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Serendipitous Synthesis of (*tert*-Butyl-*NNO*-azoxy)acetonitrile: Reduction of an Oxime Moiety to a Methylene Unit

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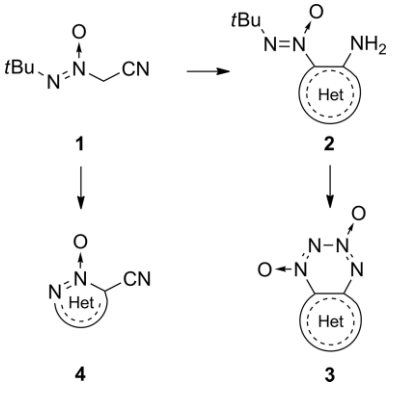
Abstract: (*tert*-Butyl-*NNO*-azoxy)acetonitrile (**1**) is a useful precursor for a number of nitrogen heterocycles. It was found that it could be obtained in good yield by treatment of the salts of (*tert*-butyl-*NNO*-azoxy)(hydroxyimino)acetonitrile with NH_2OTs. It is the first case of one-step reduction of an oxime group to a methylene unit using an aminating agent. A plausible reaction mechanism is proposed. In addition, a new strategy for the tetrazole 1-oxide ring construction was developed. This involves a diazo-group transfer to the active-methylene unit of compound **1**, followed by intramolecular coupling of the azoxy and diazo groups. The tetrazole structures were confirmed by X-ray diffraction analysis.

Introduction

Unsaturated cyclic high-nitrogen systems show considerable promise as a new generation of high-energy-density materials (HEDM).[1] 1,2,3,4-Tetrazine 1,3-dioxides (TDOs), which were synthesized for the first time by our research group,[2] are distinguished representatives of these compounds. Moreover, TDOs also show high biological activity as nitric oxide (NO) donors.[3]

A general synthetic approach to benzannulated TDOs includes a synthesis of *ortho*-amino(*tert*-butyl-*NNO*-azoxy)-benzenes followed by cyclization to give TDOs. The synthesis of these aminobenzenes usually involves a reaction of *ortho*-substituted nitrosobenzenes with *N*,*N*-dibromo-*tert*-butylamine, with a further transformation of the *ortho* substituent into an amino group.[4] This synthetic route has proved to be useful in the benzene series. However, it is often difficult to accomplish such a synthesis with a heterocyclic core; in this case, the synthesis of compounds **2** becomes a bottleneck in the preparation of new types of annulated TDOs **3** (Scheme 1).

In this paper, we report a serendipitous synthesis of (*tert*-butyl-*NNO*-azoxy)acetonitrile (**1**), which could be a useful precursor for a series of five- and six-membered heterocycles **2** (see our further publications). Moreover, this compound could be a precursor of heterocycles **4** containing an azoxy group (see Scheme 1).



Scheme 1. Nitrile **1** as a precursor of heteroannulated 1,2,3,4-tetrazine 1,3-dioxides **3** and azoxy-containing heterocycles **4**.

Results and Discussion

In the course of our studies of HEDMs, we have undertaken a search for new methods for the synthesis of tetrazole 1-oxides[5] bearing electron-withdrawing groups. Cyanotetrazole 1-oxide (**8**) was selected as a model compound. We have previously synthesized the sodium salt of tetrazole **8** starting from 4-amino-5-azidofurazan.[6] Klapötke recently used this salt as a starting material for the preparation of several new HEDMs.[7]

A new strategy for the construction of the tetrazole 1-oxide ring could involve a reaction of available oxime **5** with an aminating agent to give diazo compound **6** (Scheme 2). This could then be isomerized to give the thermodynamically more stable isomer **7**. According to quantum chemical calculations [B3LYP 6-311G(2df,2p)++], the energy released in this cyclization is 23.6 kcal/mol. Hydrolysis of tetrazole **7** could possibly lead to target compound **8**.

The amination of oxime salts to give diazo compounds is known as the Forster reaction.[8] As a rule, NH_2Cl,[8] NH_2SO_3H,[9]

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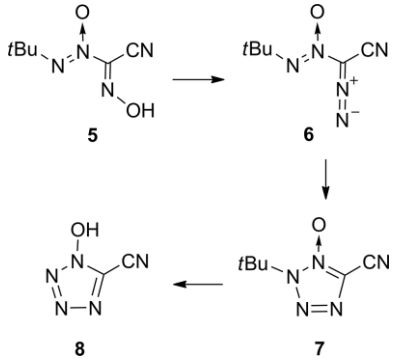
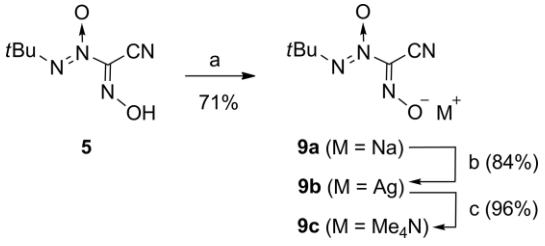


Scheme 2. The initially planned approach to the synthesis of tetrazole **8**.

or *O*-mesitylsulfonylhydroxylamine[10] have been used as the aminating agents.

The starting materials for our research were Na salt **9a** and tetramethylammonium salt **9c** (Scheme 3). The former was prepared by the reaction of oxime **5** with NaOH in methanol; this gave **9a** as a stable crystal dihydrate. The reaction of Na salt **9a** with $AgNO_3$ gave Ag salt **9b**. This was then treated with Me_4NBr in acetonitrile to give tetramethylammonium salt **9c**.

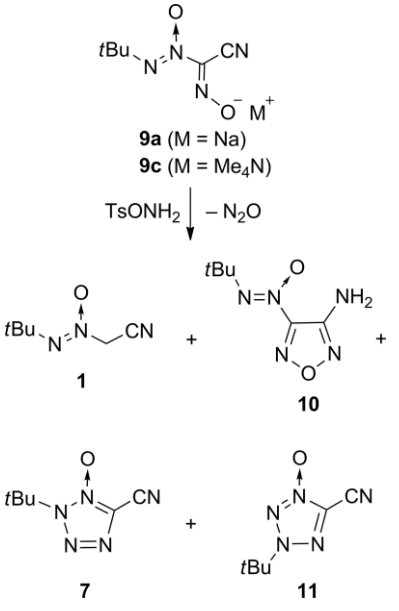


Scheme 3. Synthesis of salts **9a**–**9c**. Reagents and conditions: (a) NaOH, MeOH, 0 °C; (b) $AgNO_3$, H_2O, 25 °C; (c) Me_4NBr, MeCN, 80 °C.

$TsONH_2$ was used as an aminating agent. It was prepared according to literature procedures,[11,12] and was used either in solution in CH_2Cl_2 or as a solid.

The amination results were surprising. The reaction gave nitrile **1** as the major product. Minor products included furazan **10** and tetrazoles **7** and **11**. The product ratio varied depending on the reaction conditions (Scheme 4, Table 1).

Nitrile **1** was obtained as a colorless liquid with b.p. 65 °C (0.55 Torr). Its structure was confirmed by ^1H, ^{13}C, and ^{14}N NMR spectroscopy, IR spectroscopy, and HRMS. The ^{13}C NMR spectrum showed the signal due to the methylene unit at δ = 58.6 ppm; the signal appeared as a broad triplet [$^1J(^1H,^{13}C)$ = 153.5 Hz] in the spectrum without proton decoupling.



Scheme 4. Amination of salts **9a** and **9c**.

The highest isolated yield of nitrile **1** (68 %) was achieved when the reaction was carried out in a two-phase system of CH_2Cl_2 and H_2O in the presence of the phase-transfer catalyst Et_4NBF_4 (Table 1, entry 7). Taking into consideration the high volatility of nitrile **1**, a work-up procedure involving solvent evaporation at atmospheric pressure with a dephlegmator was used.

The highest yield by NMR spectroscopy of the mixture of tetrazoles **7** and **11** was 15 %, and was achieved when the reaction was carried out in MeCN as solvent (Table 1, entry 2). The highest isolated yield of furazan **10** (15 %) was achieved by amination of a suspension of Na salt **9a** in CH_2Cl_2 (Table 1, entry 5). In addition, the reaction mixture always contained a small amount of oxime **5** (see Table 1); this was generated from the salt (i.e., **9**), and did not react with the aminating agent.

The amination of salts **9a** and **9c** was accompanied by the release of N_2O; this was identified through ^{14}N NMR spectroscopic analysis of the reaction mixtures when the reactions were carried out in sealed NMR tubes.

