Nucleophilic substitution in the furazan series. Reactions of nitrofurazans with ammonia

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The reactions of 3-nitro-4-R-furazans with ammonia were studied. The effect of the substituent R on the specific features of the nucleophilic substitution reaction observed was considered. The nitro group attached to the furazan ring can act as both the leaving group and the activating group facilitating the displacement of the second substituent (for example, OR′ or $N(NO_2)R'$).

Key words: furazans, nitrofurazans, aminofurazans, nitramines, alkoxyfurazans, nucleophilic substitution.

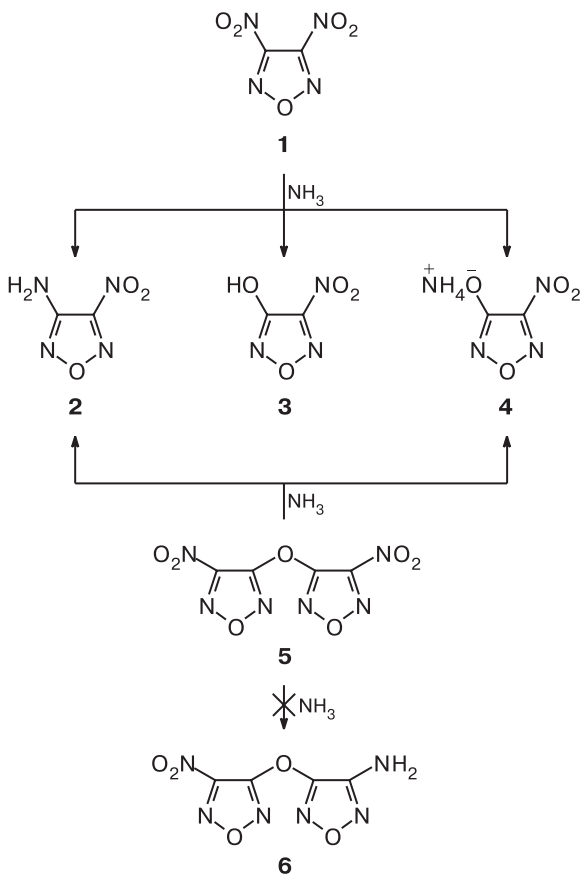
In 1968, the first publication appeared pointing to the expediency of using nitrofurazans as explosives.[1] This circumstance stimulated the development of the chemistry and research into the properties of these compounds.[2,3] Thus nitrofurazans were demonstrated to be fairly efficient as components of various energetic compositions.[4—15] It is noteworthy that the furazan ring itself is an explosophoric fragment. Therefore, even amino-, azo-, and azoxyfurazans containing no nitro groups are also of interest as components of energetic compositions.[16—22]

Study of the chemical stability and targeted modification of nitrofurazans are topical tasks. It has been shown previously that the nitro group in the furazan ring is easily displaced on treatment with nucleophiles. Thus the corresponding products have been obtained in the reactions with O-[6,23—29] and S-nucleophiles;[30] in addition, the nitro group has been successfully replaced by chlorine.[31]

This study represents further development of our research into the nucleophilic substitution in the furazan series and deals with the reaction of nitrofurazans with ammonia.

Previously, we reported that an aqueous solution of ammonia reacts with 3,4-dinitrofurazan (**1**) to give a mixture of amino- and hydroxyfurazans.[27] It is also known that anhydrous ammonia taken as a solution in MeCN is capable of displacing the nitro group in 3-amino-4-nitrofurazan (**2**) under a high pressure.[32] We found that selective displacement of one nitro group in compound **1** proceeds smoothly on treatment with an excess of a saturated solution of ammonia in anhydrous $CHCl_3$ or CCl_4 (Scheme 1). The change in the reaction temperature from −10 °C to the boiling temperature has virtually no influence on the yield of amine **2**, which equals 95—100% (GLC data, preparative yield 85—90%). Note that the displacement of one nitro group in 3,4-dinitrofurazan *N*-oxide (3,4-dinitrofuroxan) on treatment with ammonia proceeds smoothly only at −15 to −20 °C; at higher temperatures, the reaction is complicated by side processes.[33,34]

