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A Practical Anodic Oxidation of Aminofurazans to Azofurazans: an environmentally friendly route†

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Nickel oxyhydroxide, NiOOH, anode has been shown to be effective tools for the oxidation of aminofurazans to azofurazans in ca 1% aqueous alkali at room temperature. The electrochemical reaction is simple and convenient, eliminating the use of expensive and toxic organic or inorganic oxidants. The green economic preparations of desired azo compounds are very clean, producing only H₂ as a result of cathodic reduction.

Introduction

Green chemical processes play a crucial role in sustainable development, and atom-economical strategies for the enhancement of molecular complexity are the key elements for the design of new environmentally favorable synthetic processes. According to the trend, we have focused our effort on the development of a safe and efficient methods to prepare furazan (1,2,5-oxadiazole) derivatives.

Furazan chemistry has extended over a period of about 140 years, and many useful derivatives have been synthesized and investigated. Applications of these compounds are highly diverse, ranging from medicinal chemistry to explosive and propellant ingredients.[1] In this family, azofurazan structural motif is present in a range of crown ether analogs[2] and biologically active molecules that inhibit the NO-dependent activation of the soluble guanylate cyclase.[3] However, compounds incorporated azofurazan framework with a high nitrogen content and large positive heats of formation have been most extensively studied as energetic materials.[4] 4,4’-Diaminoazofurazan 1, 3,4,5 3,4-di(4-nitrofuran-3-azo)furan 2 [4,6] 4,4’-di-(5-tetrazolyl)-azofurazan,[7] 4,4-dinitrodiazononyiazofuran,[8] and tetraakis(furazano)[3,4-c:3’,4’-g:3”,4’’-h][1,2,5,6,9,10,13,14]-octazaacyclohexa-decine[4c,8] are examples of the energetic compounds (Fig. 1). Given their utility, the development of synthetic methodology to access azofurazan derivatives is continually warranted.

Azofurazans are typically prepared from aminofurazans by an oxidation reaction. Traditionally, this has been carried out using such reagents as K₅MnO₄/H⁺,[10] CrO₃/AcOH,[11] (NH₄)₂S₂O₈,[12] NaOCl or NaOBr,[13] nitronium tetrafluoroborate,[14] Br₂/H₂O,[15] or a variety of organic reagents (dibromoisocyanuric acid[16] and trichloroisocyanuric acid).[17] These procedures, however, require the use of hazardous, corrosive or expensive reagents. In a chemical oxidation, stoichiometric amounts or excess of an oxidant are needed. As a result the corresponding amounts of metal salts or acids are formed as waste. Separation of the products from the waste is often difficult. Our goal was to develop a convenient, economical and environmentally friendly synthetic protocol for a quick assembly of the azofurazan core.

Some high energetic azofurazans.

The growing social pressure for new green technologies and the promise of organic electrochemistry to deliver them has led to high academic and industrial interest in electrochemical methods.[18] The electron in electrochemistry is one of the most environmentally friendly reagents, as it produces no waste in contrast to chemical reagents; furthermore, it is the cheapest reagent in chemistry.

Organic electrooxidation has attracted much attention as one of the effective methods in carbon-carbon, carbon-nitrogen, and
carbon-oxygen bond formations.\cite{19} At the same time, electrochemical N=N bond formations is underexplored. Thus, an alkyl azo compound, di(n-butyl) diazene, than have been obtained in low yield by electrooxidation of butylamine, was described.\cite{20a} The only known electrochemical synthesis of azo-(het)arenes from amino-(het)arenes oxidation of anilines to azobenzenes (3-47% yield; the largest yields were recorded for compounds bearing electron-withdrawing substituents).\cite{20b,20c}

However, the electro-oxidation of the aniline nitrogen atom usually resulted in the formation of a radical cation, that can exist in multiple resonance forms. The latter provides an opportunity for three possible couplings: (i) nitrogen-nitrogen (head-to-head, HH), (ii) nitrogen-arene (head-to-tail, HT) and (iii) arene-arene (tail-to-tail, TT). HT and TT coupling occurs predominately, and the polymerization of anilines is a common result.\cite{21}

