

Novel illustrations of the specific reactivity of 1,1-diamino-2,2-dinitroethene (DADNE) leading to new unexpected compounds

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Abstract—1,1-Diamino-2,2-dinitroethene (DADNE) was further investigated and evaluated in oxidation and azidation reactions. DADNE gave new unexpected products as a result of its specific reactivity as previously observed. The X-ray structure determination was the key of success in this work enabling us to perfectly characterise the new products and argue about the reaction mechanisms as well. Once again, the nucleophilic *gem*-dinitrocarbon of DADNE seemed to be directly involved in these transformations. Attempts to change the regioselectivity were performed by modifying the experimental conditions.

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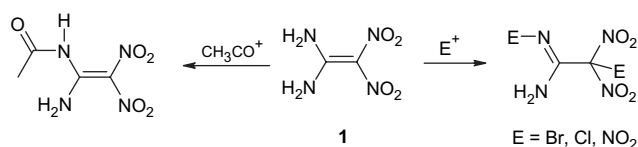
1. Introduction

Munition vulnerability is an important strategic issue. In the past several serious accidents and chain explosions onboard of military ships were reported. Consequently, huge efforts were undertaken to enhance the vulnerability standards of weapons. Energetic material researches have been focused on the improvement of material and molecule sensitivity. 5-Oxo-3-nitro-1,2,4-triazole (NTO) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) were found to be sufficiently insensitive to fulfil the new Armed Forces needs (i.e., French MURAT concept). Chemists currently design and optimise energetic molecule structures in order to find the best compromise between insensitiveness and performances. For instance, nitro and azide are known explosives functions enhancing the potential energy of energetic molecules, whereas hydrogen bonding induced by polarised NH groups stabilise the chemical structure decreasing the sensitivity.¹ More recently, 1,1-diamino-2,2-dinitroethene DADNE **1** (also called FOX-7) was prepared as a new efficient insensitive molecule.² Our work of interest consisted in modifying and optimising the DADNE structure in order to enhance its performances in respect of its insensitiveness.

We firstly started examining the chemical behaviour of DADNE³ extending the previous works.^{4,5} Two chemical behaviours of DADNE were indeed determined depending on the nature of electrophiles involved. The DADNE reactivity can be illustrated according to the following Scheme 1.

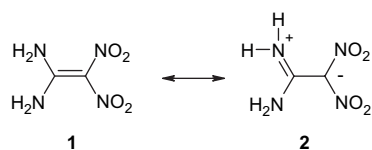
Keywords: Azidation; Peroxide oxidation; Tetrazole; Electrophilic reactions; Nitro compounds.

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Scheme 1. The reactivity of DADNE **1**.

Most studied electrophiles react rapidly with DADNE **1** at room temperature to give the di-substituted derivatives. As a nucleophile, the *gem*-dinitrocarbon can react with halogenium and nitronium electrophiles. Both reactions are then followed by a fast attack on the amidino moiety. Another DADNE reactivity was also observed since one amino group was directly attacked by a potent electrophilic complex induced under vigorous conditions (acylation catalysed by a Lewis acid in refluxing acetyl chloride).³ These experimental results indicate that the real DADNE structure **2** is far from the assumption of enamine **1** as commonly represented in the literature, but rather closer to a resonance structure such as compound **2** in accordance with the crystallographic data⁶ (see Scheme 2).



Scheme 2. DADNE and one of its more ‘real’ structural representations.

For convenience, DADNE is still represented in the paper by the unpolarised structure **1**.