Scheme 1



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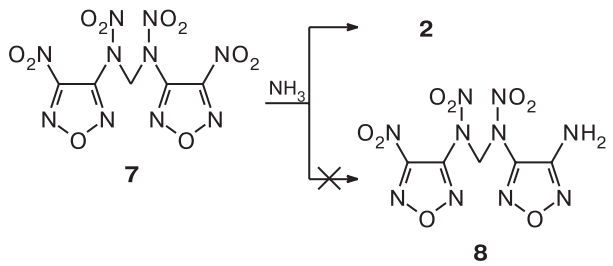
The same reaction carried out in dinitrofurazan **1** solutions in DMSO, MeCN, glyme, or benzene results in a lower yield of compound **2**. For example, in anhydrous MeCN at −10 °C and at a **1** : NH_3 ratio of 1 : 2, the yield of **2** is only 17%, the reaction giving also 3-hydroxy-4-nitrofurazan (**3**) (35%) and its ammonium salt **4** (40%). A twofold increase in the amount of ammonia increases the yield of amine **2** to 48% and only salt **4** (37%) is isolated as a side product. The formation of the hydroxy derivative is a consequence of participation of the nitrite ion,[35] capable of functioning as an O-nucleophile in a dipolar solvent. In the presence of moisture, the hydroxy derivatives are formed in even higher yields. Note that the presence of hydroxy derivatives formed as side products appreciably increases the solubility of amine **2** in water, which entails loss of the product during isolation.

It is noteworthy that for an equimolar ratio of compound **1** and ammonia, the reaction is complicated, irrespective of the solvent, by the formation of not only hydroxyfurazans but also other side products. This is due to diazotization of compound **2** and subsequent transformations of the intermediate diazonium salt; these processes normally accompany reactions with nitro group displacement.[36,37]

Amino nitro ether **6** is a fairly interesting compound from the practical standpoint. However, the reaction of 4,4′-dinitrodifurazanyl ether (**5**) with ammonia in $CHCl_3$ or CH_2Cl_2 involves only the ether bond, while the nitro groups remain intact (see Scheme 1). This results in the quantitative formation of amine **2**, and the leaving group is liberated quantitatively as salt **4** (the latter precipitates during the reaction). No even traces of the asymmetrical ether **6** (GLC and TLC data) are found in the reaction medium. A similar outcome is observed in anhydrous MeCN; however, due to the solubility of salt **4** in this solvent, the product separation becomes more difficult. Note that complete transformation of ether **5** into amine **2** takes a ~4 times longer period than the synthesis of **2** from nitro compound **1** under analogous conditions. The ability of the furazanoxy group to act as a leaving group has also been noted in our previous publication.[38]

The reaction of nitramine **7** with ammonia in $CHCl_3$ proceeds slowly and gives the same amine **2**. The possibility of cleavage of nitramines on treatment with nucleophiles has been noted in the literature.[39] In MeCN, the displacement of the nitramine fragment proceeds rapidly, and amine **2** can be isolated in 54% yield (in relation to one furazan ring) as soon as 0.5 h after the beginning of the reaction (Scheme 2). Note that under these conditions, both the yields and the rates of formation of amine **2** from nitramine **7** and ether **5** are similar. As in the case of ether **5**, no product resulting from replacement of the nitro group attached to the furazan ring, *e.g.*, such as compound **8**, was detected. The attempts to isolate the substances formed from the eliminated nitramine fragment of the initial molecule failed.

Scheme 2



Thus, the nitramino group bound to the furazan ring can be displaced on treatment with nucleophiles, like NO_2, N(O)NR, Cl, F,[40] SO_2R, and furazanoxy groups.[3]