Recently, we have shown that electrooxidation of 3-methoxy-4-nitraminofurazan 6 leads to the formation of 4,4''-dimethoxyazofurazan 7 in undivided cell in ca 40% yield (Scheme 1).\cite{22} This procedure required preparation and the use of hazardous starting nitramine 6.

\begin{center}
\includegraphics[width=0.5\textwidth]{Scheme_1.png}
\end{center}

**Scheme 1**

It should be noted that the electrooxidations for N=N bond formation in the syntheses of azocompounds mentioned above\cite{20b,20c} have been carried out with great expensive Pt anode in a non-aqueous medium (acetonitrile). An attractive perspective for synthesis of (het)aromatic azo compounds is electrooxidation of corresponding (het)aryl amines on Ni anode under galvanostatic electrolysis. The basic electrochemical reaction at Ni anode involves the formation of nickel hydroxide Ni(OH)\textsubscript{2} and its oxidation in alkaline solution (typical electrolyte is 1M NaOH/H\textsubscript{2}O) to nickel oxyhydroxide NiOOH \cite{24} which is an equivalent to the well-known oxidant, nickel peroxide.\cite{25}

Electrochemical synthesis is based on a combination of an electron transfer at the Ni anode with a chemical reaction of electrodeposited NiOOH (Figure 2). The electron transfer (re)generates the NiOOH reagent. The anode is usually used in organic synthesis for oxidation of C-H and C-C bonds of organic compounds.\cite{26} It should be noted that an example of N=N bond formation at the NiOOH anode has been described: 1,1-disubstituted hydrazines were oxidized in good yield to 1,1,4,4-tetrasubstituted tetrazenes.\cite{22} To the best of our knowledge, a synthesis of (het)aryl azo compounds using NiOOH anode has not been reported. We hypothesized that it might be possible to use the anode for oxidation of a (het)aryl amine to the corresponding azo compound.

As a part of a program aimed at the development of ecological synthetic methods for the construction of energetic materials,\cite{27} we now report a facile and reliable electrochemical oxidation of azofurazans. This clean process allows the synthesis of azofurazansin one step with high atom economy, and driven by loss of environmentally benign hydrogen gas.

**Results and discussion**

We were gratified to find that this NiOOH electrode was successful in the oxidative preparation of the azofurazans, giving clean reaction profiles (Fig. 3). We started our study by examining the oxidation of 3-amino-4-methylfurazan 8a to 4,4''-dimethoxazofurazan 9a. Cyclic voltammetry (CV) was used for an initial evaluation of the electrocatalytic process. The typical voltammetric response is exemplified in Fig. 2. Compared to the voltammogram of the Ni\textsuperscript{2+}/Ni\textsuperscript{3+} pair (E\textsubscript{1/2} = 430 mV) in absence of a substrate (solid line), the peak current increases when amine 8a was added (dotted line). The observation is similar to that fixed at the electrodeoxidation urea on NiOOH catalyst surface in alkaline medium.

\begin{center}
\includegraphics[width=0.5\textwidth]{Figure_2.png}
\end{center}

**Figure 2.** CVs of Ni/NiOOH in 0.2 M NaOH with (black dotted line) and without (gray solid line) amine 8a (20 mmol L\textsuperscript{-1}, 100 mV s\textsuperscript{-1}).

However, preparative-scale evaluation is crucial in order to establish the actual performance and efficiency of the Ni\textsuperscript{2+}/Ni\textsuperscript{3+} catalytic systems under synthetic conditions. Preparative electrolysis of compound 8a under galvanostatic conditions involved using a four-neck jacketed flask as an undivided cell, a cylindrical Ni anode, a cylindrical net Ti cathode, and an aqueous solution of an alkali as the supporting electrolyte.
Figure 3. Schematic illustration of the possible electrochemical mechanism for the oxidation of aminofurazans on Ni(OH)₂.

