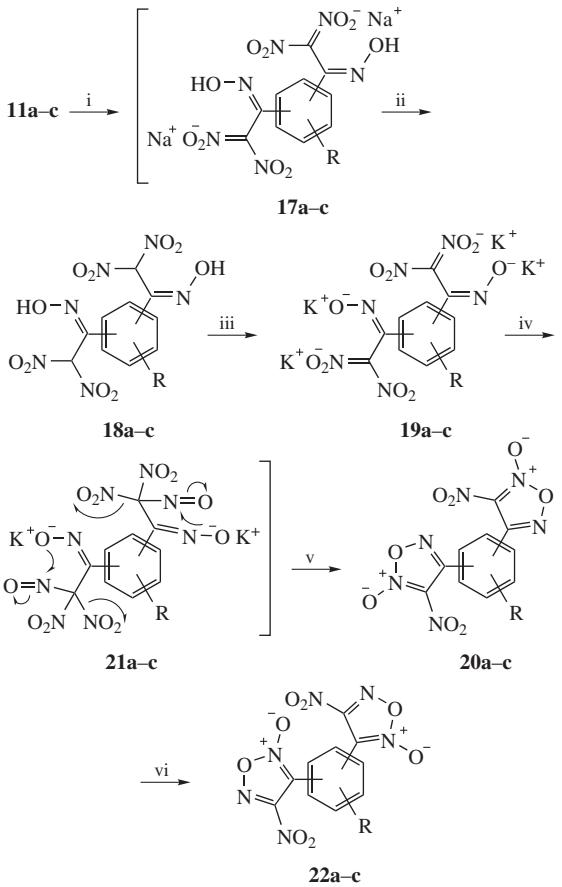
12a,**b**, which were prepared according to Scheme 2, do not occur in the *amfi*-configuration. Therefore, they cannot be oxidized to aminofuroxans.

More successful results were obtained in the synthesis of nitrofurazanyl derivatives from bis(aminoglyoximes) **12a**,**b**. These compounds were dehydrated to 1,3- and 1,4-bis(3-aminofurazan-4-yl)benzenes **15a**,**b** by their refluxing in aqueous NaOH solution and the amino groups in compounds **15a**,**b** were then oxidized to the nitro groups with H_2O_2 in CF_3COOH. Target 1,3- and 1,4-bis(3-nitrofurazan-4-yl)benzenes **16a**,**b** were synthesized in 56 and 95% yields, respectively (Scheme 3).‡



Scheme 3 *Reagents and conditions*: i, $K_3Fe(CN)_6$ (4 mol), 2.4% aqueous NH_3, H_2O, 5 °C, 20 min; ii, 2 N NaOH, 100 °C, 1.5 h; iii, 30% H_2O_2 (100 mol)/CF_3COOH (25 mol), 50 °C, 2 h.

To obtain 1,3- and 1,4-bis(nitrofuroxanyl)benzenes, the reaction of all three bis(hydroximoyl) chlorides **11a–c** with an excess of dinitromethane sodium salts at low temperature in DMF was examined. Sodium salts of 1,3- and 1,4-bis(2,2-dinitro-1-oximinoethyl)benzenes (**17a–c**) were obtained and purified from dinitromethane by extraction with $CHCl_3$. The salts were acidified with H_2SO_4 to 1,3- and 1,4-bis(2,2-dinitro-1-oximinoethyl)benzenes **18a–c** and transformed to tetrapotassium salts of 1,3- and 1,4-bis(2,2-dinitro-1-oximinoethyl)benzenes (**19a–c**) by treatment with AcOK in MeOH. Nitrosylation of salts **19a–c** with $NaNO_2$ in AcOH afforded 1,3- and 1,4-bis(3-nitrofuroxan-4-yl)benzenes **20a–c**. The reaction evidently runs through intermediates **21a–c**. Then, 3-nitrofuroxan derivatives **20a–c** were thermally isomerized to 1,3- and 1,4-bis(4-nitrofuroxan-3-yl)-benzenes **22a–c** in high yields by refluxing in toluene (Scheme 4).§



Scheme 4 *Reagents and conditions*: i, $NaCH(NO_2)_2$ (4 mol), DMF, –20 °C, 48 h; ii, $CHCl_3$; iii, 20% H_2SO_4; iv, AcOK (10 mol), MeOH, 5 °C, 1 h; v, $NaNO_2$ (5 mol), $AcONa{\cdot}3H_2O$, AcOH, 20–30 °C, 30 min; vi, toluene, 2 h.