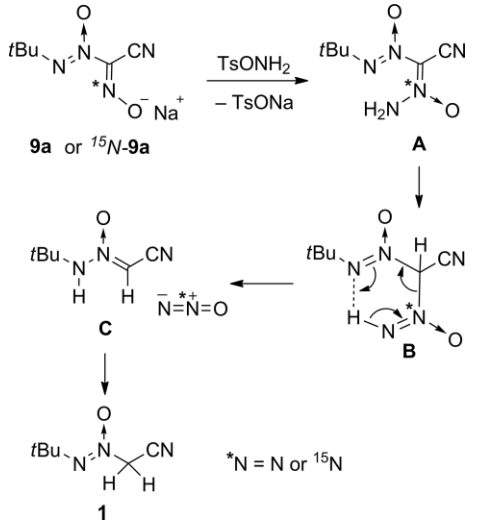
The formation of nitrile **1** can be understood as occurring through the following sequence of transformations (Scheme 5).

Table 1. Amination of salts **9a** and **9c**.

Entry	Salt **9**	M^+	Solvent	Reaction conditions	Yield [%]				
					5	**1**	**10**	**7**	**11**
1	**9a**	Na^+	CD_3OD	25 °C, 1 h	20[a]	59[a] [c]	6[a]	11[a]	4[a]
2	**9a**	Na^+	CD_3CN	2–5 °C, 0.5 h	11[a]	62[a]	12[a]	13[a]	2[a]
3	**9c**	NMe_4^+	$CDCl_3$	2–5 °C, 0.5 h	8[a]	55[a]	5[a]	1[a]	5[a]
4	**9a**	Na^+	CD_2Cl_2	suspension of **9a**, 25 °C, 1 h	10[a]	41[a]	16[a]	8[a]	2[a]
5	**9a**	Na^+	CH_2Cl_2	suspension of **9a**, 25 °C, 1 h	–	35[b]	15[b]	–	6[b]
6	**9a**	Na^+	CH_2Cl_2/H_2O	Et_4NBF_4 (10 mol-%), 2–5 °C, 1 h	3[a]	73[a]	7[a]	1[a]	–
7	**9a**	Na^+	CH_2Cl_2/H_2O	Et_4NBF_4 (10 mol-%), 2–5 °C, 1 h	3[b]	68[b]	6[b]	–	1[b]

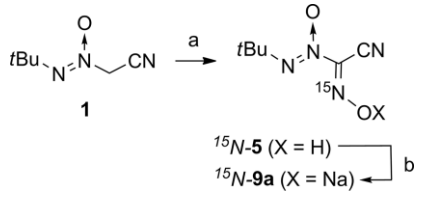
[a] Yield determined by NMR spectroscopy using an internal standard. [b] Isolated yield. [c] Deuterium-substituted **1**.

Initially, in analogy to the Forster reaction, amination proceeds at the N atom of the oxime to give intermediate **A**. Then, instead of H_2O elimination, as in the Forster reaction, tautomerization occurs to give intermediate **B**. Extrusion of N_2O, and a further proton transfer results in nitrile **1**.



Scheme 5. Plausible mechanism for the formaton of nitrile **1**.

^{15}N-labeled Na salt ^{15}N-**9a** was used to confirm this mechanism. This salt was prepared by the reaction of nitrile **1** with Na$^{15}NO_2$ in AcOH, followed by neutralization of the intermediate oxime (i.e., ^{15}N-**5**) with NaOH (Scheme 6).

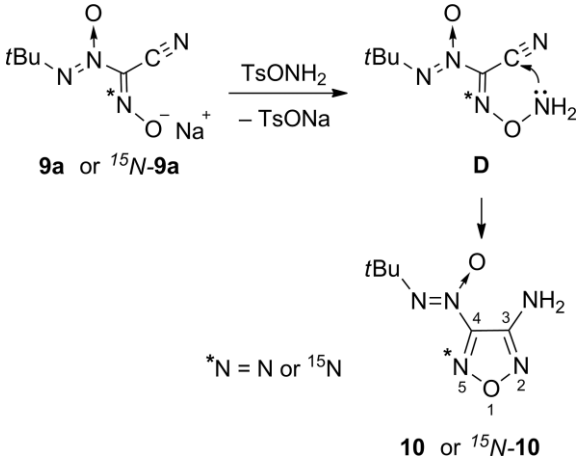


Scheme 6. Synthesis of salt ^{15}N-**9a**. Reagents and conditions: (a) Na$^{15}NO_2$, AcOH, 0–5 °C, 1 h, then 25 °C, 5 h (99 %); (b) NaOH, MeOH, 25 °C (99 %).

The nitrous oxide released in the reaction of Na salt ^{15}N-**9a** with the aminating agent contained ^{15}N at the central N atom (see Scheme 5). This was demonstrated through ^{15}N NMR spectroscopic analysis of the reaction mixture when the reaction was carried out in a sealed NMR tube.

To explain the formation of furazan **10** in the reaction of Na salt **9a** with $TsONH_2$, we suggest that the amination proceeds at the O atom of the oxime moiety to give intermediate **D**, and that this species then undergoes cyclization (Scheme 7). The reaction of Na salt ^{15}N-**9a** with $TsONH_2$ in CH_2Cl_2 led to furazan ^{15}N-**10**, with ^{15}N at the N-5 atom of the ring. To the best of our knowledge, this method has not been used before to prepare a furazan ring.

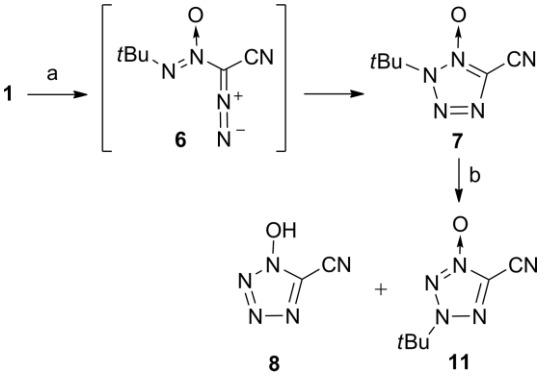
In the course of the amination of Na salt **9a**, the reaction proceeded to a small extent according to the Forster reaction mechanism, and diazo compound **6** cyclized into tetrazole **7** (see Scheme 2). The latter isomerized, to some extent, to the thermodynamically more stable isomer **11** directly in the reaction mixture (NMR tube experiments, see Table 1, entries 1–4). Complete isomerization took place with heating during the distillation of nitrile **1** (see Table 1, entry 7).



Scheme 7. Plausible mechanism for furazan ring formation.

According to the calculations [B3LYP 6-311G(2df,2p)++], isomer **11** was more stable thermodynamically than **7** by 5.3 kcal/mol.

Having established a method for the synthesis of nitrile **1**, we turned our attention to our initial goal of preparing 1-hydroxy-5-cyanotetrazole (**8**; see Scheme 2). Tetrazole **7** was synthesized by the reaction of nitrile **1** with TsN_3 in the presence of triethylamine in 46 % yield (Scheme 8). Intermediate diazo compound **6** was not observed in the reaction mixture (TLC). Tetrazole **7** was isolated as white crystals (m.p. 62–63 °C).



Scheme 8. Synthesis of tetrazoles **7**, **8**, and **11**. Reagents and conditions: (a) TsN_3, NEt_3, CH_2Cl_2, 25 °C, 5 h (49 %); (b) see Table 2.

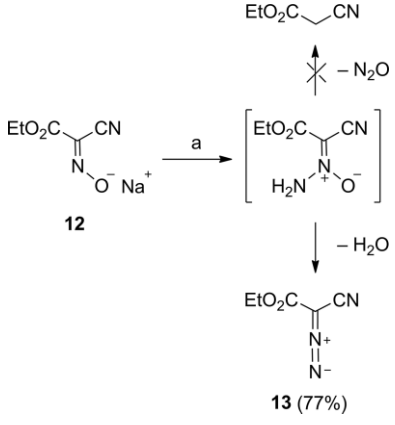
Several methods for the transformation of tetrazole **7** to H-form **8** were tested (Scheme 8, Table 2). Heating tetrazole **7** without a solvent at 100 °C for 10 min gave only a small yield of tetrazole **8** (10 %). The major product was isomeric tetrazole **11** (86 %). Keeping tetrazole **7** deposited on silica gel (60 Merck 15–40 μm) at 25 °C for 5 h gave a mixture of tetrazole **8** (42 %) and tetrazole **11** (53 %). The best yield of tetrazole **8** (73 %) was achieved by treatment of tetrazole **7** with excess HCl in diethyl ether at 25 °C for 15 min. A separate experiment showed that compound **11** remained unchanged under these reaction conditions. Thus it can be stated that tetrazole **7** takes part in two parallel reactions, viz. the loss of the *tert*-butyl group, and isom-

erization to tetrazole **11**. The latter loses the *tert*-butyl group under much more drastic conditions, and yields a number of by-products. Compound **8** was obtained as hygroscopic white crystals (m.p. 80–83 °C).