Further works on DADNE deal with oxidation and azidation reactions leading to new unexpected products. They are all

characterised by X-ray analysis. The mechanisms are also discussed taking into consideration the established reactivity of DADNE.³

2. Results and discussion

2.1. Oxidation of DADNE with peroxide reagents

Several works report efficient oxidation methods of deactivated primary amines producing a mixture of nitro, azo and azoxy products in the furazane series (Scheme 3).^{7a–d}

Selectivity depends on the nature of the substrate, the oxidant strength and on the employed experimental conditions.^{8,9} Sheremetev suggested a correlation between the ionisation potentials of deactivated primary amines and the oxidative capacity of the mixtures so that a wide variety of nitrofurazanes, bearing both electron-withdrawing and electron-donating groups, have been prepared in this way.⁹ In order to reach an azoxy derivative of DADNE, we chose to carry out the DADNE oxidation in a mixture of diluted hydrogen peroxide (30% in H₂O₂) and concentrated sulfuric acid (Scheme 4) as previously described in the furazane series.^{7a}

A white insoluble product rapidly precipitated in the mixture. Analyses were difficult to undertake since the product had a very low solubility in all solvents including water. However, we succeeded in preparing suitable crystals for X-ray analysis. Surprisingly, unexpected amidinoformic acid **5** was identified as the oxidised product. This compound was firstly synthesised by Yoshimura et al. from potassium thiooxamide and ammonia.¹⁰ Wieland and Seeliger then suggested other synthetic ways to access amidinoformic acid from dithioacetic acid sulfide and from hydroxyacetonitrile.¹¹ Finally, Nii et al. reported a new synthesis of amidinoformic acid using benzyl cyanofornates.¹² In spite of many reports, no full analytical characterisation of amidinoformic acid was performed. No X-ray and full IR data were reported.^{10–12} Figure 1 displays the X-ray structure of amidinoformic acid **5**.

As an obvious zwitterionic molecule, the two C–NH₂ bonds (1.31 Å) are similar due to a full π -electron delocalisation

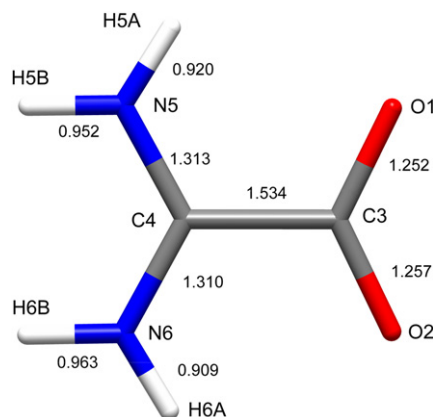
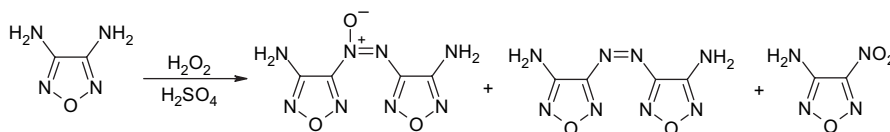


Figure 1. X-ray crystal structure of amidinoformic acid **5**.

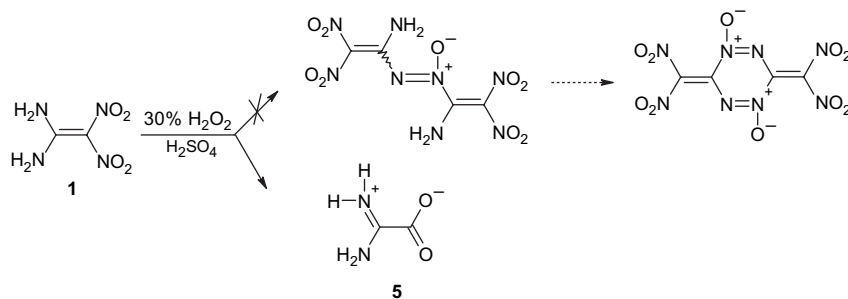
between both the nitrogens. They have almost a double bond character (1.31 Å instead of 1.25 Å for an exact double bond). The C–C bond is an exact single bond (1.53 Å) and the carboxylate C=O bond has a standard value (1.25 Å). The zwitterionic structure is a result of the acid–base amidinoformic acid properties as the amidino moiety is sufficiently basic to abstract the acidic proton. The IR spectrum displayed two characteristic peaks. The amidinium moiety (CNH₂⁺) absorbs at 1715 cm⁻¹, which is very close to the frequency of formamidinium chloride (1717 cm⁻¹). The ionised carboxyl group absorbs at 1645 cm⁻¹ and fairly flanks standard values reported in the amino-acid series.¹³ This value is also close to the strong vibrations of sodium formate carbonyl (1611 and 1632 cm⁻¹).