Anodic oxidations of amine 8a were carried out at stirring under various conditions. The reactions were generally clean when monitored by NMR, only target azo compound 9a and unreacted starting material have been identified components. Details on the experimental protocol are summarized in Table 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (concentration, mol/L)</th>
<th>Current density (mA/cm²)</th>
<th>Electricity passed, Q/Qn(e)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>a</th>
<th>Recovery of 8a</th>
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<tr>
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<td>57</td>
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<td>59</td>
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<tr>
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<td>46</td>
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<td>22 (20)</td>
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<td></td>
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<tr>
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<td>97 (95)</td>
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<td>7</td>
<td>19</td>
<td>66</td>
<td>33.0</td>
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</table>

*Reactions were run under galvanostatic conditions on 2 mmol scale of compound 8a in 100 ml of H₂O (0.02 mol/L) at room temperature. b Before the experiment, the Ni anode (ca. 48 cm²) was activated according to the next procedure.\(^{[23]}\) A thin NiOOH surface layer was deposited on the anode at preliminary electrolysis in a solution 0.1 M NiSO₄, 0.1 M NaOAc, and 0.005 M NaOH, at j = 1 mA cm⁻² with periodical reverse of the electrode polarization. Here Q is the amount of electricity (F), and Qn( theor) = 2F per a mole of compound 8a. Determined by ¹H NMR spectroscopy using 4,4'-dimethoxyazoazurazan as an internal standard at 298 K. reaction (averages of two runs); isolated yields are shown in parentheses. Reaction conducted at 70°C.

The results in Table 1 indicate that in the electrooxidation, all of the bases (entries 1–3) favored the formation of azo compound 9a with comparable selectivity. It appeared that NaOH is optimum with respect to overall yield and cost. We found that the use of 0.1 M NaOH in H₂O at 22°C under an air atmosphere produced 9a after 22 min in 59% yield with a moderate conversion of 8a (Table 1, entry 2). Using 0.2 M NaOH as a basic medium, the conversion was enhanced, but the resulting yield of 9a remained below 80% (Table 1, entry 4). Increase of the temperature (entry 7) or prolongation of the reaction time (entry 8) did not lead to an improvement in the yield. However, an excellent result was obtained when double quantity of electricity was passed; a 97% yield of azo compound 9a and almost complete conversion of amine 8a were observed (Table 1, entry 14).

Next, the scope of this oxidation was examined (Table 2). It was found that the solubility of aminofurazans in water is a key parameter to the success of the electrochemical process. Thus, the solubility of alkyl and alkoxy compounds 8a–g is much better than that of aryl 8i and hetarylfurazans 8j, 8k, and 8m. As a result, a variety of groups, including Me (a), Et (b), Pr (c), Bu (e), cyclopropyl (d), MeO (f), PrO (g), and OH (h) were perfectly tolerated under these reaction conditions to produce the corresponding azofurazans 9a–h in excellent yields. On the other hand, aminofurazans bearing aryl and pyridyl substituents showed little conversion into the desired azofurazans 9i and 9j. Aminofurazan 8k with 1,2,4-oxadiazolyl group is insoluble in water. As a result, attempts to oxidize this amine to azocompound 9k were unsuccessful and only unreacted starting material was observed. On the other hand, tetrazolylfurazanylamine 8l have higher water solubility and produced the desired azo compound 9l in excellent yield. Obviously, this protocol could be feasible for large scale production of the product 9l.

Table 2 Electrooxidative synthesis of azofurazans from aminofurazans on NiOOH anode.

| Reaction conditions: 8 (2 mmol), 0.2 M NaOH in H₂O (100 ml), 25°C, current density j = 6 mA cm⁻², Qn( theor) = 2F per a mole of compound 8a, NiOOH coated anode, Ti cathode. General procedure was used. Isolated yields are an average of three runs; in all cases where the reaction was unsuccessful or the yield of azo compound 9 was low, significant amounts of starting material were recovered. Electricity passed: Q/Qn( theor) = 3. Reaction was performed at 70°C. 3-Amino-4-nitrozofuranazan 8r was used in place of 3-amino-4-hydroxyazoazurazan 8o.