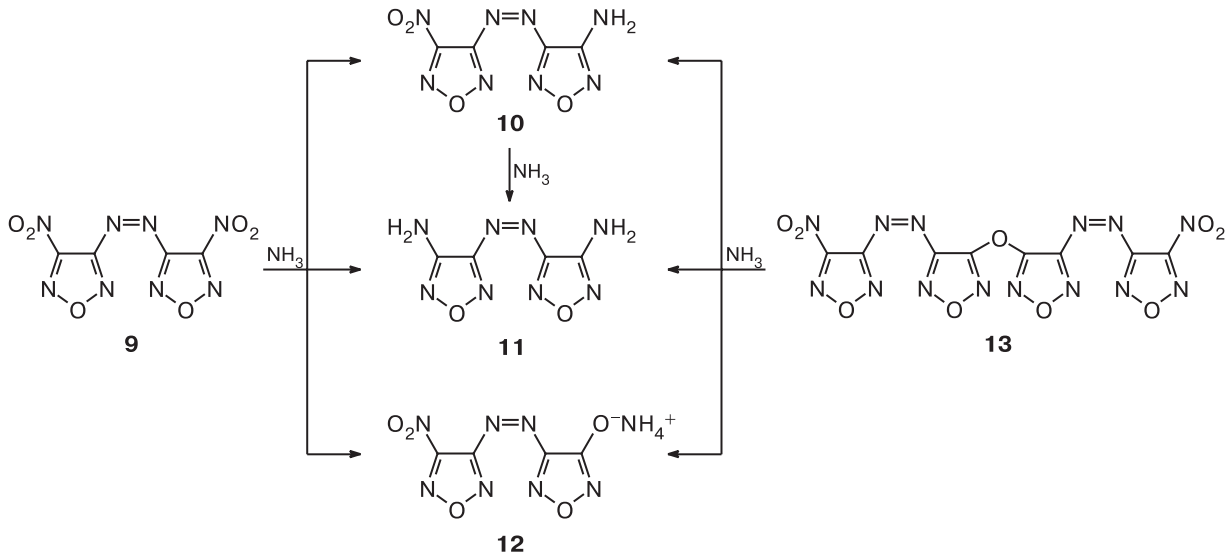
4,4-Dinitroazofurazan (**9**) reacts with ammonia in anhydrous $CHCl_3$ as readily as compound **1**. However, this may give both monoamine **10** and diamine **11** (Scheme 3). Salt **12** formed as a minor impurity (yield 1—7%) can be easily washed out by water and the corresponding hydroxy derivative can be isolated upon acidification. In the case of compound **9**, predominant formation of a definite product can be attained by changing the reactant ratio or temperature. For instance, diamine **11** is the major product (yield 86%) with a 10-fold excess of NH_3 and a temperature of 35—45 °C. Evidently, the reaction proceeds as successive displacement of both nitro groups. Indeed, under similar conditions, monoamine **10** is converted almost quantitatively (yield 96%) into diamine **11**.

The use of a 1.25 *N* solution of NH_3 in $CHCl_3$ at ~20 °C and a **9** : NH_3 ratio of 1 : 2 affords monoamine **10** in 79% yield; in this case, diamine **11** is formed in 13% yield. The formation of diamine **11** cannot be avoided completely even when the reaction is carried out at −5 °C. It is worth noting that the synthesis of monoamine **10** by oxidation of diamine **11** is a very laborious procedure resulting in a low product yield,[41,42] whereas the use of readily available dinitro compound **9** permits the preparation of rather large amounts of this product.

When compound **13** is treated with a $CHCl_3$ solution of ammonia, the ether bond is the first to be cleaved (as in ether **5**), resulting in precipitation of salt **12** (see Scheme 3). However, as in the case of azo compound **9**, the nitro group in the resulting amino nitro compound **10** is substituted to give diamine **11**. Nevertheless, at 0 °C and at a **13** : NH_3 ratio of 1 : 2.5, the yield of monoamine **10** can reach 85%. It is noteworthy that although nitro compound **1** and ether **5** differ appreciably in reactivity, compounds **9** and **13** differ only slightly in this respect.

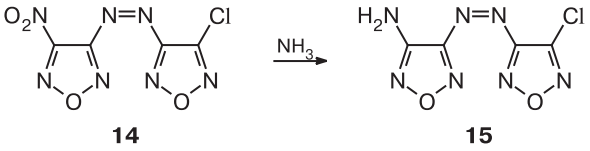
An interesting result was obtained in the reaction of ammonia with 4-nitro-4′-chloroazofurazan (**14**) in $CHCl_3$. Even with a large excess of ammonia, only the nitro group was displaced (Scheme 4). A many-day stir-

Scheme 3



ring of amino chloro derivative **15** in a 1.25 *N* solution of NH_3 in $CHCl_3$ did not result in chlorine displacement. Note that displacement of only the nitro group was observed in a previous study[29] for reactions of 4-(4-chlorofurazan-3-*N*(*O*)*N*-azoxy)-3-nitrofurazan with O- and C-nucleophiles.

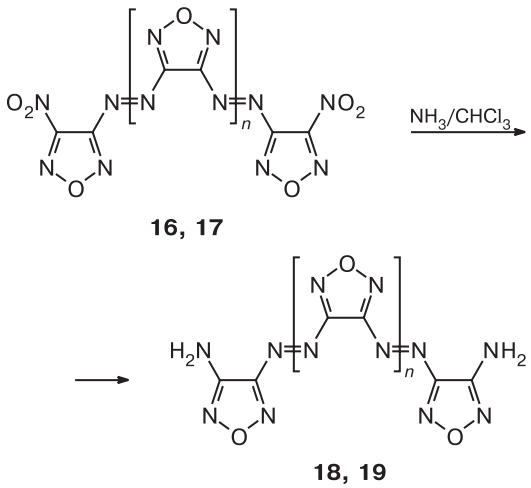
Scheme 4



Both nitro groups in bis- and tris-azo compounds **16** and **17** are readily substituted on treatment with ammonia in $CHCl_3$ both at room temperature and at lower temperatures (Scheme 5). When excess ammonia was used, diamines **18** and **19** were formed in almost quantitative yields (91—94%). The attempts to prepare monosubstituted products using a nitro compound to ammonia ratio of 1 : 2 proved unsuccessful. The reaction gave a complex mixture of products (according to TLC, more than six products), from which no individual compounds could be isolated. Evidently, in this case, too, the nitrite ion evolved upon displacement of the nitro group induces side processes.