We obviously assumed that the nucleophilic *gem*-dinitrocarbon was attacked instead of amino moieties as initially expected. We therefore attempted to modify the regioselectivity by treating DADNE **1** with a non-aqueous and highly-concentrated pertrifluoroacetic acid solution. However, despite using more severe oxidation conditions, no change was observed, amidino acid **5** being isolated again.

Such an unexpected result prompted us to investigate the oxidation mechanism. The literature regarding the conversion of a nitrocarbon into a carboxyl derivative is

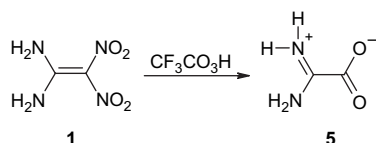


Scheme 3. Oxidation of diaminofurazane in hydrogen peroxide.

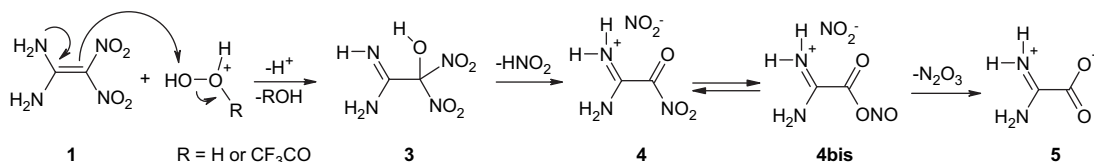


Scheme 4. Oxidation of DADNE in diluted hydrogen peroxide and concentrated sulfuric acid.

well-documented.¹⁴ The well-known Nef reaction consists in an acid-catalysed hydrolysis of nitro compounds to give the corresponding carbonyl derivatives. The mechanism was shown to proceed via an addition of H₂O onto the protonated nitro group leading to the coloured α -hydroxynitroso intermediate. Since the reaction occurred in a non-aqueous pertrifluoroacetic acid solution (see Scheme 5) and assuming that the *gem*-dinitrocarbon was nucleophilic,³ a transfer of hydroxylum 'HO⁺' onto the *gem*-dinitrocarbon was a more likely and valuable explanation. The primary amine oxidation by peroxide reagents is a well-known process giving mixtures of nitro, azo and azoxy products.^{7a,15} Several hydroxylum transfers are required to reach these compounds.^{7a} In this reaction, the involved hydroxylum electrophile was suspected to attack the nucleophilic *gem*-dinitrocarbon of DADNE **1** (as in nitrations and halogenations).³ Therefore, we suggested the following mechanism (Scheme 6).



Scheme 5. Oxidation of DADNE in concentrated pertrifluoroacetic acid mixture.

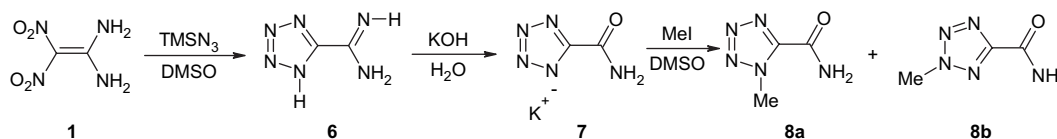


Scheme 6. Suggested oxidation mechanism of DADNE. The reaction is presented as an acid-catalysed electrophilic reaction.