The electrooxidation of an amino group in 3,4-diaminofuranazan 8o was first expected to provide the desired azo compound 9o. An amino group of this product can further react with itself or...
An asymmetric unit cell of azo compound \( \text{9o} \) to azo compound \( \text{9o} \) in good yield (92%):[56] however, the reaction takes up to 20 h to complete.

Table 2 illustrates a generalized protocol implemented for the synthesis of azo compounds of interest in the energetic material chemistry arena such as 4,4Hdihydroxyazofurazan \( \text{9h} \) (identical with compound 3 from Fig.1),[7] compound \( \text{9m} \),[46] \( \text{9} \)H-diaminoazofurazan \( \text{9o} \) (identical with compound 1 from Fig.1),[46,53] and compound \( \text{9p} \) (the latter is an intermediate in the synthesis of nitrodiacenenoxides, \( \text{R} \)-N(O)=N-NO2).[38]

Notably, these electrochemical conditions provide access to the products derived from 3-amino-4-azidoazofurazan \( \text{8n} \).[32] At room temperature, highly sensitive azo compound \( \text{9n} \) can be made in 74% yield (Table 2). On the other hand, at higher temperatures, energetic pentalene \( \text{11} \)[33] (Scheme 2) was synthesized in good yield.

\[ \text{NH}_2 \text{N} \text{N} \text{N} \text{O} \text{O} \text{N} \text{N} \text{N} \text{H} \]

\[ \text{8n} \]

\[ \text{11} \]

**Scheme 2**

The products were identified from their characteristic spectroscopic properties by comparison with those of similar compounds in the literature. Their \( ^{13} \text{C} \) NMR data are all consistent with the presence of the azofurazan core in the proposed structures. In particular, the \( \delta \) values for \( \text{C}-\text{N}=\text{N} \) (155-163 ppm), and \( \text{C}-\text{R} \) (148-151 ppm) are typical of azofurazans.[34] The structures of 4,4Hcyclopropylazofurazan \( \text{9d} \) and 5(4H-azidofurazan-3-yl)-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazol-5-im-4-ide \( \text{11} \) were established by X-ray crystallography(Fig. 4).[36]

An asymmetric unit cell of azo compound \( \text{9d} \) contains half of the molecule located at the center of symmetry which adopts planar structure and \( \text{ap-ap-ap} \) conformation that is typical for azofurazans.[10,36]

An asymmetric unit cell of fused furazan \( \text{11} \) contains one molecule, and this structure is characterized by high density

(1.859 g cm\(^{-3}\) at 100 K). The molecule is somewhat nonplanar probably due to steric repulsion between substituents at the furazan ring. For the analysis of the crystal packing we used combination of the common visual analysis of the crystal packing based on consideration of the close contacts and the approach based on intermolecular pair energies[37] for which the M052X/aug-cc-pvdz level of approximation was utilized. Both methods and the basis set were successfully applied in our recent studies on isolated molecules and their aggregates.[38] The details of the crystal packing analysis are given as electronic supporting information (ESI).

**Conclusions**

In summary, we have reported a novel, efficient, and easy to perform green method for \( \text{N=N} \) bond formation to the synthesis of azofurazans. Key features of the approach include the electrooxidation of aminofurazans in \( \text{ca} \) 1% aqueous alkalion \( \text{NiOOH} \) anodewithout the use of inorganic/organic oxidants or other solvents. The process run in water produces from good to excellent yields of the azofurazans, promising candidates for
energetic material formulations. Given the high yield, “greenness”, and possibility of scaling-up, the process has considerable potential for adoption by pilot plant.

Current research from this laboratory is directed towards developing new applications of the electrooxidation in azoheterocycle synthesis.

Sectional experiment

Caution! Some substances prepared herein are highly energetic compounds and sensitive to various stimuli. Safety precautions, such as face shields, a leather apron, gloves, and hearing protection should be employed. These compounds should be handled with great care.