Table 2. Preparation of tetrazoles **8** and **11**.

Entry	Starting material	Reaction conditions	Yield [%] **8**	**11**
1	**7**	without solvent, 100 °C, 10 min	10	86
2	**7**	silica gel, 25 °C, 5 h	42	53
3	**7**	HCl/Et_2O, 25 °C, 30 min	73	9
4	**11**	HCl/Et_2O, 25 °C, 30 min	0	99

To understand the scope of the reduction of the oxime moiety to a methylene unit, amination of the Na salt of ethyl cyano(hydroxyimino)acetate (**12**) was carried out under the same conditions as for the amination of Na salt **9a** (Scheme 9; a two-phase system CH_2Cl_2/H_2O in the presence of the phase-transfer catalyst Et_4NBF_4). However, a Forster reaction took place to give diazo compound **13** in 77 % yield. Ethyl cyanoacetate, an expected product of oxime reduction to the methylene unit, was not found in the reaction mixture, even in trace amounts (checked by ^1H NMR spectroscopy).



Scheme 9. Amination of Na salt **12**. Reagents and conditions: (a) $TsONH_2$, Et_4NBF_4 (10 mol-%), CH_2Cl_2, H_2O, 2–5 °C, 1 h.

The possibility that isomerism at the C=N double bond of the oxime group could play a key role in the reaction mechanism seems unlikely because rotation around the double bond in the oxime anion should be unhindered.

Structure Confirmation

The structure of tetrazole **7** was confirmed by X-ray diffraction (XRD) analysis of a suitable powder (Figure 1).

The structures of tetrazoles **8** and **11** were ascertained by X-ray diffraction (XRD) analysis of suitable single crystals (Figures 2 and 3).

Although the structural peculiarities of each of these molecules could be anticipated to some extent (see Figures 1, 2, and 3), it is nevertheless desirable to look at the crystal packing motifs in more detail, since the compounds can all be considered to be precursors of high-energy materials.

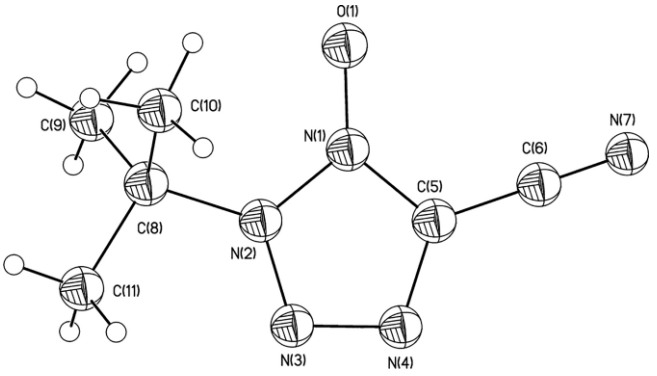


Figure 1. General view of the crystal structure of tetrazole **7**. Non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 30 %). Selected bond lengths [Å]: O(1)–N(1) 1.242(4), N(4)–N(3) 1.310(3), N(4)–C(5) 1.345(3), N(3)–N(2) 1.323(4), N(2)–N(1) 1.382(2), N(2)–C(8) 1.507(2), N(1)–C(5) 1.362(2).

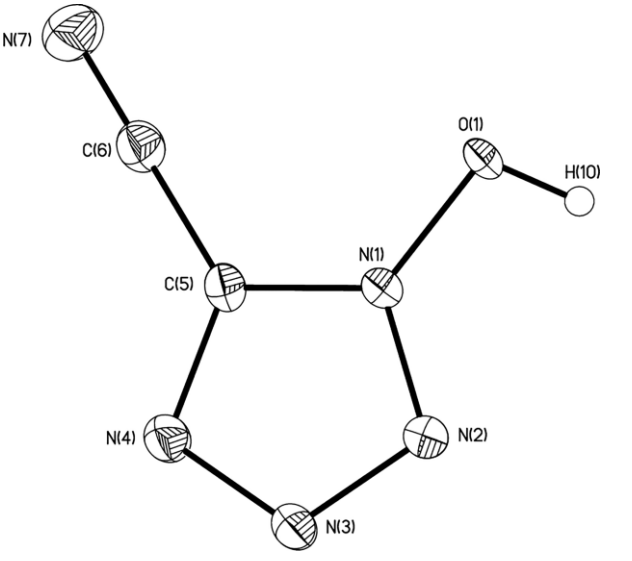


Figure 2. General view of the crystal structure of tetrazole **8**. Non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50 %). Selected bond lengths [Å]: N(1)–N(2) 1.320(2), N(1)–O(1) 1.3394(1), N(1)–C(5) 1.341(2), N(2)–N(3) 1.312(2), N(3)–N(4) 1.344(2), N(4)–C(5) 1.325(2).

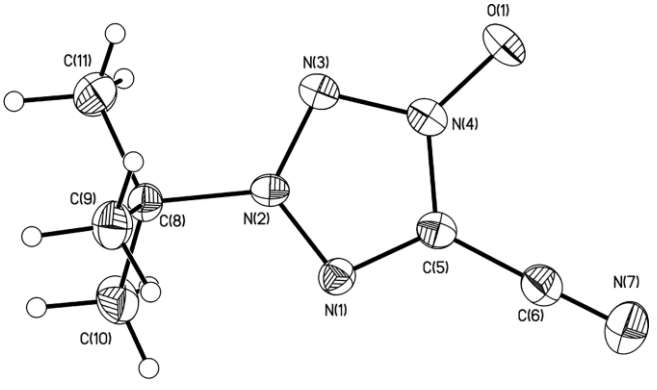


Figure 3. General view of the crystal structure of tetrazole **11**. Non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50 %). Selected bond lengths [Å]: O(1)–N(4) 1.270(2), N(1)–N(2) 1.316(2), N(1)–C(5) 1.323(2), N(2)–N(3) 1.328(2), N(2)–C(8) 1.506(2), N(3)–N(4) 1.337(2), N(4)–C(5) 1.367(2).

Given that the geometry of **7** was obtained by powder diffraction, some caution is needed when analyzing and comparing the distribution of bond lengths with those in **8** and **11**. The most interesting features of the crystal structures of compounds **7**, **8**, and **11** were found in a packing-pattern analysis.

The analysis of crystal packing in **11** revealed that the molecules are assembled into columns directed along the *a* axis by means of both stacking (N···N) and O···π-type interatomic interactions (Figure 4). For the two centrosymmetric pairs within the column, the distances N(4)···N(4A) and O···N_4C_{cent} (N_4C_{cent} – centroid of the 5-membered cycle) are almost equal [3.019(2)–3.024(2) and 3.014(2)–3.021(2) Å, respectively]. The O···N distances for the O···π interaction vary in the range 3.154(2)–3.269(2) Å [the shortest contact was with the N(2) atom], while the O···C distances are in the range 3.199(2)–3.273(2) Å. These columns are kept together by weak C–H···NC and C–H···O interactions.

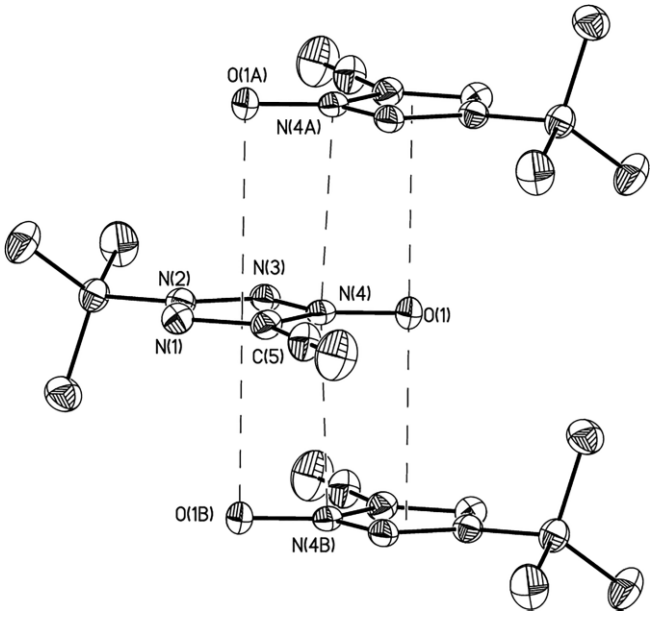


Figure 4. Fragment of a column in the crystal of tetrazole **11**.