1-Amidino-2-hydroxy-2,2-dinitroethane **3** can be seen as the first intermediate. A subsequent HNO₂ elimination followed by a nitro–nitrite rearrangement afforded amidinoformic acid **5**. Nitrite nucleophilic substitution is known to produce hydroxyl derivatives as the ambident nitrite ion can react according to both N- and O-attack.^{16a} The O-attack leads to the nitrite ester, which breaks down very rapidly to the final product delivering dinitrogen trioxide (N₂O₃).^{16a} Broxton reported that in the deficient aromatic series the O-attack was 20 times greater than the N-attack. Many nitrite O-attacks giving hydroxyl products are exemplified in the literature.^{16b–c} So we supposed that equilibrium between **4** and **4bis** did exist due to the presence of the ambident nitrite counter-ion to further produce amidino acid **5** by delivering N₂O₃.

2.2. The particular reaction of DADNE and TMSN₃

The reactivity of DADNE **1** was also previously evaluated towards dipolar reactants in presence of unsubstituted and substituted azides,³ but all attempts failed and no 1,3-



Scheme 7. Derivatisation work for complete identification of tetrazole **6**.

cycloaddition on the carbon–carbon bond was observed. Surprisingly, the reaction of **1** and trimethylsilylazide (TMSN₃) gave an unexpected white product. However, once again no cycloaddition occurred. IR spectrum displayed NH or/and NH₂ absorption bands, whereas ¹⁴N NMR analysis revealed no evidence of nitro groups. The product formula (C₂N₆H₄) was given thanks to elementary analyses and mass spectrometry. Being an insoluble product, the full characterisation could not be completed by X-ray determination. The new structure **6** was only perfectly assigned after an efficient derivatisation work (Scheme 7).

X-ray determinations of derivatives **7** and **8a**, obtained after alkaline hydrolysis and subsequent methylation, provided an unambiguous proof of structure **6**. Compounds **8a** and **8b** as a mixture of regioisomers (4:1, mol:mol) were separated from the crude mixture by selective crystallisation. The regioselectivity of the alkylation depends on the substituent on C(5), and also on the exact form (neutral or ionised) in which the substrate reacts with the alkylating agent.¹⁷ The derivatives **7** and **8a** have standard N–N tetrazole bonds ranging from 1.31 to 1.35 Å (Fig. 2). Both structures also have standard C=O and C(O)–NH₂ bonds, which respectively measure 1.23 and 1.32 Å close to usual standard values. Both ionic and neutral structures have the same average N–N cyclic bond lengths. No significant structural

differences between the two tetrazole cycles are observed. Nevertheless, we can notice a slight longer N(4)–C(5) bond in tetrazolate **7** compared to tetrazole **8a** due to a delocalisation of the anionic charge.

As a confirmation of the structure **6**, a disulfilimine by-product **9** slowly crystallised from the crude reaction mixture (see X-ray structure in Fig. 3). This compound was formed by condensation of **6** with two molecules of dimethylsulfoxide (used as a solvent).

At a first glance, we assumed after a rough evaluation of the X-ray data that the disulfilimine by-product might have a simple and symmetrical structure as represented in Figure 4. Yet experimental X-ray observations (i.e., bond lengths) could not match the structure **9a**.

The exocyclic C(5)–C(6) bond is single (1.49 Å) and the heterocycle is clearly a usual tetrazole. All cyclic tetrazole bonds are fairly similar to those of tetrazoles **7** and **8a** as described above (see Fig. 2). The N(1)–N(2), N(3)–N(4),

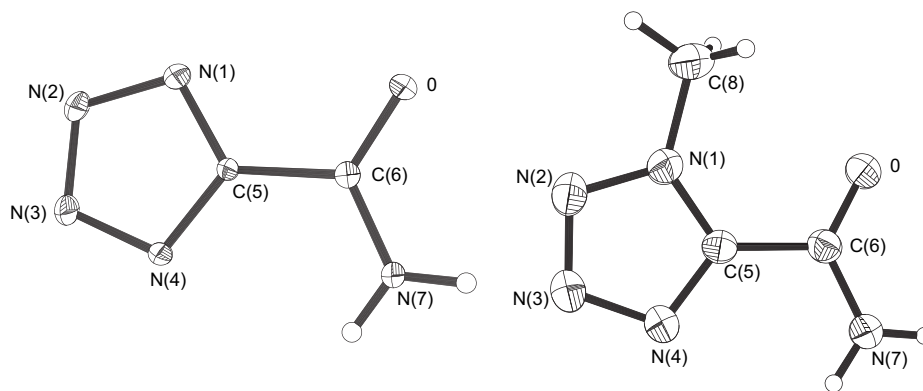


Figure 2. X-ray structures of tetrazoles **7** and **8a**.