Treatment of 4,4′-dinitro-3,3′-bifurazan (**20**) with ammonia in $CHCl_3$ gives mainly diamino derivative **22**, in addition to monoamine **21** (Scheme 6). Even at −30 °C and a deficiency of ammonia, monoamine **21** can be prepared in a yield of ≤35%, the reaction mixture containing both the initial compound **20** and diamine **22**

Scheme 5

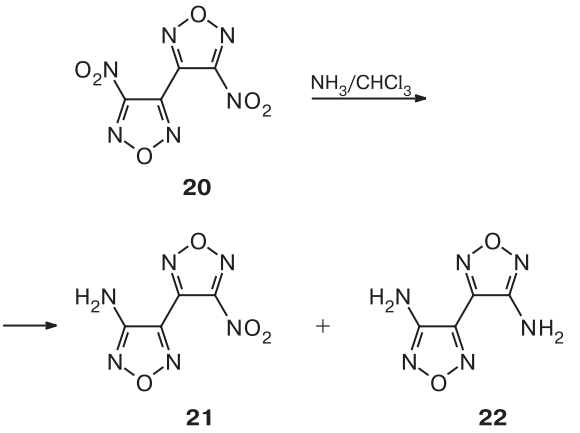


n = 1 (**16**, **18**), 2 (**17**, **19**)

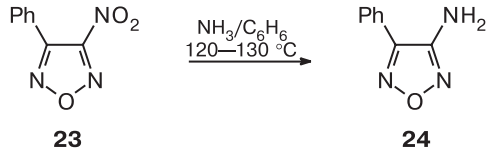
(the mixture was separated by preparative chromatography). The side products resulting from the concomitant reactions of the nitrite ion do not interfere much with the isolation of compound **21**.

Although the furazan ring is similar to the dinitrophenyl fragment in electron-withdrawing properties,[43,44] nitrofurazans containing no strong electron-withdrawing substituents are rather inert with respect to solutions of ammonia. Thus 3-nitro-4-phenylfurazan (**23**) reacts with a $CHCl_3$ solution of ammonia very slowly (a 10-fold excess of NH_3, 20—60 °C). However, heating of compound **23** with an excess of ammonia as a benzene solution in an autoclave at 120—130 °C for 3 h affords amine **24** in 89% yield (Scheme 7).

Scheme 6

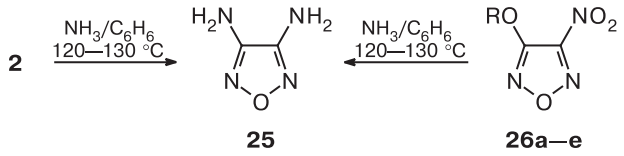


Scheme 7



A similar autoclave treatment of compound **2** affords 3,4-diaminofurazan (**25**) in 83% yield (Scheme 8). Moreover, diamine **25** is formed in 65—85% yield upon a similar autoclave treatment of any nitro derivative (compound **1**, **5**, or **7**), which is converted into amine **2** under mild conditions.

Scheme 8

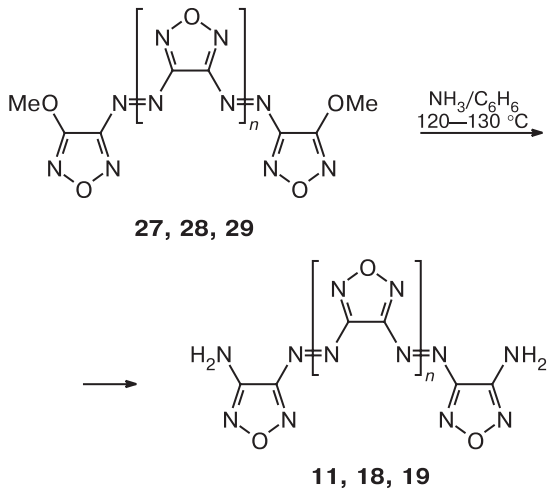


R = Me (**a**), Et (**b**), Pr^i (**c**), Bn (**d**), Ph (**e**)