The molecules in the crystal of tetrazole **7** also participate in O···π interactions. However, a principally different type of mutual arrangement of molecules was observed (Figure 5). It can be seen in **7** that the C–O bond is nearly perpendicular to the N_4C plane of the ring, and that the O···N_4C_{cent} distance is 2.91 Å (O···N and O···C in **7** are 3.02–3.26 Å and 3.06 Å, respectively). In contrast to **11**, these interactions lead to construction of zig-zag chains. The other intermolecular interactions in **7** are of the C–H···NC and C–H···O types.

In the crystal of tetrazole **8**, the molecules are, as expected, assembled into infinite chains by strong N–H···O hydrogen bonds O(1)–H(1O)···N(3A) [H(1O)···N(3A) 1.78 Å, O(1)···N(3A) 2.642(2) Å, O(1)–H(1O)···N(3A) 174°] (Figure 6). It should be noted that, in addition to hydrogen bonds, rather unusual intermolecular HO···OH and O···N contacts were observed between the molecules within the chains [O···O distance 2.735(2) Å, and O(1)···N(2D) distance 2.926(2) Å]. Both of these contacts can, in principle, be regarded as forced or even repulsive interactions.

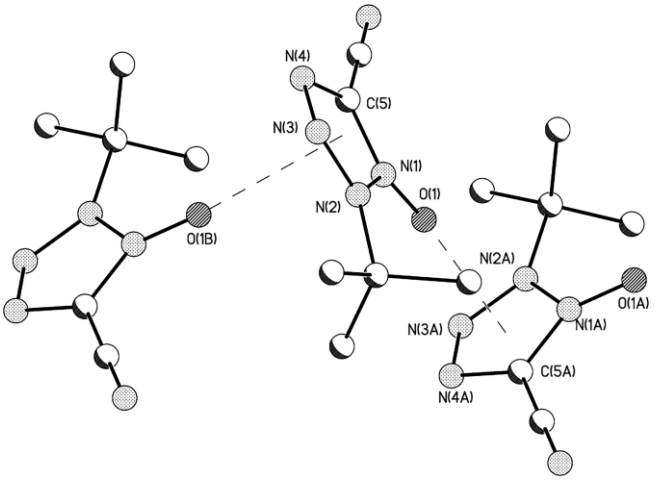


Figure 5. Fragment of a zig-zag chain in the crystal of tetrazole **7**.

The O···N contact, however, could be caused by an interaction between the oxygen lone pair and the antibonding orbital of the N(2)–N(1) bond, and this possibility was partly confirmed by geometric analysis (the O–N–N angle is 159.3°). The HO···OH interaction type has previously been observed for OH groups participating in intramolecular hydrogen bonds.[13]

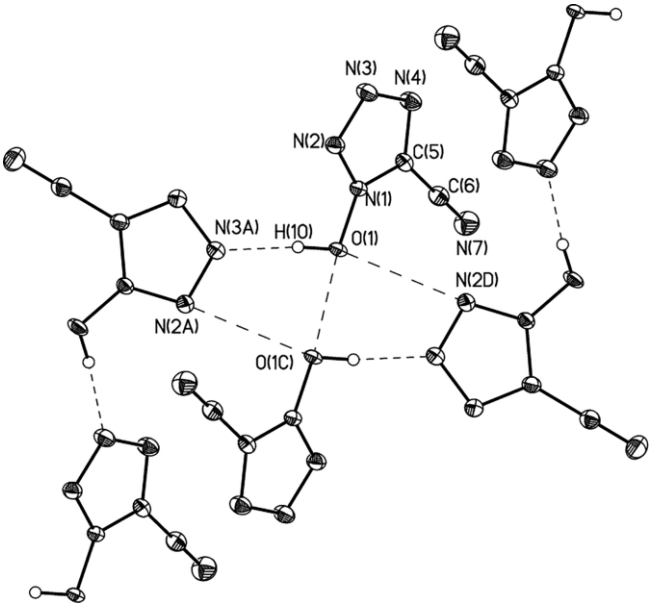


Figure 6. Fragment of the crystal packing of tetrazole **8**.

Taking into account the fact that geometry data are irrelevant for the unambiguous determination of the bonding nature of any weak interaction, we carried out DFT calculations of model dimers from crystals of **7** and **11** (Figures 7 and 8). In order to thoroughly analyze all the noncovalent interactions in the two model dimers, we resorted to the QTAIM (quantum theory of atoms in molecules) theory.[14] This approach gives the opportunity to locate all bonding interactions through a search of (3,–1) critical points of charge density, and to estimate the energy of weak interactions by means of the Espinosa correlation scheme.[15]

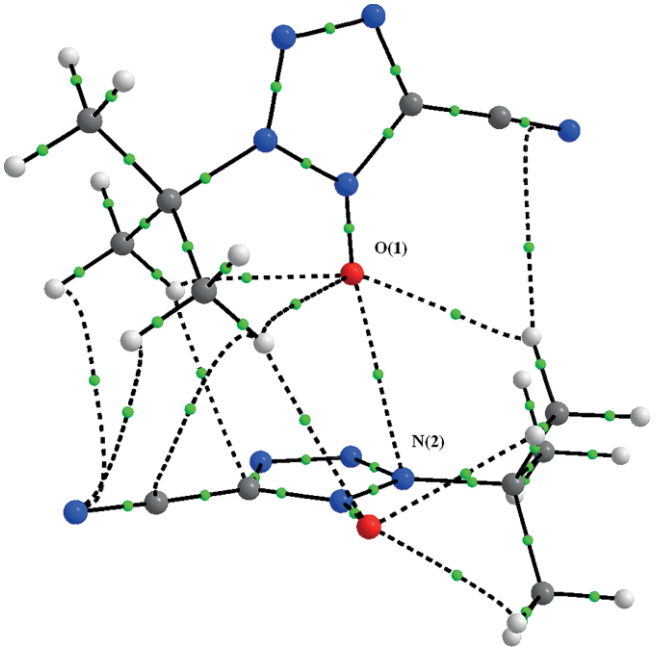


Figure 7. Illustration of the model dimers, showing the O···π interactions in **7** according to the B97D/6-311G** calculations. The critical points (3,–1) are shown by green balls, and the bond paths for intermolecular bonds by dashed lines. The critical points (3,+1) and (3,+3) are omitted for clarity.

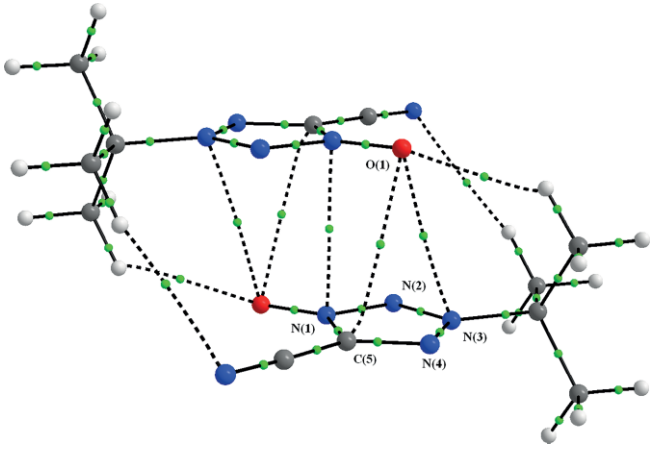


Figure 8. Illustration of the model dimers, showing the O···π interactions in **11** according to the B97D/6-311G** calculations. The critical points (3,–1) are shown by green balls, and the bond paths for intermolecular bonds by dashed lines. The critical points (3,+1) and (3,+3) are omitted for clarity.

Geometry optimization at the B97d/6-311G** level of theory led to structures that were very similar to the experimental ones for both dimer types. For dimer **7**, the N(4)···N(4A) and O···N_4C_{cent} distances were equal to 2.978 and 2.961 Å, respectively. Note that the shortest O···N contact (3.085 Å) was again detected for the N(2) atom. For dimer **11**, the perpendicular arrangement of molecules was also observed in the isolated state. Here, the O···N_4C_{cent} separation was equal to 2.910 Å, and the shortest O···N(2) contact was 3.044 Å. The binding energies of these dimers, corrected by ZPE (zero-point energy) and BSSE (basis-set-superposition error) values, were 10.74 and 8.06 kcal/mol for **7** and **11**, respectively. These values can be explicitly considered as a measure of the above-mentioned interactions. Indeed, the search of critical points revealed that, apart from the O···π interactions, a number of C–H···O and C–H···N interactions were also formed (see Figures 7 and 8).