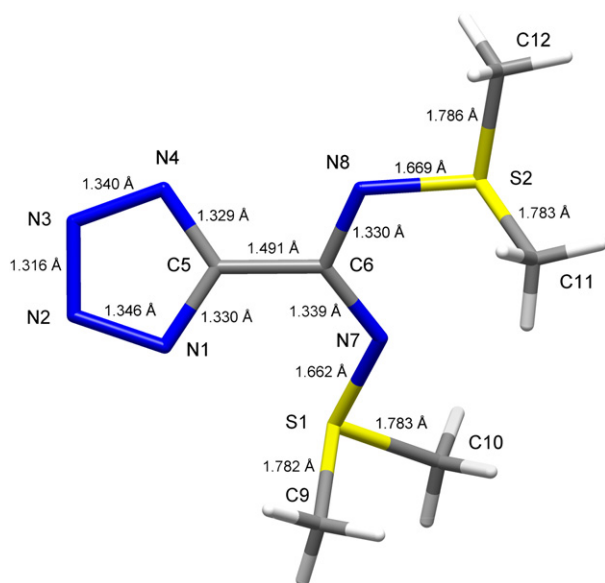
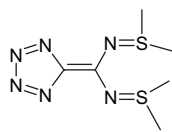


Figure 3. A disulfilimine by-product characterised by X-ray analysis.

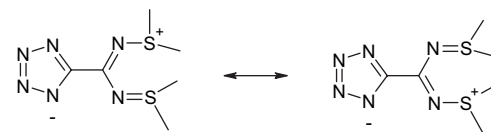


9a

Figure 4. Symmetrical disulfilimine structure **9a** as an unsuitable representation.

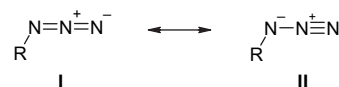
N(1)–C(5) and N(4)–C(5) bonds range from 1.33 to 1.34 Å, whereas the shortest ‘double-character’ N(2)–N(3) bond has a 1.32 Å length. It is noteworthy that the two C–N bonds of the disulfilimine moiety have almost the same length (1.33–1.34 Å) indicating a full electron delocalisation between both the nitrogens N(7) and N(8). A full delocalisation is also allowed onto the two sulfur atoms (both N–S bonds measure 1.66–1.67 Å). Consequently, the real disulfilimine structure can be represented by the two zwitterionic mesomers as represented in Scheme 8.

This surprising result prompted us to investigate the mechanism of the reaction. We first speculated an interaction between the nucleophilic *gem*-dinitrocarbon and TMSN₃ as



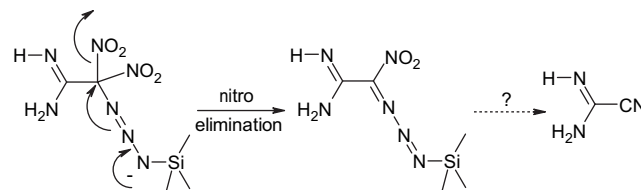
Scheme 8. Representation of disulfilimine **9**.

observed with other electrophiles.³ But to the best of our knowledge no electrophilic behaviour of TMSN₃ has been reported before in the literature. The only example described by Olah consists in an activated system involving trimethylsilylazide and a super acid to induce a potent aminating [NH₂N₂]⁺ reagent.¹⁸ Our gentle experimental conditions are definitely far from those described by Olah. A deeper bibliographic investigation on azides let us to consider trimethylsilylazide as an ambivalent reagent as nitrogen atoms have both electron-donating and electron-withdrawing properties.¹⁹ These linear compounds can be represented by two mesomeric structures. Resonance of **I** and **II**, with equal contributions, leads to bond order 1.5 and 2.5 for N_a–N_b and N_b–N_c, respectively (Scheme 9).