It is of interest that heating in a autoclave of 3-methoxy-4-nitrofurazan (**26a**) with ammonia results in the displacement of both nitro and methoxy groups to give 3,4-diaminofurazan (**25**) in 78% yield (see Scheme 8). Similar results were obtained by using alkoxyfurazans **26b—d** and phenoxy derivative **26e** (yields 75—81%). Evidently, the reaction proceeds as a stepwise displacement of substituents. Although the displacement of the alkoxy group bound to the polynitrophenyl fragment is a well-studied reaction,[36] it is quite unusual for alkoxyazoles. We would like to emphasize the importance of the possibility of displacing the RO group attached to the furazan ring. In some cases, it is necessary to exclude the presence of the nitrite ion, which could give rise to side hydroxy derivatives[35] and is also reactive toward N-nucleophiles.[36,37]

Although displacement of the methoxy groups in methoxy azofurazans **27—29** occurs at usual pressure, this reaction is very slow. Conducting the reaction in an autoclave at 120—130 °C provides efficient (30 min, yields 80—93%) synthesis of amines **11**, **18**, and **19**, respectively (Scheme 9). It should be emphasized that the use of the methoxy analogs instead of the nitro compounds makes the synthesis of these amines safe.

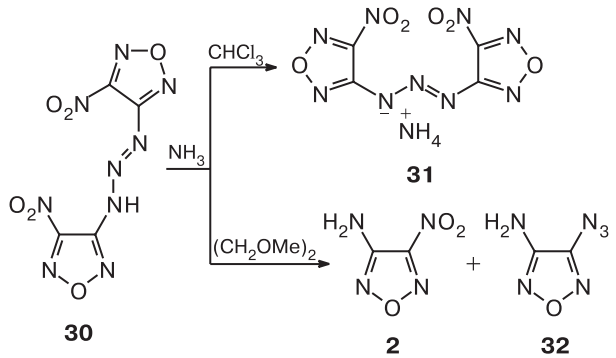
Scheme 9



n = 0 (**11**, **27**), 1 (**18**, **28**), 2 (**19**, **29**)

Dinitrotriazene **30** reacts with ammonia in $CHCl_3$ at ~20 °C to give salt **31**, which is quantitatively precipitated and is not further converted. Heating of compound **30** with ammonia in glyme gives a mixture of amine **2** and azide **32** in ~30% yields (Scheme 10).

Scheme 10



In conclusion, note that the nitro group bound to the furazan ring can act as both a leaving and an activating group, which facilitates the displacement of the second substituent (for example, OR or $N(NO_2)R$). The data

about the groups able to be displaced by nucleophiles are exceptionally important for choosing the synthetic pathways to furazan derivatives. The use of OR or $N(NO_2)R$ as the leaving groups in the furazan series can be recommended for efficient application in processes where the presence of nitrite ions, supplied to the reaction medium upon displacement of the nitro group, is undesirable.

Experimental

Melting points were determined on a Köffler stage. ^1H, ^{13}C, and ^{14}N NMR spectra for natural isotope abundances were recorded on a Bruker AM-300 spectrometer operating at 300.13, 75.7, and 21.5 MHz, respectively. The ^{14}N NMR chemical shifts were determined in the δ scale relative to external $MeNO_2$. Mass spectra were registered on Varian MAT CH-6 and Varian MAT CH-111 instruments (70 eV). IR spectra were measured on a Specord IR-75 spectrometer (KBr pellets for solids and thin films for liquids). The reactions were monitored and the product purity was checked by TLC on Silufol UV-254 plates; silica gel was used for preparative chromatography.

The starting nitrofurazans **1**,[41] **5**,[23] **7**,[45] **9**,[41] **13**,[24] **14**,[31] **16**,[6,46] **17**,[47] **19**,[41] **23**,[41] **26**,[41] and **30** [28] were prepared by previously described procedures.

Caution! Most of nitrofurazans are explosive. The precautions recommended by the appropriate instructions must be taken.

Reaction of 3,4-dinitrofurazan (1) with NH_3. ***A.*** A 1.25 *N* solution of NH_3 in $CHCl_3$ (5—10 mL) was added dropwise with stirring to a solution of compound **1** (1.6 g, 10 mmol) in anhydrous $CHCl_3$ (15 mL). The mixture was stirred until the initial compound was no longer detected by TLC (elution with a CCl_4—CH_2Cl_2 mixture). The reaction mixture was evaporated to dryness *in vacuo* and the residue was recrystallized from water to give 1.25 g (96%) of **3-amino-4-nitrofurazan (2)** as primrose-colored crystals, m.p. 124—125 °C (*cf.* Ref. 48: m.p. 122.5—123 °C, *cf.* Ref. 41: m.p. 125 °C). The spectroscopic characteristics corresponded to the published data.