† All new compounds exhibited satisfactory elemental analyses. IR spectra were measured on a UR-20 spectrometer; ^1H and ^{13}C NMR spectra were recorded on Bruker AC200-31 (200 MHz for ^1H and 50.3 MHz for ^{13}C) and Bruker AM300 (300 MHz for ^1H and 75.5 MHz for ^{13}C) spectrometers ($CDCl_3$ was used as the internal standard). ^{13}C NMR spectra were recorded under proton decoupling conditions. ^{14}N NMR spectra were recorded on a Bruker AM300 (22 MHz) spectrometer ($MeNO_2$ was used as the internal standard). Mass spectra were measured on a Finnigan MAT INCOS-50 instrument. TLC was carried out on Silufol UV-254 plates. Melting points were measured on a Gallenkamp instrument (Sanyo).

1,3-Bis(2-aminoglyoximo-1-yl)benzene **12a**: yield 69%, mp 180–182 °C, R_f 0.31 (EtOAc). ^1H NMR ($[^2H_6]$DMSO) δ: 5.7 (br. s, 4H, NH_2), 7.35 (t, 1H, C^5H in Ar, ^3J 7.5 Hz), 7.6 (d, 2H, C^4H, C^6H in Ar, ^3J 7.5 Hz), 7.9 (s, 1H, C^2H in Ar), 9.45 (br. s, 2H, OH), 11.6 (br. s, 2H, OH). IR (ν/cm^{-1}): 3464 (NH_2), 3350 (OH), 2850 (CH), 2360, 1652 (C=N), 1484, 1376, 1280, 980, 872, 812, 700.

1,4-Bis(2-aminoglyoximo-1-yl)benzene **12b**: yield 31%, mp 214–215 °C, R_f 0.16 (EtOAc). ^1H NMR ($[^2H_6]$DMSO) δ: 5.76 (br. s, 4H, NH_2), 7.56 (s, 4H in Ar), 9.48 (br. s, 2H, OH), 11.70 (br. s, 2H, OH). IR (ν/cm^{-1}): 3472 (NH_2), 3400 (OH), 3020 (CH), 2980 (CH), 1684 (C=N), 1584, 1416, 1372, 1260, 1140, 1060, 1026, 960, 844, 828.

1,3-Bis(cyanooximinomethyl)benzene **13a**: yield 79%, mp 195–196 °C, R_f 0.38 ($CHCl_3$:EtOAc, 5:1). ^1H NMR ($[^2H_6]$DMSO) δ: 7.65 (t, 1H, C^5H in Ar, ^3J 5.9 Hz), 7.85 (d, 2H, C^4H, C^6H in Ar, ^3J 5.9 Hz), 8.05 (s, 1H, C^2H in Ar), 14.00 (s, 2H, OH). IR (ν/cm^{-1}): 3384 (OH), 3236 (OH), 3028 (CH), 2988 (CH), 2872 (CH), 2236 (CN), 1612 (C=N), 1440, 1380, 1328, 1256, 1112, 1064, 1016, 896, 864, 800, 620.

1,4-Bis(cyanooximinomethyl)benzene **13b**: yield 90%, mp 192–194 °C, R_f 0.55 ($CHCl_3$:EtOAc, 5:1). ^1H NMR ($[^2H_6]$DMSO) δ: 7.88 (s, 4H in Ar), 14.1 (br. s, 2H, OH). IR (ν/cm^{-1}): 3528 (OH), 3488 (OH), 3008 (CH), 2984 (CH), 2384, 2232 (CN), 1624 (C=N), 1532, 1452, 1304, 1288, 1224, 1072, 1044, 980, 848, 832.

‡ *1,3-Bis(3-aminofurazan-4-yl)benzene* **15a**: yield 39%, mp 220–221 °C, R_f 0.42 ($CHCl_3$:EtOAc, 1:1). ^1H NMR ($[^2H_6]$DMSO) δ: 6.35 (br. s, 4H, NH_2), 7.7 (t, 1H, C^5H in Ar, ^3J 8.6 Hz), 7.9 (d, 2H, C^4H, C^6H in Ar, ^3J 8.6 Hz), 8.1 (s, 1H, C^2H in Ar). ^{13}C NMR ($[^2H_6]$DMSO) δ: 126.4 (C^1, C^3 in Ar), 126.8, 129.8, 130.1 (C^2, C^4, C^5 and C^6 in Ar), 146.5, 155.4 (C^3, C^4 in furazan ring). IR (ν/cm^{-1}): 3472 (NH_2), 3244 (CH), 2852 (CH), 2368 (CH), 1632 (C=N), 1572, 1516, 1396, 1280, 980, 872, 812, 700. MS, *m*/*z*: 244 (M^+).