Scheme 9. Resonance structures of substituted azides.

According to Scheme 9 resonance **II** can be seen as both an acceptor and an electron-donor reagent. Since the amino moiety of DADNE was not affected, we assumed a likely interaction between the DADNE *gem*-dinitrocarbon and TMSN₃ (see Scheme 10). Thus, the remaining negative charge located on the azide function could lead to a rapid elimination of NO₂⁻. The final expected product formed in this process could be, after several eliminations,



Scheme 10. Amidinoacetone nitrile as a possible precursor of product **6**?

amidinoacetonitrile (Scheme 10). Therefore, we decided to pursue our experimental works to check this hypothesis by several means. We first tried to detect amidinoacetonitrile by following the reaction by IR, but no significant nitrile absorption band was noticed.²⁰

No acidic activation of TMSN_3 was successfully achieved and no yield improvement was observed either.²¹ Anhydrous runs were carried out to prevent hydrolysis of TMSN_3 , but no yield improvement was reached. A longer reaction time was required to obtain **6**.²² A run with a large excess of hydrazoic acid (HN_3) in the presence of DADNE **1** was also attempted, but no trace of **6** was detected, even after a one-week reaction. This indicates that HN_3 cannot be solely involved in this transformation.

All of these trials are proof that the mechanism is not trivial and worth being investigated in further depth. More than solving a particular and interesting problem, there is a fundamental reactivity issue around the role and the chemical behaviour of trimethylsilylazide.

3. Conclusion

These further works on DADNE highlighted once again the particular reactivity of such a compound. The X-ray structures unambiguously characterised the novel and unexpected compounds obtained from oxidation and azidation of DADNE. As previously demonstrated,³ we reasonably suspect for both reactions an obvious contribution of the DADNE *gem*-dinitrocarbon in these transformations. TMSN_3 was suspected to behave in a different way as usually observed. The DADNE regioselectivity has not been successfully modified by varying the experimental conditions, as already noticed with harder activated electrophiles $[\text{Cl}]^+$ in the presence of DADNE.²³

4. Experimental section

4.1. General

Melting points were determined by using a DSC823 Mettler Toledo apparatus (8 °C/min). Reagents had commercial

grades and were purchased from Aldrich. DADNE was prepared as previously described by Latypov et al.² IR spectra were recorded on a Nicolet Avatar 320 FTIR instrument in dry KBr pellets. NMR spectra were recorded with a Bruker Avance 400 spectrometer fitted with a 10 mm broadband ATM probe. Chemical shifts were referred to TMS for ^1H and ^{13}C and to nitromethane for ^{15}N . Mass spectra (MS) were recorded by using a Nermag R10-10H mass spectrometer by electronic impact (IE, 70 eV), positive chemical ionisation (Cl^+ , NH_3) and negative chemical ionisation (Cl^- , NH_3). Elementary analyses were performed with an NA2500 ThermoElectron Corporation apparatus. Sensitivities to impact (CSI) and to friction (CSF) were determined using the Julius Peter apparatus. It was shown (see below) that compounds **5–7** are insensitive. These values can be compared to 2,4,6-trinitrotoluene (TNT) as a reference compound (CSI=30 J and CSF=300 N).

4.2. X-ray crystallography

Compounds **5**, **7**, **8a** and **9** were analysed by J. Marrot at the University of Versailles (France). Colourless crystals were glued to a glass fibre. Intensity data were collected at room temperature with a Siemens SMART diffractometer equipped with a CCD two-dimensional detector [λ Mo $K\alpha=0.71073$ Å].