Furthermore, the only bonding path corresponding to the O···π interaction was found in **7** for the O(1), N(2) atomic pair; in contrast, in **11**, (3,–1) critical points were located for the N(4)···N(4A), O(1)···C(5), and O(1)···N(3) interactions. It is noteworthy that in both cases, the oxygen atom interacted with the nitrogen atom bearing the *tert*-butyl group. The choice of which molecules will form interactions with this nitrogen atom cannot be governed by the N atom charge (–0.24 and –0.29 e in **7** and **11**, respectively), and is definitely influenced by auxiliary C–H···O interactions. Indeed, the energies of the O(1)···N(2) interaction in **7** and the N(4)···N(4A), O(1)···C(5), and O(1)···N(3) interactions in **11** were equal to 1.8, 1.8, 1.3, and 1.7 kcal/mol, respectively; the energy of the C–H···O interactions was only slightly lower (0.8–1.15 kcal/mol). We noted that the total energy values for all the intermolecular interactions in **7** and **11** (12.4 and 8.16 kcal/mol, respectively) were rather close to the dimer binding energy values. One can conclude that the formation of the above-mentioned intermolecular O···π interactions is forced, and that the difference in the mutual orientation of the molecules within the dimers is the consequence only of the isomer choice, and is caused by cooperative effects from both O···N and C–H···O interactions.

The DFT calculations for tetramer **8** (two O–H···N bonded molecules assembled by the above-mentioned HO···OH and O···N interactions) failed to help elucidate the nature of the intermolecular contacts observed in the crystal structure of **8**:

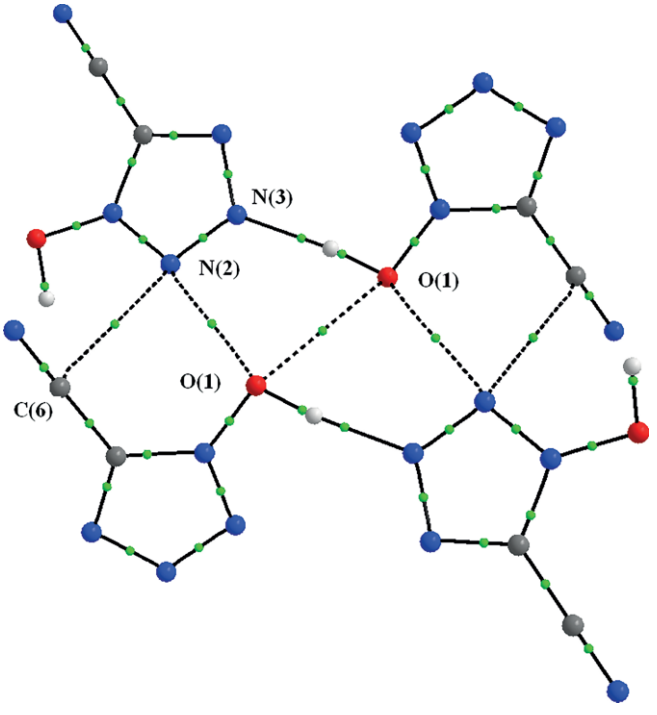


Figure 9. Illustration of the model tetramer, showing the O···N and HO···OH interactions in **8** according to the B97D/6-311G** calculations. The critical points (3,–1) are shown by green balls, and the bond paths for intermolecular bonds by dashed lines. The critical points (3,+1) and (3,+3) are omitted for clarity.

geometry optimization of the tetramer led to a principally different geometry due to the presence of "free" OH groups (Figure 9).

The single-point calculation of the tetramer's experimental geometry was carried out instead with O–H bond-length normalization to the value derived from the DFT calculations discussed above. The (3,–1) critical points were found for the HO···OH, O···N contacts, and for the O–H···N hydrogen bond, with energies equal to 2.6, 1.9, and 19.1 kcal/mol, respectively. Furthermore, the critical point (3,–1) was also located for the N(2)···C(6) contact (3.211 Å, 1.0 kcal/mol). It should be noted that according to atomic-charge analysis, the N(3) atom participating in hydrogen-bond formation in **8** was characterized by the maximum negative charge (–0.46 e), whereas the electron accumulation was significantly smaller for all the other in-ring nitrogen atoms [(–0.07) – (–0.04) e]. One can suppose that, in contrast to **7** and **11**, the supramolecular organization in the crystals of **8** is controlled by intramolecular forces and, to a greater extent, by the corresponding charge distribution.

Conclusions

A new method for the one-step reduction of an oxime group to a methylene unit was developed, as exemplified by the reaction of (*tert*-butyl-*NNO*-azoxy)-(hydroxyimino)acetonitrile salts with NH_2OTs to give (*tert*-butyl-*NNO*-azoxy)acetonitrile **1**. Nitrile **1** could be a useful starting material for the synthesis of new types of heteroannulated 1,2,3,4-tetrazine-1,3-dioxides (see our further publications).

Moreover, a new method for tetrazole 1-oxide ring formation was developed, involving the intramolecular coupling of azoxy and diazo groups. In addition, a new method for furazan ring formation was found. It involves amination of a cyanoxime at the oxygen atom of the oxime group, followed by cyclization.

Experimental Section

General Remarks: ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded with Bruker DRX-500 (500.1, 125.8, 36.1, and 50.7 MHz, respectively) and Bruker AV600 (600.1, 150.9, 43.4, and 60.8 MHz, respectively) spectrometers. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from internal tetramethylsilane (^1H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N; negative values of δ_N correspond to upfield shifts). IR spectra were recorded with a Bruker ALPHA-T spectrometer in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}) as pellets with KBr or as a thin layer. Low-resolution mass spectra were recorded with a Varian MAT-311A instrument (EI, 70 eV). High-resolution ESI mass spectra (HRMS) were recorded with a Bruker micrOTOF II instrument. Melting points were determined with a Kofler melting-point apparatus. Silica gel 60 Merck (15–40 μm) was used for preparative column chromatography. Silica gel "Silpearl UV 254" was used for preparative thin-layer chromatography. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F254. All reagents were purchased from Acros and Sigma–Aldrich. Solvents were purified before use, according to standard procedures. All other reagents were used without further purification. (*tert*-Butyl-*NNO*-azoxy)(hydroxyimino)acetonitrile,[16] ethyl *O*-(*p*-tolylsulfonyl)acetohydroximate,[12] *O*-(*p*-tolylsulfonyl)-hydroxylamine,[11] *p*-tolylsulfonyl azide,[17] ethyl cyano(hydroxyimino)acetate,[18] and ethyl cyano(diazo)acetate[19] were prepared according to the reported procedures.

The X-ray powder diffraction pattern of compound **7** was measured using Cu-K_α[20] radiation in transmission mode with a Bruker D8 Advance Vario diffractometer equipped with a LynxEye 1D detector and a Ge^{III} monochromator. The pattern was indexed using the SVD (singular value decomposition) index algorithm[20] as implemented in Bruker TOPAS 5.0,[21] and solved in direct space using parallel tempering as implemented in FOX.[22] The Rietveld refinement (in Bruker TOPAS 5.0) of this model was restraint consistent,[23] with a half uncertainty window (HUW) of 0.20(16) Å, indicating a reliable determination of the bonding pattern. The conventional *R* values were acceptably low, and the root-mean-square deviation (RMSD) of the Rietveld refined non-hydrogen atomic positions from the PW-DFT-D optimized ones was 0.092 Å, within the limits proposed by van de Streek and Neumann for correct single-crystal[24] or powder[25] structures (see Supporting Information for details). X-ray structure determination for single crystals of compounds **8** and **11** was carried out with a Bruker APEX DUO CCD diffractometer, and for compound **8** with a Bruker SMART APEX II CCD diffractometer (Mo-K_α radiation). The crystal structure of compound **11** was refined as two twin components with relative occupancies equal to 0.55 and 0.45. The structures of **8** and **11** were solved by direct methods, and were refined using an anisotropic approximation for non-hydrogen atoms.[26] The crystal data and structure-refinement parameters for compounds **7**, **8**, and **11** can be found in the Supporting Information.