General: All the reagents and solvents were of analytical grade, purchased from commercial sources, and used as received.

Alkyldiazofuran 8a-e,[39] alkoxy- and hydroxydiazofurans 8f-h,[40] aryl derivatives 8i and 8j,[41] 1,2,4-oxidiazole 8k,[42] tetrazole 8l,[43] compound 8m,[44] and butylazoxy derivative 8p[45] were synthesized by using previously reported methods. Infrared spectra were determined in KBr pellets on a Perkin-Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311A instrument. High resolution mass-spectra and NMR spectra are identical with those reported in the literature. HRMS (ESI-TOF) calcd for C_{10}H_{12}NiO_{4}NaO_2^- ([M + Na^-]) = 245.0763, found 245.0779.

4,4'-Diethylazofuranaz (9b). Yellow solid, R_t = 0.62 (1:1 hexane/CH_2Cl_2); mp 108-109 °C (lit.[46] mp 107 °C); 1H and 13C NMR spectra are identical with those reported in the literature.[34a]

By analogous methodology were obtained azofurazans 9b-9g, 9h-9j, 9l-9n and 9p.

4,4'-Diethylazofuranaz (9b). Yellow solid, R_t = 0.62 (1:1 hexane/CH_2Cl_2); mp 59-60°C (hexane); IR (KBr) v/cm^-1: 2987, 2930, 1562, 1460, 1425, 1387, 1324, 1205, 1035, 979, 916, 800, 738, 719, 618; 1H NMR (300 MHz, DMSO-d_6): δ 1.98 (t, J = 7.4 Hz, 6H, CH_3); 2.98 (k, J = 7.4 Hz, 4H, CH_2); 13C NMR (75.5 MHz, DMSO-d_6): δ 10.9 (s, CH_3), 18.1 (s, CH_3), 150.7 (s, C=C), 162.5 (s, C=N=N); Anal.Calcd for C_8H_12NiO_2 (222.40); C 37.42, H 4.54, N 37.82; found: C 37.48, H 4.52, N 37.76. HRMS (ESI-TOF) calcd for C_8H_12NiO_2Na^- ([M + Na^-]) = 245.0763, found 245.0779.

4,4'-Diethylazofuranaz (9c). Orange oil, R_t = 0.62 (1:1 hexane/CH_2Cl_2); IR (KBr) v/cm^-1: 2967, 2937, 2877, 1559, 1463, 1245, 1201, 1092, 1027, 918, 806, 720, 616; 1H NMR (300 MHz, CDCl_3): δ 1.01 (t, J = 7.4 Hz, 6H, CH_3); 1.76 (k, J = 7.4 Hz, 4H, CH_2); 2.95 (t, J = 7.4 Hz, 4H, CH_2); 13C NMR (75.5 MHz, CDCl_3): δ 13.5 (s, CH_3), 20.2 (s, CH_3), 26.3 (s, CH_3), 148.3 (s, C=C), 162.6 (s, C=N=N); Anal.Calcd for C_{11}H_{14}NiO_2 (250.26); C 47.99, H 5.64, N 33.58; found: C 48.01, H 5.60, N 33.46.

4,4'-Dicyclopropylazofuranaz (9d). Yellow solid, R_t = 0.62 (1:1 hexane/CH_2Cl_2); mp 108-110°C (MeOH); IR (KBr) v/cm^-1: 1557, 1461, 1431, 1341, 1213, 1177, 1094, 1064, 1025, 925, 885, 819, 724, 617, 607; 1H NMR (300 MHz, CDCl_3): δ 1.16 (m, 4H, CH_2); 2.37 (m, 1H, CH); 13C NMR (75.5 MHz, CDCl_3): δ 5.5 (s, CH), 10.0 (s, CH), 151.5 (s, C=C), 162.9 (s, C=N=N); Anal.Calcd for C_{11}H_{14}NiO_2Na^- (246.23); C 47.88, H 4.09, N 34.13; found: C 47.82, H 4.02, N 34.02. HRMS (ESI-TOF) calcd for C_{11}H_{14}NiO_2Na^- ([M + Na^-]) = 269.0763, found 269.0765.