1,4-Bis(3-aminofurazan-4-yl)benzene **15b**: yield 68%, mp 205–207 °C, R_f 0.32 ($CHCl_3$:EtOAc, 1:1). ^1H NMR ($[^2H_6]$DMSO) δ: 6.30 (br. s, 4H, NH_2), 7.90 (s, 4H, CH in Ar). ^{13}C NMR ($[^2H_6]$DMSO) δ: 127.15 (C^1, C^4 in Ar), 128.30 (C^2, C^3 in Ar), 146.26, 155.24 (C^3, C^4 in furazan ring). IR (ν/cm^{-1}): 3432 (NH_2), 3344 (NH_2), 3204, 3201 (CH), 2352 (CH), 1644 (C=N), 1552, 1480, 1388, 1280, 1068, 984, 844, 736. MS, *m*/*z*: 244 (M^+).

1,3-Bis(3-nitrofurazan-4-yl)benzene **16a**: yield 56%, mp 81–83 °C, R_f 0.26 (CCl_4:$CHCl_3$, 1:1). ^1H NMR ($[^2H_6]$acetone) δ: 7.93 (t, 1H, C^5H in Ar, ^3J 7.9 Hz), 8.22 (d, 2H, C^4H, C^6H in Ar, ^3J 7.9 Hz), 8.37 (s, 1H, C^2H in Ar). ^{13}C NMR ($CDCl_3$) δ: 128.71 (C^1, C^3 in Ar), 129.43, 131.01 (C^2, C^5 in Ar), 132.83 (C^4, C^6 in Ar), 149.81 (C^4 in furazan ring), 159.01 (C^3 in furazan ring). ^{14}N NMR ($[^2H_6]$acetone) δ: –35.07 (s, NO_2). IR (ν/cm^{-1}): 2850 (CH), 2360 (CH), 1652 (C=N), 1540 (NO_2), 1484, 1344 (NO_2), 1280, 980, 872, 812, 700.

1,4-Bis(3-nitrofurazan-4-yl)benzene **16b**: yield 95%, mp 125–127 °C, R_f 0.28 (CCl_4:$CHCl_3$, 1:1). ^1H NMR ($[^2H_6]$acetone) δ: 8.12 (s, 4H, Ar). ^{13}C NMR ($[^2H_6]$acetone) δ: 125.99 (C^1, C^4 in Ar), 130.08 (C^2, C^3 in Ar), 149.84 (C^4 in furazan ring), 159.79 (C^3 in furazan ring). ^{14}N NMR ($[^2H_6]$acetone) δ: –35.11 (s, NO_2). IR (ν/cm^{-1}): 3100 (CH), 2850 (CH), 1572, 1544 (NO_2), 1372 (NO_2), 1224, 1060, 1000, 912, 840, 824, 764.

To summarize, 1,3- and 1,4-bis(3-nitrofurazan-4-yl)benzenes and isomeric 1,3- and 1,4-bis[3(4)-nitrofuroxan-4(3)yl]benzenes were for the first time synthesized in this work. Their structures were established by spectral (^{1}H, ^{13}C, ^{14}N NMR, IR and mass spectra) and elemental analysis data. It was shown that synthesized 1,3- and 1,4-bis(aminoglyoximoyl)benzenes are not evidently in *amfi*-configuration that hindered their oxidation to corresponding 1,3- and 1,4-bis(3-aminofuroxan-4-yl)benzenes.

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§ *1,3-Bis(3-nitrofuroxan-4-yl)benzene* **20a**: yield 56%, mp 139.5–140.5 °C, R_f 0.29 (CCl_4:EtOAc, 1:1). ^{1}H NMR ([$^2H_6$]acetone) δ: 7.92 (t, 1H, C^{5}H in Ar, ^3J 7.9 Hz), 8.15 (d, 2H, C^{4}H, C^{6}H in Ar, ^3J 7.9 Hz), 8.28 (s, 1H, C^{2}H in Ar). ^{13}C NMR ([$^2H_6$]acetone) δ: 125.42 (C^1, C^3 in Ar), 127.33 (C^3 in furoxan ring), 129.02, 129.82 (C^2, C^5 in Ar), 132.22 (C^4, C^6 in Ar), 151.35 (C^4 in furoxan ring). ^{14}N NMR ($CDCl_3$) δ: –38.35 (s, NO_2). IR (ν/cm^{-1}): 3096 (CH), 1632 (furoxan ring), 1544 (NO_2), 1468, 1448, 1392 (NO_2), 1264, 1220, 1172, 1040, 1000, 984, 856, 808, 756, 720.