CCDC 1469470 (for **8**), 1454604 (for **7**) and 1406899 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

The DFT calculations were carried out using the Gaussian 09 program.[27] A dispersion-corrected B97D density functional[28] together with a split-valence triple-zeta gaussian basis set containing two additional polarization functions (6-311G**) were used. All geometry optimizations were carried out using default limitations on forces and displacements. The type of a stationary point on the potential-energy surface was confirmed by calculations of normal vibrations for all optimized systems. All the optimized structures correspond to ground states. Binding energies for all supramolecular associates were calculated using corrections to both zero-point vibrations and basis-set superposition errors. The QTAIM analysis (charge-density critical points searches as well as integrations of charge density within atomic basins) was carried out using the AIMAll software.[29]

Sodium Salt of (*tert*-Butyl-*NNO*-azoxy)(hydroxyimino)acetonitrile Dihydrate (9a): A solution of NaOH (4.0 g, 0.1 mol) in MeOH (50 mL) was added to a stirred solution of oxime **5** (17.0 g, 0.1 mol) in MeOH (100 mL) at 0–5 °C. The resulting mixture was concentrated under reduced pressure, and the residue was recrystallized from water (100 mL) to give Na salt **9a** (13.7 g, 60 mmol, 71 %) as yellow crystals, m.p. 242–246 °C (decomp.). An analytical sample of Na salt **9a** was obtained by crystallization from MeCN as yellow crystals, m.p. 243–246 °C (decomp.). ^1H NMR (500.1 MHz, [D_6]DMSO): δ = 1.39 (s, 9 H, CMe_3) ppm. ^{13}C NMR (125.8 MHz, [D_6]DMSO): δ = 26.2 (CMe_3), 57.7 (CMe_3), 111.7 (C≡N), 142.5 (br., C=N) ppm. ^{14}N NMR (36.1 MHz, [D_6]DMSO): δ = –52 [*N*(O)N*t*Bu, $\Delta\nu_{1/2}$ = 320 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 3609 (s), 3490 (s), 2214 (w), 1621 (m), 1495 (m), 1451 (w), 1431 (w), 1362 (w), 1305 (s), 1264 (s), 1235 (m), 1145 (m) cm^{-1}. $C_6H_{13}N_4NaO_4$ (228.18): calcd. C 31.58, H 5.74, N 24.55; found C 31.48, H 5.69, N 24.85.

Tetramethylammonium Salt of (*tert*-Butyl-*NNO*-azoxy)(hydroxyimino)acetonitrile (9c): A solution of Na salt **9a** (1.14 g, 5 mmol) in distilled water (20 mL) was added to a solution of $AgNO_3$ (0.85 g, 5 mmol) in distilled water (10 mL). The resulting yellow precipitate was collected by filtration, washed with distilled water (2 × 15 mL), and dried in a vacuum desiccator over P_2O_5 to give Ag salt **9b** (1.17 g, 84 %) as a yellow powder, m.p. 163–165 °C (decomp.). $C_6H_9AgN_4O_2$ (277.03): calcd. C 26.01, H 3.27, N 20.22; found C 26.03, H 2.93, N 20.22.

A solution of Ag salt **9b** (1.00 g, 3.6 mmol) in MeCN (30 mL) was added to a boiling solution of Me_4NBr (556 mg, 3.6 mmol) in MeCN (500 mL). The reaction mixture was cooled to 25 °C, and the solvent was removed under reduced pressure. The dry residue was extracted with CH_2Cl_2 (50 mL). The extract was concentrated under reduced pressure, and the resulting residue was dried in a vacuum desiccator over P_2O_5 to give tetramethylammonium salt **9c** (842 mg, 96 %) as red-orange crystals, m.p. 93–97 °C. ^{1}H NMR (600.1 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, CMe_3), 3.34 (s, 12 H, NMe_4^+) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 26.2 (CMe_3), 55.9 (t, $^1J_{C,N}$ = 3.7 Hz, NMe_4^+), 58.7 (CMe_3), 112.0 (C≡N), 142.7 (br., C=N) ppm. ^{14}N NMR (43.4 MHz, $CDCl_3$): δ = –55 [*N*(O)N*t*Bu, $\Delta\nu_{1/2}$ = 520 Hz], –337 (NMe_4^+, $\Delta\nu_{1/2}$ = 25 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3014 (w), 2976 (s), 2933 (m), 2213 (m), 1638 (s), 1488 (s), 1452 (m), 1425 (w), 1404 (w), 1362 (m), 1306 (s), 1269 (s), 1229 (s), 1211 (s), 1147 (m), 948 (s) cm^{-1}. $C_{10}H_{21}N_5O_2$ (243.31): calcd. C 49.36, H 8.70, N 28.78; found C 49.20, H 8.87, N 28.70.

General Procedure for the Reactions of Salts 9 with *O*-(*p*-Tolylsulfonyl)hydroxylamine in Deuterated Solvents: Freshly prepared solid $TsONH_2$ (130 mg, 0.7 mmol) was added to a solution of salt **9** (0.5 mmol) in deuterated solvent (see Table 1, entries 1–3, 6) (2 mL) at 2–5 °C. The reaction mixture was stirred (for the temperature and the reaction time, see Table 1), then it was filtered, and the internal standard *p*-dichlorobenzene (36.8 mg, 0.25 mmol) was added. A portion (0.55 mL) of the reaction mixture was transferred to an NMR tube, and a ^{1}H NMR spectrum was recorded. The yields of the products are given in Table 1.

Reaction of Sodium Salt 9a with *O*-(*p*-Tolylsulfonyl)hydroxylamine in CD_2Cl_2: Freshly prepared $TsONH_2$ (140 mg, 0.75 mmol) was added to a stirred suspension of finely powdered Na salt **9a** (114 mg, 0.5 mmol) in CD_2Cl_2 (2 mL) at 25 °C. The reaction mixture was vigorously stirred for 1 h at 25 °C, then it was filtered, and the internal standard *p*-dichlorobenzene (36.8 mg, 0.25 mmol) was added. A portion (0.55 mL) of the reaction mixture was transferred to an NMR tube, and a ^{1}H NMR spectrum was recorded. The yields of the products are given in Table 1, entry 4.

Reaction of Sodium Salt 9a with *O*-(*p*-Tolylsulfonyl)hydroxylamine. Synthesis of (*tert*-Butyl-*NNO*-azoxy)acetonitrile (1): A solution of *O*-(*p*-tolylsulfonyl)hydroxylamine in CH_2Cl_2 was obtained by a slight modification of the method used by Klapötke.[11] *O*-(*p*-Tolylsulfonyl)acetohydroximate (20.5 g, 80 mmol) was added to $HClO_4$ (70 % aq.; 75 mL) at 25 °C. The resulting suspension was stirred for 2 h, then it was poured into ice water (1.5 L), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine (2 × 50 mL), and then immediately added to a solution of Na salt **9a** (11.4 g, 50 mmol) and Et_4NBF_4 (1.10 g, 5 mmol) in water (150 mL) at 2–5 °C with vigorous stirring. The reaction mixture was stirred for 1 h at 2–5 °C, then the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (25 mL). The combined organic extracts were dried with Na_2SO_4, and concentrated at atmospheric pressure. The resulting residue was distilled at 65 °C (0.55 Torr) to give (*tert*-butyl-*NNO*-azoxy)acetonitrile (**1**; 4.60 g, 33 mmol, 65 %) as a colorless oil. The distillation residue was extracted with hexane (3 × 25 mL), and the combined organic extracts were concentrated under reduced pressure to give an additional amount of nitrile **1** (0.21 g, 1.5 mmol, 3 %) as a colorless oil.

The residue insoluble in hexane was dissolved in boiling EtOH (5 mL), then cooled to –18 °C. The resulting white precipitate was collected by filtration, and dried in air to give furazan **10** (0.48 g, 2.6 mmol, 5 %) as a white solid, m.p. 163–165 °C. The product obtained was identical (m.p., TLC, ^{1}H NMR) to furazan **10** prepared by a literature procedure.[30] The mother liquor was concentrated under reduced pressure, and the residue was purified by preparative TLC (petroleum ether/ethyl acetate, 2:1) to give an additional amount of furazan **10** (66 mg, 0.4 mmol, 1 %) as a white solid, tetrazole **11** (56 mg, 0.4 mmol, 1 %) as a white solid, and oxime **5** (222 mg, 1.3 mmol, 3 %) as a white solid (m.p. 83–85 °C). This last compound was identical (m.p., TLC, ^{1}H NMR) to oxime **5** prepared by a literature procedure.[16] An analytical sample of tetrazole **11** was obtained by crystallization from petroleum ether/CH_2Cl_2, as colorless crystals, m.p. 102–105 °C.