B. A solution of NH_3 (0.68 g, 40 mmol) in anhydrous MeCN (20 mL) was added dropwise at −10 °C to a solution of compound **1** (1.6 g, 10 mmol) in anhydrous MeCN (15 mL). After spontaneous heating of the reaction mixture to ~20 °C, the solvent was removed *in vacuo*. Extraction of the residue with an ether—hexane mixture (10 : 1, 100 mL) gave compound **2**, which was obtained in 48% yield after solvent evaporation and recrystallization from water. The residue insoluble in the ether mixture was recrystallized from a $CHCl_3$—AcOH mixture (15 : 2) to give 0.55 g (37%) of the **ammonium salt of 3-hydroxy-4-nitrofurazan (4)**, m.p. 110—112 °C. Found (%): C, 16.27; H, 2.71; N, 37.81. $C_2H_4N_4O_4$. Calculated (%): C, 16.22; H, 2.72; N, 37.84. IR, ν/cm^{-1}: 3350, 3250—2900, 1610, 1540, 1500, 1470, 1420, 1390, 1320, 1205, 1020, 910, 870. ^{14}N NMR (DMSO-d_6), δ: −23.6 (NO_2); −359.4 (NH_4^+).

C. A solution of NH_3 (0.68 g, 40 mmol, 25 mL) in anhydrous glyme was added dropwise with stirring at ~20 °C over a period of 0.5 h to a solution of compound **1** (1.6 g, 10 mmol) in the same solvent (15 mL). The mixture was stirred for an additional 0.5 h and the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (200 mL) and washed with water (4×30 mL). The organic layer was dried with $MgSO_4$ and evaporated *in vacuo*. The crude product was recrystallized from water to give 0.55 g (42%) of compound **2**. The aqueous layer was acidified with HCl and extracted with ether (3×30 mL). The ethereal extract was dried with $MgSO_4$ and concentrated *in vacuo* to give 0.72 g (55%) of **3-hydroxy-4-nitrofurazan (3)** as a thick oil. The spectroscopic characteristics corresponded to published data.[23,26,27]

Reaction of 4,4′-dinitrodifurazanyl ether (5) with NH_3. A 1.25 *N* solution of NH_3 in $CHCl_3$ (10 mL) was added dropwise with stirring to a solution of compound **5** (1.22 g, 5 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred for an additional 2 h, the precipitate was filtered off, washed with CH_2Cl_2, and dried in air to give 0.73 g (98%) of salt **4**, m.p. 110—111 °C. The filtrate was concentrated to dryness, and the residue was recrystallized from water to give 0.63 g (97%) of compound **2**, m.p. 124—125 °C.

Reaction of methylene-*N*,*N*′-bis[(4-nitrofurazan-3-yl)nitramine] (7) with NH_3. Ammonia gas was passed for 0.5 h at ~20 °C through a stirred solution of compound **7** (1.81 g, 5 mmol) in anhydrous MeCN (30 mL). The solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with water (4×30 mL). The organic layer was dried with $MgSO_4$ and evaporated *in vacuo*, and the residue was recrystallized from water to give 0.35 g (54%) of compound **2**.

Reaction of 4,4′-dinitroazofurazan (9) with NH_3. ***A.*** Ammonia gas was passed for 0.5 h through a stirred solution of compound **9** (2.56 g, 10 mmol) in $CHCl_3$ (60 mL) heated to 35—40 °C. The residue was filtered off and recrystallized from DMSO to give 1.88 g (96%) of **4,4′-diaminoazofurazan (11)** as a yellow amorphous powder, m.p. 325—326 °C (dec.) (*cf.* Ref. 48: m.p. 325 °C (dec.)). ^1H NMR (DMSO-d_6), δ: 6.89 (NH_2). ^{13}C NMR (DMSO-d_6), δ: 150.7 (CNH_2); 155.8 (CNN). The other spectroscopic characteristics corresponded to published data.[48]