1,4-Bis(3-nitrofuroxan-4-yl)benzene **20b**: yield 45%, mp 180–203 °C, R_f 0.31 (CCl_4:EtOAc, 1:1). ^{1}H NMR ([$^2H_6$]acetone) δ: 8.13 (s, 4H in Ar). ^{13}C NMR ($CDCl_3$) δ: 128.17 (C^3 in furoxan ring), 129.75 (C^1, C^4 in Ar), 129.78 (C^2, C^3, C^5 and C^6 in Ar), 151.84 (C^4 in furoxan ring). ^{14}N NMR ([$^2H_6$]acetone) δ: –38.30 (s, NO_2). IR (ν/cm^{-1}): 3112 (CH), 2800 (CH), 2332, 1632 (furoxan ring), 1548 (NO_2), 1436, 1340 (NO_2), 1200, 1012, 984, 844, 792, 712.

1,3-Bis(3-nitrofuroxan-4-yl)-5-methylbenzene **20c**: yield 42%, mp 122–124 °C, R_f 0.20 (CCl_4:$CHCl_3$, 1:1). ^{1}H NMR ([$^2H_6$]acetone) δ: 2.60 (s, 3H, Me), 7.97 (s, 2H in Ar), 8.08 (s, 1H in Ar). ^{13}C NMR ($CDCl_3$) δ: 20.33 (Me), 125.73 (C^3 in furoxan ring), 127.41 (C^5 in Ar), 132.93 (C^4, C^6 in Ar), 139.72 (C^2 in Ar), 151.78 (C^4 in furoxan ring). ^{14}N NMR ([$^2H_6$]acetone) δ: –38.35 (s, NO_2). IR (ν/cm^{-1}): 2932 (CH), 2876 (CH), 1648 (furoxan ring), 1628 (Ar), 1536 (NO_2), 1468, 1412, 1348 (NO_2), 1260, 1172, 1076, 880, 844, 776.

1,3-Bis(4-nitrofuroxan-3-yl)benzene **22a**: yield 91%, mp 142–144 °C, R_f 0.21 (CCl_4:$CHCl_3$, 1:1). ^{1}H NMR ([$^2H_6$]acetone) δ: 7.92 (t, 1H, C^{5}H in Ar, ^3J 7.9 Hz), 8.09 (d, 2H, C^{4}H, C^{6}H in Ar, ^3J 7.9 Hz), 8.22 (s, 1H, C^{2}H in Ar). ^{13}C NMR ([$^2H_6$]acetone) δ: 110.00 (C^3 in furoxan ring), 121.90 (C^1, C^3 in Ar), 129.53, 131.04 (C^2, C^5 in Ar), 132.84 (C^4, C^6 in Ar), 158.87 (C^4 in furoxan ring). ^{14}N NMR ($CDCl_3$) δ: –34.88 (s, NO_2). IR (ν/cm^{-1}): 1632 (furoxan ring), 1568 (NO_2), 1512, 1484, 1372 (NO_2), 1296, 1268, 1144, 1116, 1072, 1028, 1000, 988, 896, 828, 796, 792, 704.

1,4-Bis(4-nitrofuroxan-3-yl)benzene **22b**: yield 90%, mp 212–214 °C, R_f 0.20 (CCl_4:$CHCl_3$, 1:1). ^{1}H NMR ([$^2H_6$]acetone) δ: 8.09 (s, 4H in Ar). ^{13}C NMR ($CDCl_3$) δ: 110.08 (C^3 in furoxan ring), 123.91 (C^1, C^4 in Ar), 130.23 (C^2, C^3, C^5 and C^6 in Ar), 158.85 (C^4 in furoxan ring). ^{14}N NMR ([$^2H_6$]acetone) δ: –34.91 (s, NO_2). IR (ν/cm^{-1}): 1624 (furoxan ring), 1612 (Ar), 1536 (NO_2), 1488, 1408, 1364 (NO_2), 1292, 1268, 1132, 1076, 992, 840, 792.

1,3-Bis(4-nitrofuroxan-3-yl)-5-methylbenzene **22c**: yield 70%, mp 138–141 °C, R_f 0.20 (CCl_4:$CHCl_3$, 1:1). ^{1}H NMR ([$^2H_6$]acetone) δ: 2.56 (s, 3H, Me), 7.88 (s, 2H in Ar), 7.99 (s, 1H in Ar). ^{13}C NMR ($CDCl_3$) δ: 20.33 (Me), 109.95 (C^3 in furoxan ring), 121.81 (C^1, C^3 in Ar), 128.19 (C^2 in Ar), 133.10 (C^4, C^6 in Ar), 139.80 (C^5 in Ar), 158.85 (C^4 in furoxan ring). ^{14}N NMR ([$^2H_6$]acetone) δ: –35.07 (s, NO_2). IR (ν/cm^{-1}): 2920 (CH), 1624 (furoxan ring), 1560 (NO_2), 1504, 1356 (NO_2), 1272, 1136, 1076, 1016, 872, 832, 776, 704.