4,4'-Dibutylazofuranaz (9e). Yellow oil, R_t = 0.62 (1:1 hexane/CH_2Cl_2); IR (KBr) v/cm^-1: 2962, 2935, 2875, 1558, 1466, 1382, 1238, 1197, 1102, 1031, 917, 766, 730, 656, 616; 1H NMR (300 MHz, CDCl_3): δ 0.96 (t, J = 7.3 Hz, 6H, CH_3); 1.44 (m, J = 7.4 Hz, 4H, CH_2); 1.72 (m, J = 7.3 Hz, 4H, CH_2); 2.99 (t, J = 7.4 Hz, 4H, CH_2); 13C NMR (75.5 MHz, CDCl_3): δ 13.7 (s, CH_3), 22.2 (s, CH_2), 24.2 (s, CH_3), 29.0 (s, CH_3), 148.6 (s, C=C), 162.7 (s, C=N-N); Anal.Calcd for C_{15}H_{20}NiO_2Na^- (278.31); C 51.79, H 6.52, N 30.20; found: C 51.82, H 6.47, N 30.08. HRMS (ESI-TOF) calcd for C_{15}H_{20}NiO_2Na^- ([M + Na^-]) = 301.1383, found 301.1421.

4,4'-Dimethoxyazofuranaz (9f). Yellow solid, R_t = 0.62 (1:1 hexane/CH_2Cl_2); mp 180-182 °C (EtOH) (lit.[47] mp 177-178 °C); 1H NMR (300 MHz, CDCl_3): δ 4.22 (s, 3H, OMe); 13C NMR (75.5 MHz, CDCl_3): δ 60.0 (s, OCH_3); 155.0 (s, C-C); 158.8 (s, C=N-N); Anal.Calcd for C_{11}H_{12}NiO_2Na^- (226.15); C 31.87, H 2.67, N 37.16; found: C 31.91, H 2.62, N 37.02. IR spectra are identical with those reported in the literature.[48]

4,4'-Dipropoxyazofuranaz (9g). Yellow solid, R_t = 0.62 (1:1 hexane/CH_2Cl_2); mp 52-53°C (hexane); 1H NMR (300 MHz, DMSO-d_6): δ 1.02 (t, J = 7.4 Hz, 6H, CH_3); 1.78 (k, J = 7.4 Hz, 4H, CH_2); 4.45 (t, J = 7.4 Hz, 4H, OCH_3); Anal.Calcd for C_{17}H_{24}NiO_4 (282.26); C 42.55, H 5.00, N 29.77; found: C 42.59, H 4.55, N 29.52. HRMS (ESI-TOF) calcd for C_{17}H_{24}NiO_4Na^- ([M + Na^-]) = 305.0974, found 305.0977.

4,4'-Diphenylazofuranaz (9i). Yellow solid, R_t = 0.62 (1:1...
4,4-Di-4-(pyridin-3-yl)-azofurazan (9j). Yellow solid, \( R_1 = 0.62 \) (1:1 hexane/CH\(_2\)Cl\(_2\)); mp 145-146°C (hexane); IR (KBr) v/cm\(^{-1}\): 1593, 1576, 1531, 1476, 1465, 1416, 1383, 1337, 1283, 1133, 1074, 928, 917, 872, 827, 732, 707, 688, 621, 587; \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): 7.48 (dd, \( J = 4.8, 1.1, 1.1 \) H, CH\(_3\)); 8.10 (d, \( J = 7.9, 1.1, 1.1 \) H, CH\(_3\)); 8.74 (d, \( J = 4.6, 1.1, 1.1 \) H, CH\(_3\)); 8.91 (s, 1 H, CH\(_3\)); 10 \(^3\)C NMR (75.5 MHz, DMSO-d\(_6\)): \( \delta = 120.4, 123.7, 136.8, 148.7, 1.1 \) (C, C), 149.2, 152.0, 161.8 (s, C=N=N); Anal.Ca: C\(_{13}\)H\(_9\)N\(_3\)O\(_3\) (220.27): C 52.50, H 2.52, N 34.99; found: C 52.53, H 2.49, N 34.85.