B. A 1.25 *N* solution of NH_3 in $CHCl_3$ (5 mL) was added dropwise with stirring to a solution of compound **9** (2.56 g, 10 mmol) in anhydrous $CHCl_3$ (45 mL). After 20 min of stirring, the reaction mixture was washed with water (3×15 mL), dried with $MgSO_4$, filtered through a thin silica gel layer, and concentrated *in vacuo*. The residue was recrystallized from CCl_4 to give 1.78 g (79%) of **4-amino-4′-nitroazofurazan (10)** as orange crystals, m.p. 92—93 °C (*cf.* Ref. 41: m.p. 93 °C). The spectroscopic characteristics corresponded to published data.[41,42]

Reaction of 4,4′-bis(4-nitrofurazan-3-ylazo)difurazanyl ether (13) with NH_3. A 1.25 *N* solution of NH_3 in $CHCl_3$ (7 mL) was added with stirring at 0 °C to a solution of compound **13** (2.18 g, 5 mmol) in anhydrous CCl_4 (50 mL). Then CH_2Cl_2 (50 mL) was added and after stirring for 20 min at 0 °C, the reaction mixture was allowed to warm up to ~20 °C. The mixture was washed with water (3×15 mL), dried with $MgSO_4$, filtered through a thin layer of silica gel, and concentrated *in vacuo*. The residue was recrystallized from CCl_4 to give 0.96 g (85%) of compound **10**, m.p. 92—93 °C.

Reaction of 4-nitro-4′-chloroazofurazan (14) with NH_3. A 1.25 *N* solution of NH_3 in $CHCl_3$ (60 mL) was added to a solution of compound **14** (0.49 g, 2 mmol) in anhydrous $CHCl_3$ (10 mL) at ~20 °C. The resulting solution was stirred for 2 h, washed with water (3×60 mL), dried with $MgSO_4$, filtered through a thin layer of silica gel, and concentrated *in vacuo*. The residue was recrystallized from CCl_4 to give 0.37 g (86%) of **4-amino-4′-chloroazofurazan (15)** as orange crystals, m.p.

121—122.5 °C. Found (%): C, 22.26; H, 1.00; Cl, 16.39; N, 45.41. $C_4H_2ClN_7O_2$. Calculated (%): C, 22.29; H, 0.94; Cl, 16.45; N, 45.49. MS, *m/z*: 215, 216 $[M]^+$, 132, 131, 84. IR, ν/cm^{-1}: 3472, 3320, 1628, 1540, 1528, 1476, 1432, 1388, 1187, 1028, 1012, 765, 680. ^{13}C NMR (DMSO-d_6), δ: 141.6 (CCl); 149.2 (CNH_2); 156.0 ($\underline{C}CNH_2$); 159.5.

Reaction of 3,4-bis(4-nitrofurazan-3-ylazo)furazan (16) with NH_3. Ammonia gas was passed for 0.5 h at ~20 °C through a solution of compound **16** (3.52 g, 10 mmol) in a mixture of $CHCl_3$ (50 mL) and CCl_4 (20 mL). The reaction mixture was cooled to 0 °C and at this temperature, the product was filtered off and washed with cold water. Recrystallization from Pr^iOH gave 2.66 g (91%) **4,4´-bis(4-aminofurazan-3-ylazo)furazan (18)** as fine yellow-orange crystals, m.p. 205—207 °C. Found (%): C, 24.71; H, 1.37; N, 57.51. $C_6H_4N_{12}O_3$. Calculated (%): C, 24.67; H, 1.38; N, 57.53. MS, *m/z*: 292 $[M]^+$, 208, 112. IR, ν/cm^{-1}: 3430, 3310, 1615, 1400, 1230, 1090, 1045. ^{13}C NMR (DMSO-d_6), δ: 149.1 (CNH_2); 156.1; 157.4 (CNN).

Reaction of 4,4´-bis(4-nitrofurazan-3-ylazo)azofurazan (17) with NH_3. The reaction carried out as described above using compound **17** (4.48 g, 10 mmol) gave 3.65 g (94%) of **4,4´-bis(4-aminofurazan-3-ylazo)azofurazan (19)**, m.p. 264—266 °C. Found (%): C, 24.78; H, 1.06; N, 57.72. $C_8H_4N_{16}O_4$. Calculated (%): C, 24.75; H, 1.04; N, 57.73. MS, *m/z*: 388 $[M]^+$, 304, 208, 180. IR, ν/cm^{-1}: 3344, 3232, 1630, 1610, 1580, 1490, 1410, 1290, 1110, 1040, 790. ^{13}C NMR (DMSO-d_6), δ: 149.0 (CNH_2); 155.9; 156.4; 158.3 (CNN).