Data for nitrile **1**: ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, CMe_3), 5.06 (s, 2 H, CH_2) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 25.2 (CMe_3), 58.5 (br., CH_2), 60.2 (CMe_3), 111.2 (C≡N) ppm. ^{13}C NMR (without proton decoupling [GATED]; 125.8 MHz, $CDCl_3$): δ = 25.3 (q, $^1J_{H,C}$ = 127.6 Hz, CMe_3), 58.6 (br. t, $^1J_{H,C}$ = 153.5 Hz, CH_2), 60.3 (dec, $^2J_{H,C}$ = 4.0 Hz, CMe_3), 111.3 (t, $^2J_{H,C}$ = 8.9 Hz, C≡N) ppm. ^{14}N NMR (36.1 MHz, $CDCl_3$): δ = –3 [N(O)*N*t*Bu*, $\Delta\nu_{1/2}$ = 750 Hz], –64 [*N*(O)N*t*Bu, $\Delta\nu_{1/2}$ = 35 Hz], –119 (C≡N, $\Delta\nu_{1/2}$ = 680 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2975 (s), 2266 (w), 1512 (s), 1508 (s), 1456 (w), 1364 (w), 1301 (s), 1239 (m), 1207 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 141 [M]$^{+\cdot}$. HRMS (ESI): calcd. for $C_6H_{11}N_3O$ [M + Na]$^+$ 164.0794; found 164.0797.

Data for tetrazole **11**: ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.76 (s, 9 H, CMe_3) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 28.6 (CMe_3), 69.7 (CMe_3), 105.3 (C≡N); 126.8 (br., C-5) ppm. ^{14}N NMR (36.1 MHz, $CDCl_3$): δ = –59 (N→O, $\Delta\nu_{1/2}$ = 170 Hz), –109 (N*t*Bu, $\Delta\nu_{1/2}$ = 440 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2995 (m), 2255 (w), 1458 (s), 1378 (m), 1293 (w), 1259 (m), 1220 (w), 1188 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 167 [M]$^{+\cdot}$. HRMS (ESI): calcd. for $C_6H_9N_5O$ [M + H]$^+$ 168.0880; found 168.0878.

Reaction of Solid Sodium Salt 9a with *O*-(*p*-Tolylsulfonyl)-hydroxylamine in CH_2Cl_2: Freshly prepared $TsONH_2$ (3.00 g, 16 mmol) was added to a stirred suspension of finely powdered salt **9a** (2.28 g, 10 mmol) in dry CH_2Cl_2 (30 mL) at 25 °C. The reaction mixture was vigorously stirred for 1 h, and then it was concentrated under reduced pressure. The resulting residue was purified by column chromatography (petroleum ether/ethyl acetate, 5:1) to give tetrazole **11** (100 mg, 6 %) as white crystals (m.p. 97–103 °C), and also a mixture of nitrile **1** and furazan **10**. The latter mixture was extracted with hexane (2 × 10 mL), and the extract was concentrated under reduced pressure to give nitrile **1** (0.50 g, 35 %) as a colorless oil. The residue after the extraction was furazan **10** (0.28 g, 15 %), a white solid (m.p. 163–165 °C). The products obtained were identical (m.p., TLC, ^{1}H NMR) with authentic samples.

(*tert*-Butyl-*NNO*-azoxy)(^{15}N-hydroxyimino)acetonitrile (^{15}N-5): $Na^{15}NO_2$ (200 mg, 2.85 mmol) was added in several portions over 10 min to a stirred mixture of nitrile **1** (282 mg, 2 mmol), AcOH (0.4 mL), and H_2O (0.6 mL) at 0–5 °C. The reaction mixture was stirred for 1 h at 0–5 °C, and then for 5 h at 25 °C. After the reaction was complete, CH_2Cl_2 (30 mL) was added. The organic layer was separated, washed with brine (10 mL), dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to give oxime ^{15}N-**5** (338 mg, 99 %) as a white solid. An analytical sample of oxime ^{15}N-**5** was obtained by crystallization from petroleum ether as color-

less crystals, m.p. 93–95 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.46 (s, 9 H, CMe_3) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 25.3 (CMe_3), 61.5 (CMe_3), 104.7 (C≡N), 136.4 (br., C=N) ppm. ^{14}N NMR (36.1 MHz, $CDCl_3$): δ = –65 [*N*(O)N*t*Bu, $\Delta\nu_{1/2}$ = 180 Hz] ppm. ^{15}N NMR ([GATED], 60.8 MHz, CD_3OD): δ = 27.5 (^{15}N-OH) ppm. IR (KBr): $\tilde{\nu}$ = 3386 (m), 3287 (s), 2985 (s), 2752 (m), 2658 (m), 1489 (s), 1455 (m), 1369 (m), 1295 (m), 1238 (m), 1209 (m), 1164 (s), 1081 (s), 1060 (m), 1039 (w) cm^{-1}. $C_6H_{10}N_2{}^{15}NO_2$: calcd. C 42.06, H 5.84, N 33.30; found C 41.97, H 5.65, N 33.25.

Sodium Salt of (*tert*-Butyl-*NNO*-azoxy)(^{15}N-hydroxyimino)acetonitrile Dihydrate (^{15}N-9a): A solution of NaOH (51 mg, 1.3 mmol) in MeOH (1 mL) was added dropwise to a stirred solution of oxime ^{15}N-**5** (200 mg, 1.3 mmol) in MeOH (3 mL) at 0–5 °C. The solvent was removed under reduced pressure, the residue was dissolved in boiling MeCN (3 mL), and the resulting solution was cooled to –20 °C. The precipitate was collected by filtration, and dried in a vacuum desiccator to give Na salt ^{15}N-**9a** (173 mg, 63 %) as yellow crystals, m.p. 230–234 °C (decomp.). ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 1.39 (s, 9 H, CMe_3) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 26.2 (CMe_3), 57.7 (CMe_3), 111.7 (C≡N), 142.5 (br., C=N) ppm. ^{14}N NMR (36.1 MHz, [D$_6$]DMSO): δ = –52 [*N*(O)N*t*Bu, $\Delta\nu_{1/2}$ = 320 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 3609 (s), 3490 (s), 2214 (w), 1621 (m), 1495 (m), 1451 (w), 1431 (w), 1362 (w), 1305 (s), 1264 (s), 1235 (m), 1145 (m) cm^{-1}. $C_6H_{13}N_3{}^{15}NNaO_4$: calcd. C 31.42, H 5.67, N 24.87; found C 31.48, H 5.69, N 24.85.

Reaction of Sodium Salt ^{15}N-9a with *O*-(*p*-Tolylsulfonyl)hydroxylamine in a Sealed NMR Tube: Freshly prepared $TsONH_2$ (30 mg, 0.16 mmol) was added to a solution of Na salt ^{15}N-**9a** (23 mg, 0.1 mmol) in CD_3OD (0.5 mL) in an NMR tube at –78 °C under an argon atmosphere. The cooled tube was sealed, then warmed to 25 °C, and kept for 1 h. The ^{1}H, ^{14}N, and ^{15}N NMR spectra were recorded (see Supporting Information). In the ^{1}H NMR spectrum, signals due to nitrile **1**, oxime **5**, furazan **10**, and tetrazoles **7** and **11** were observed. Data for nitrous oxide: ^{14}N NMR (43.4 MHz, CD_3OD): δ = –148 [t, the central N atom in NNO, $\Delta\nu_{1/2}$ = 10 Hz, $^1J(^{14}N,^{14}N)$ = 4.2 Hz (cf. ref.[31])], –232 [d, the terminal N atom in N^{15}NO and NNO, $\Delta\nu_{1/2}$ = 10 Hz, $^1J(^{14}N,^{15}N)$ = 6.2 Hz (cf. ref.[32])] ppm. ^{15}N NMR (60.8 MHz, CD_3OD): δ = –147.2 [t, the central N atom in N^{15}NO, $^1J(^{14}N,^{15}N)$ = 6.2 Hz (cf. ref.[32])] ppm.