4,4'-Bis(4-(1H-tetrazol-5-yl)-azofurazan (9k). Yellow solid, mp 249-250°C (lit.\(^{[7]}\) mp 238°C); \(^1\)H and \(^13\)C NMR spectra are identical with those reported in the literature.\(^{[7]}\)

4,4'-[1,2,3]Triazolo[4,5-c][1,2,5]oxadiazol-4-yl]-3,3'-azofurazan (9m). Orange solid, \( R_1 = 0.80 \) (1:1 hexane/CH\(_2\)Cl\(_2\)); mp 128-129°C (dec), (lit.\(^{[33]}\) mp 128-129°C); \(^1\)H and \(^13\)C NMR spectra are identical with those reported in the literature.\(^{[33]}\)

Electrooxidation of 3,4-diaminoazofurazan (8o). A 0.2 M solution of NaOH (100 mL) and amine 8o (0.26 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 6F per mole of starting amine were passed (\( Q = 1158 \) C), the electrolysis was stopped, the reaction mixture was stirred for 15 min. After completion of the reaction, aqueous HCl solution was added to pH 1 and the mixture was extracted with ether (3×30 mL). The organic phase was dried over Na\(_2\)SO\(_4\) and then evaporated. The residue was purified by recrystallization to give 4,4'-di-(5-tetrazolyl)-azofurazan, (9i).

4,4-Dihydroxyazofurazan (9h) was obtained by similarly to compound 9f: A yellow solid, mp 262-265°C (lit.\(^{[40]}\) mp 263-265°C); \(^1\)H and \(^13\)C NMR spectra are identical with those reported in the literature.\(^{[40]}\)

Electrooxidation of 3-amino-4-nitroazofurazan 8r. A 0.2 M solution of NaOH (100 mL) and amine 8r (0.26 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 6F per mole of starting amine were passed (\( Q = 1158 \) C), the electrolysis was stopped, the reaction mixture was stirred for 15 min. After completion of the reaction, aqueous HCl solution was added to pH 1 and the mixture was extracted with ether (3×30 mL). The organic phase was dried over Na\(_2\)SO\(_4\) and then evaporated. The residue was purified by recrystallization to give 4,4-dihydroxyazofurazan (9h), mp 262-265°C, (lit.\(^{[40]}\) mp 263-265°C); \(^1\)H and \(^13\)C NMR spectra are identical with those reported in the literature.\(^{[40]}\)

5-(4-Azidofurazan-3-yl)-1,2,3-triazolo[4,5-c][1,2,5]oxadiazol-5-ium-4-ide (11). A 0.2 M solution of NaOH (100 mL) and amine 8m (0.26 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 6F per mole of starting amine were passed (\( Q = 1158 \) C), the electrolysis was stopped, the reaction mixture was diluted with benzene (100 mL) and stirred for 15 min. The benzene extract was dried over MgSO\(_4\) and refluxed for 2 h. The solvent was removed under vacuum. The residue was purified by recrystallization to give the product 11; mp 103-104°C (lit.\(^{[33]}\) mp 103-104°C); \(^1\)H NMR (DMSO-d\(_6\), 75.5 MHz, \(^13\)C NMR (DMSO-d\(_6\), 30.4 MHz): \( \delta = 139.7, 135.2, 138.2, 23.5, 36.2, 38.8, 43.9 \) (lit.\(^{[40]}\) \( \delta = 147.7, 143.8, 139.7, 135.2, 138.2, 23.5, 36.2, 38.8, 43.9 \). \(^1\)H and \(^13\)C NMR spectra are identical with those reported in the literature.\(^{[33]}\)

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Notes and references