Reaction of 4,4´-dinitrobifurazan (20) with NH_3. The reaction carried out as described in the previous procedure using compound **20** (2.28 g, 10 mmol) gave 1.63 g (97%) of **4,4´-diaminobifurazan (22)**, m.p. 300 °C (dec.) (*cf.* Ref. 49, 50: m.p. 298—299 °C, *cf.* Ref. 1: 305 °C (dec.)). The spectroscopic characteristics corresponded to published data.

Reaction of 3-nitro-4-phenylfurazan (23) with NH_3. A solution of compound **23** (1.91 g, 10 mmol) in benzene (30 mL) was placed into a 150 mL autoclave. The autoclave was purged with nitrogen and evacuated, and NH_3 gas was supplied up to a pressure of 15 atm. The reaction mixture was stirred for 3 h at 120—130 °C. After cooling, the pressure was relieved and the autoclave was purged with nitrogen. Ether (30 mL) was added, the mixture was washed with water (3×30 mL), and the organic layer was dried with $MgSO_4$. After removal of the solvent, the residue was recrystallized from 95% propan-2-ol to give 1.43 g (89%) of **3-amino-4-phenylfurazan (24)** as light-cream-colored crystals, m.p. 97—98 °C (*cf.* Ref. 49, 51: m.p. 98—99 °C). The spectroscopic characteristics corresponded to published data.

Reaction of 3-methoxy-4-nitrofurazan (26a) with NH_3. The reaction carried out as in the previous experiment with compound **26a** (2.9 g, 20 mmol) gave 1.56 g (78%) **3,4-diaminofurazan (25)**, m.p. 179—180 °C (*cf.* Ref. 52: m.p. 179—180 °C, *cf.* Ref. 1: m.p. 180 °C). The spectroscopic characteristics corresponded to published data.

Other 3-alkoxy-4-nitrofurazans react in a similar way.

Reaction of 4,4´-dimethoxyazofurazan (27) with NH_3. A solution of compound **27** [27] (2.26 g, 10 mmol) in benzene (20 mL) was placed in a 50-mL autoclave. The autoclave was purged with nitrogen and evacuated, and then NH_3 gas was supplied up to a pressure of 15 atm. The reaction mixture was stirred for 20 min at 120—130 °C. After cooling, the pressure was relieved and the autoclave was purged with nitrogen. The reaction mixture was concentrated *in vacuo* to dryness and the residue was washed with water and recrystallized from DMSO to give 1.82 g (93%) of compound **11**, m.p. 325—326 °C (dec.).

Reaction of 3,4-bis(4-methoxyfurazan-3-ylazo)furazan (28) with NH_3. The reaction carried out similarly to the previous experiment using 3.22 g (10 mmol) of compound **28** gave 2.54 g (87%) of compound **18**, m.p. 205—207 °C.

Reaction of 4,4´-bis(4-methoxyfurazan-3-ylazo)azofurazan (29) with NH_3. The reaction carried out similarly to the previous experiment using compound **29** (4.18 g, 10 mmol) gave 3.1 g (80%) of **4,4´-bis(4-aminofurazan-3-ylazo)azofurazan (19)**, m.p. 264—266 °C.

Reaction of 1,3-bis(4-nitrofurazan-3-yl)triazene (30) with NH_3. ***A.*** A 1.25 *N* solution of NH_3 in $CHCl_3$ (10 mL) was added dropwise with stirring to a solution of compound **30** (2.71 g, 10 mmol) in anhydrous $CHCl_3$ (50 mL). Then ether (50 mL) was added, the mixture was stirred for 20 min, and the ammonium salt **31** was filtered off. Reprecipitation with ether from MeCN at 0 °C gave 0.96 g (85%) of product **31** as yellow crystals, m.p. 102—106 °C (dec.). Found (%): C, 16.59; H, 1.45; N, 48.67. $C_4H_4N_{10}O_6$. Calculated (%): C, 16.67; H, 1.40; N, 48.61. Acidification of salt **31** with HCl gave the initial triazene **30**, m.p. 96—97 °C (*cf.* Ref. 28: m.p. 95—96 °C).

B. Ammonia gas was passed for 0.5 h at 40—50 °C through a stirred solution of compound **30** (2.71 g, 10 mmol) in anhydrous glyme (30 mL). After stirring (1 h), the reaction mixture was concentrated to dryness. The residue was separated on a chromatographic column (SiO_2 40/100, elution with $CHCl_3$—MeCN, 7 : 1). The first fraction (0.36 g, yield 29%) was **3-azido-4-aminofurazan (32)**, m.p. 85—86 °C (*cf.* Ref. 53: m.p. 86.5—87.5 °C). The second fraction (0.4 g, yield 31%) was compound **2**, m.p. 124—125 °C.

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