Reaction of Solid Sodium Salt ^{15}N-9a with *O*-(*p*-Tolylsulfonyl)-hydroxylamine in CH_2Cl_2: 4-(*tert*-Butyl-*NNO*-azoxy)-1,2,5(^{15}N)-oxadiazol-3-amine (^{15}N-10): Freshly prepared $TsONH_2$ (550 mg, 2.9 mmol) was added to a stirred suspension of finely powdered salt ^{15}N-**9a** (474 mg, 2.1 mmol) in dry CH_2Cl_2 (10 mL) at 25 °C. The reaction mixture was vigorously stirred for 1 h, and then it was concentrated under reduced pressure. Then H_2O (10 mL) and EtOAc (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried with Na_2SO_4, and concentrated under reduced pressure. The resulting solid was extracted with hexane (10 × 10 mL), and the solid residue was purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate, 4:1) to give furazan ^{15}N-**10** (47 mg, 12 %) as white crystals (m.p. 163–165 °C). The product obtained was identical (m.p., TLC, ^{1}H NMR) with an authentic sample of unlabeled furazan **10**. ^{15}N NMR (60.8 MHz, CD_3OD): δ = 26.1 (^{15}N of furazan ring) ppm. Nitrile **1** and tetrazole **11** were not isolated in this experiment.

3-*tert*-Butyl-2*H*-tetrazole-5-carbonitrile 4-Oxide (7): A solution of Et_3N (0.85 mL, 6.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 15 min to a stirred solution of TsN_3 (1.20 g, 6.2 mmol) and nitrile **1** (705 mg, 5 mmol) in CH_2Cl_2 (7 mL) at 0–5 °C. The resulting mixture was stirred at 20 °C for 5 h, then the solvent was removed under reduced pressure, and the residue was extracted with hexane (10 × 15 mL). The combined extracts were concentrated under reduced pressure to a volume of ca. 50 mL, and kept overnight at –20 °C. The resulting precipitate was collected by filtration, and dried in vacuo to give tetrazole **7** (380 mg, 46 %) as white crystals (m.p. 61–62 °C). An analytical sample of tetrazole **7** was obtained by recrystallization from hexane as white crystals, m.p. 62–63 °C. ^{1}H NMR (600.1 MHz, $CDCl_3$): δ = 1.86 (s, 9 H, CMe_3) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 26.2 (CMe_3), 69.6 (CMe_3), 105.7 (C≡N); 127.5 (br., C-5) ppm. ^{14}N NMR (43.4 MHz, $CDCl_3$): δ = –21 (tetrazole ring, $\Delta\nu_{1/2}$ = 1700 Hz), δ = –45 (tetrazole ring, $\Delta\nu_{1/2}$ = 870 Hz), δ = –72 (N→O, $\Delta\nu_{1/2}$ = 230 Hz), –83 (N*t*Bu, $\Delta\nu_{1/2}$ = 690 Hz), –160 (C≡N, $\Delta\nu_{1/2}$ = 1430 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2995 (m), 2252 (w), 1503 (s), 1455 (m), 1400 (w), 1376 (w), 1288 (w) cm^{-1}. HRMS (ESI): calcd. for $C_6H_9N_5O$ [M + Na]$^+$ 190.0699; found 190.0693.

Reaction of Tetrazole 7 with HCl/Et_2O. Synthesis of 1-Hydroxy-1*H*-tetrazole-5-carbonitrile (8): Tetrazole **7** (388 mg, 2.3 mmol) was dissolved in a saturated solution of HCl in Et_2O (15 mL) at 25 °C. The reaction mixture was kept at 25 °C for 2 h and the solvent was removed under reduced pressure. The residue was dissolved in boiling CH_2Cl_2 (50 mL), the solution was filtered and the filtrate was cooled to –20 °C and kept for 12 h. The white precipitate was formed. The mother liquor was decanted and the precipitate was dried in vacuo to give was tetrazole **8** (35 mg, 14 %) as hygroscopic white crystals, m.p. 80–83 °C. The mother liquor was concentrated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to give additional amount of tetrazole **8** (153 mg, 59 %) as hygroscopic white crystals and tetrazole **11** (35 mg, 9 %) as white crystals, m.p. 97–103 °C.

Data for tetrazole **8**: ^{13}C NMR (150.9 MHz, CD_3OD): δ = 106.7 (C≡N), 128.8 (br., C-5) ppm. ^{14}N NMR (43.4 MHz, CD_3OD): δ = –4 (tetrazole ring, $\Delta\nu_{1/2}$ = 380 Hz), –14 (tetrazole ring, $\Delta\nu_{1/2}$ = 240 Hz), –41 (tetrazole ring, $\Delta\nu_{1/2}$ = 460 Hz), –106 (C≡N and tetrazole ring, $\Delta\nu_{1/2}$ = 630 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3362 (s), 3235 (s), 2269 (w), 1696 (s), 1616 (m), 1496 (s), 1409 (m), 1375 (s), 1239 (s), 1216 (s), 1124 (m), 1060 (m), 1039 (w) cm^{-1}. C_2HN_5O (111.06): calcd. C 21.63, H 0.91, N 63.06; found C 21.85, H 1.03, N 62.87.

Thermolysis of Tetrazole 7. Synthesis of 2-*tert*-Butyl-2*H*-tetrazole-5-carbonitrile 4-Oxide (11): Tetrazole **7** (77 mg, 0.5 mmol) was heated in a thin layer without solvent at 100 °C for 10 min. The resulting residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate, 2:1) to give tetrazole **11** (66 mg, 86 %) as a white solid (m.p. 97–103 °C); and tetrazole **8** (5 mg, 10 %) as a yellow oil. The products obtained were identical to tetrazoles **8** and **11** prepared by the procedures described above.

Rearrangement and De-*tert*-butylation of Tetrazole 7 on Silica Gel: Tetrazole **7** (334 mg, 2 mmol) was added to a suspension of silica gel 60 (Merck; 15–40 μm; 3.0 g) in CH_2Cl_2 (10 mL), and the solvent was removed under reduced pressure. The residue was kept at 25 °C for 5 h, then it was transferred onto a Schott filter, and eluted with MeOH (50 mL). The eluate was concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel "Silpearl UV 254" (ethyl acetate) to give tetrazole **11** (177 mg, 53 %) as white crystals, and tetrazole **8** (93 mg, 42 %) as hygroscopic white crystals. The products obtained were identical to tetrazoles **8** and **11** prepared by the procedures described above.

Sodium Salt of Ethyl Cyano(hydroxyimino)acetate (12):[33] A solution of NaOH (1.20 g, 30 mmol) in MeOH (20 mL) was added dropwise to a stirred solution of ethyl cyano(hydroxyimino)acetate (4.26 g, 30 mmol) in MeOH (20 mL) at 25 °C. The solvent was removed under reduced pressure. The residue was crystallized from

MeCN (40 mL) and dried in a vacuum desiccator over P_2O_5 to give Na salt **12** (1.87 mg, 38 %) as yellow crystals, m.p. >260 °C (decomp.). $C_5H_5N_2NaO_3$ (164.10): calcd. C 36.60, H 3.07, N 17.07; found C 36.58, H 3.06, N 16.99.

Reaction of Sodium Salt 12 with *O*-(*p*-Tolylsulfonyl)hydroxylamine. Synthesis of Ethyl Cyano(diazo)acetate (13): *O*-(*p*-Tolylsulfonyl)acetohydroximate (0.75 g, 2.9 mmol) was added to $HClO_4$ (70 % aq.; 4 mL) at 25 °C. The resulting suspension was stirred for 2 h, then it was poured into ice water (75 mL), and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (2 × 5 mL), concentrated under reduced pressure to a volume of ca. 10 mL, and then immediately added to a solution of Na salt **12** (326 mg, 2 mmol) and Et_4NBF_4 (43 mg, 0.2 mmol) in water (6 mL) at 2–5 °C with vigorous stirring. The reaction mixture was stirred for 1 h at 2–5 °C, then the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were washed with H_2O (2 × 5 mL), and brine (10 mL), dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) to give diazo compound **13** (214 mg, 77 %) as a yellow oil. The product obtained was identical (TLC, ^1H, ^{13}C NMR) to diazo compound **13** prepared according to the reported procedure.[19]

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Keywords: Synthetic methods · Reduction · Amination · Nitrogen heterocycles · Diazo compounds

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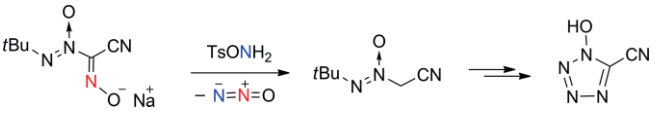

(*tert*-Butyl-*NNO*-azoxy)acetonitrile was obtained by a new one-step transformation of an oxime group into a methylene unit using an aminating agent. This active-methylene compound has played a key role in creating a new approach to the synthesis of tetrazole 1-oxides.

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