Slightly more than one hemisphere of data was collected in 1271 frames with ω scans (width of 0.30° and exposure time of 30 s per frame (**7**), 10 s per frame (**5**), (**8a**) and (**9**)). Data reduction was performed with SAINT software. Data were corrected for Lorentz and polarisation effects, and a semi-empirical absorption correction based on symmetry equivalent reflections was applied by using the SADABS program.²⁴ Lattice parameters were obtained from least-squares analysis of all reflections. The structure was solved by direct method and refined by full matrix least-squares, based on F^2 , using the SHELX-TL software package.²⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located with geometrical restraints in the riding mode.

CCDC 294504, 620086, 620087, 620088 contain the supplementary crystallographic data. These data can be obtained

Compd	Crystal size (mm)	Crystal system	Space group	Unit cell dimensions (lengths, Å)	Unit cell dimensions (angles, °)	Volume (Å ³)	Z	Density
5	0,10 0,08 0,02	Triclinic	<i>P</i> -1	<i>a</i> =3.5490(3), <i>b</i> =5.2822(4), <i>c</i> =9.4294(6)	α =80.332(3), β =87.856(4), γ =75.043(3)	168.35(2)	2	1.737
7	0,75 0,30 0,10	Monoclinic	<i>P</i> ₂ / <i>c</i>	<i>a</i> =3.7277(1), <i>b</i> =21.0790(3), <i>c</i> =7.2773(2)	α =90, β =113.268(2), γ =90	525.31(2)	4	1.912
8a	0,73 0,42 0,24	Monoclinic	<i>P</i> ₂ / <i>c</i>	<i>a</i> =4.2299(2), <i>b</i> =21.4700(5), <i>c</i> =6.9942(4)	α =90, β =114.148(2), γ =90	579.60(5)	4	1.457
9	0,48 0,22 0,08	Monoclinic	<i>P</i> ₂ / <i>c</i>	<i>a</i> =7.4196(4), <i>b</i> =13.5605(6), <i>c</i> =10.6268(5)	α =90, β =90.425(1), γ =90	1069.17(9)	4	1.443

free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Caution: DADNE is an insensitive compound, nevertheless it has a high potential energy and must be handled with care and proper shielding.

4.3. Amidinoformic acid (5)

DADNE **1** (400 mg, 2.70 mmol) was rapidly added to a stirred solution containing 30% hydrogen peroxide (8 g) and concentrated sulfuric acid (4.4 g) at room temperature. The mixture was kept at room temperature for 18 h and poured into iced water (60 mL). The precipitate was collected by filtration. It was washed twice with cold water and dried over P₂O₅. A white insoluble solid was obtained (80% yield). Mp 275 °C. ¹H NMR (DMSO) δ=9.34 (2s, 1H, 1H) ppm. ¹³C NMR (DMSO) δ=164.7, 166.3 ppm. IR (KBr) 3354, 3323, 3025, 1715 (C=N), 1645 (C=O), 1491, 1130, 1106, 885, 853, 826, 757, 671, 538, 466 cm⁻¹. MS (CI⁺, NH₃): *m/z*=107 (100) [MH+18]⁺; MS (CI⁻, NH₃): *m/z*=106 (37) [MH+18]⁻; Elem. analysis calcd (%): C 27.3, H 4.5, N 31.8; found: C 26.3, H 4.1, N 30.8. CSI>50.1 J; CSF>353 N.

4.4. 5-Amidino-tetrazole (6)

DADNE **1** (28.5 g, 0.193 mol) and trimethylsilylazide (208.0 g, 1.806 mol) were stirred in DMSO (360 mL) for 3–5 days at ambient temperature. The mixture was filtered and washed with a small amount of DMSO. The crude 5-amidino-tetrazole **6** was washed with water (twice) and with acetone. 5-Amidino-tetrazole (4.68 g) was obtained (22%) as a white solid (DSC: decomposition started from 260 °C, onset: 323 °C). ¹H NMR (DMSO) δ=8.96 (br s) ppm. ¹³C NMR (DMSO) δ=152.8, 156.7 ppm. IR (KBr) 3223, 3051, 1704, 1579, 1474, 1391, 1370, 1122, 787, 757, 689, 520, 458 cm⁻¹. MS (IE): *m/z*=112 (5); MS (CI⁺, NH₃): *m/z*=113 (100), 225 (7); Elem. analysis calcd (%): C 21.4, H 3.6, N 75.0; found: C 21.0, H 3.8, 71.3. CSI>50.1 J; CSF>353 N.

4.5. Potassium tetrazole-5-carboxamide salt (7)

5-Amidino-tetrazole (0.49 g, 4.4 mmol) was heated in refluxing potassium hydroxide solution (0.25 g, 4.5 mmol, 25 mL) until completely dissolved (40 min). The mixture was evaporated to dryness under vacuum. The residue was dried over P₂O₅ and washed with THF. A white solid was yielded (84%). ¹H NMR (DMSO) δ=7.13 (br s, 1H), 7.44 (br s, 1H) ppm. ¹³C NMR (DMSO) δ=157.7, 162.8 ppm. ¹⁵N NMR (D₂O) δ=-278 (weak signal), -68, -1 ppm; Elem. analysis calcd (%): C 15.9, H 1.3, N 46.3; found: C 15.1, H 1.5, N 43.2. CSI>50.1 J; CSF>353 N.

4.6. 1-Methyltetrazole-5-carboxamide (8a)

Potassium tetrazole-5-carboxamide salt **7** (1.83 g, 12.2 mmol) was dissolved in 100 mL of DMSO at 75–80 °C. Iodomethane (5 mL, 11.4 g, 80.3 mmol) was quickly introduced with a syringe. The mixture became dark (iodine was formed) and was stirred for 30 min. DMSO was distilled (bp 60 °C) under vacuum. Water (30 mL) was poured onto

the red residue and a small amount of sodium bisulfite was added to remove iodine. A white solid precipitated and was collected by filtration. The solid was washed with water (twice), dried over P₂O₅ and further triturated with acetone. The remaining salts were removed by filtration. Evaporation of acetone afforded 0.30 g of pure 1-methyltetrazole **8a**. The aqueous filtrate was left for 2 days under ambient air and another portion of 1-methyltetrazole **8a** was filtered and washed with iced water (0.30 g). Both fractions were combined to afford the pure product **8a** as a white solid with 33% yield. Mp 164 °C (lit. 164 °C).²⁶ ¹H NMR (acetone) δ=7.13 (br s, 1H), 7.44 (br s, 1H), 4.36 (3H, s) ppm. ¹³C NMR (acetone) δ=148.3, 157.8, 36.5 ppm. ¹⁵N NMR (acetone) δ=-280, -236, -51, -4, 7 ppm. IR (KBr) 3348, 3192, 2963, 2880, 2798, 1714, 1624, 1508, 1459, 1401, 1374, 1228, 1195, 952, 722, 704, 598, 526 cm⁻¹. MS (CI⁺, NH₃): *m/z*=128 (100), 145 (68); MS (CI⁻, NH₃): *m/z*=126 (100); Elem. analysis calcd (%): C 28.3, H 3.9, N 55.1; found: C 28.1, H 3.8, N 53.6. The combined filtrates were further extracted with ethyl acetate (3×30 mL). The organic layers were combined, dried over MgSO₄ and concentrated under vacuum. A pale yellow product (0.72 g) was isolated and analysed by ¹H NMR. A mixture of 1-methyltetrazole **8a** and 2-methyltetrazole **8b** was thus obtained in a 4:1 molar ratio.

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20. Only few broad weak bands around 2200 cm⁻¹ in the nitrile characteristic absorption range were observed.
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22. The same reaction in freshly distilled DMSO was run for 10 days. After 1–2 days no formation of **6** was observed. The mixture was kept for one additional week to recover **6** with 17% yield.
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