Energetic Materials

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High-Density Energetic Mono- or Bis(Oxy)-5-Nitroiminotetrazoles**

*Young-Hyuk Joo and Jean'ne M. Shreeve**

Dedicated to Professor Malcolm M. Renfrew on the occasion of his 100th birthday

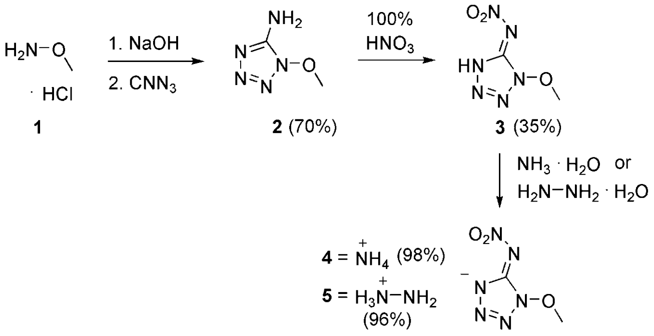
In the last decade, the investigation of energetic tetrazoles—cyanotetrazole, aminotetrazole, azidotetrazole, nitrotetrazole, and nitroiminotetrazole—has led to major developments in the area of high-energetic materials by many research groups.[1] Several exciting classes of 5-substituted tetrazole moieties are introduced in the literature.[2]

Tetrazoles can be protonated to form tetrazolium salts[3] or deprotonated to give tetrazolates.[4] While deprotonation increases the thermal stability of tetrazoles, protonation can lower the decomposition temperature.[5] These energetic materials based on high nitrogen content are derived from their high heats of formation due to the large number of N–N and C–N bonds.[6] The combination of a tetrazole ring with energetic substituent groups containing oxygen atoms, such as nitro groups, nitrate esters, or nitramine, is of interest leading to excellent oxidizers. Current research issues in the field of high energetic materials include increasing oxygen content, which may result in the replacement of ammonium perchlorate in an effort to decrease pollution. Organic 5-nitrotetrazole derivatives,[1k,7] especially for synthesis of the highly energetic 1-methyl-5-nitrotetrazole, were synthesized in good yields. These were calculated to be endothermic with heats of formation of 2.16 $\mathrm{kJ\,g^{-1}}$, which was assessed by means of standard tests and quantum chemical calculations.[7] In addition, the highly energetic, nitrogen-rich 1-methyl-5-nitroiminotetrazole[8] and its salts[8c] can easily be obtained by nitration of aminotetrazole followed by metathesis reactions using silver 1-methyl-5-nitroiminotetrazolate and the guanidinium family of chlorides in aqueous solution with high yields. Although 5-nitroiminotetrazole derivatives and their salts are energetic materials with high nitrogen content, they show good stabilities towards friction and impact, and good thermal stability.[8c,9] The development of new energetic compounds with similar attractive properties exhibit significant promise in optimizing environmentally benign replacements for toxic materials.[10]

In the past few years, the most convenient route to 1-substituted 5-aminotetrazole is the addition of amine or hydrazine to cyanogen azide,[11] which was found to be an efficient reagent for the synthesis of readily purified 1-substituted 5-aminotetrazoles from primary amines under non-catalytic mild conditions. Nitration of these aminotetrazoles using 100 % nitric acid has been shown to form mono-, di-, or tri- substituted nitroiminotetrazole derivatives.[12] With these features in mind, our group became interested in examining the analogous chemistry using alkoxy amine derivatives.

Here we describe the work leading to a series of nitroiminotetrazole derivatives of oxy nitroiminotetrazoles and their salts, with potentially significant physical and energetic properties. The aim of our study was to elucidate the structures in the crystalline state using X-ray diffraction analysis and to find new, potent oxygen- and nitrogen-rich tetrazoles. Alkoxy 5-nitroiminotetrazolates may be of interest as a new class of ionic energetic materials, which have good thermal stabilities, high densities, good oxygen balance, and high heats of formation and which are realizable in high yields though straightforward routes.

The synthesis of 1-methoxy-5-aminotetrazole (**2**) was achieved from the reaction of cyanogen azide[11] with methoxy amine (obtained by neutralization of **1** with sodium hydroxide) (Scheme 1). At ambient temperature, nitration of aminotetrazole **2** using 100 % nitric acid without solvent has been shown to form 1-methoxy-5-nitroiminotetrazole (**3**) in good yield. The new energetic salts **4** and **5** were easily obtained by reacting **3** with a slight excess of 28 % aqueous ammonia or 97 % hydrazine hydrate in water, respectively. The structures of methoxy nitroiminotetrazole and its salts are supported by IR, and ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic data as well as elemental analysis. Structural confirmation of **3** and **5** by single-crystal X-ray diffraction analyses is given in Figure 1 a for **3**, and for **5** in the Supporting Information.[13]



Scheme 1. Synthesis and reaction of **3**.

Methylene bridged nitroiminotetrazoles are particularly exciting molecules as high-energy density materials. We were

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[*] Dr. Y.-H. Joo, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho
Moscow, ID 83844-2343 (USA)
Fax: (+1) 208-885-9146
E-mail: jshreeve@uidaho.edu

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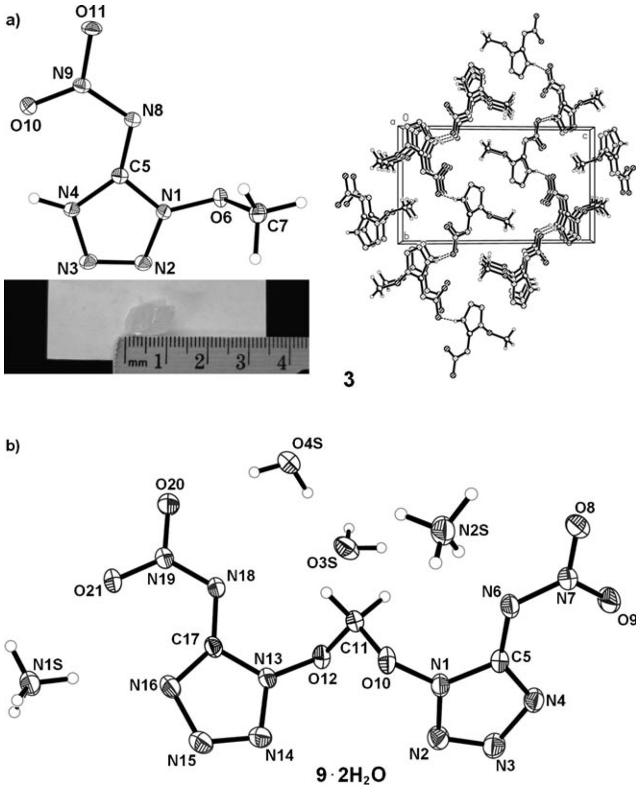
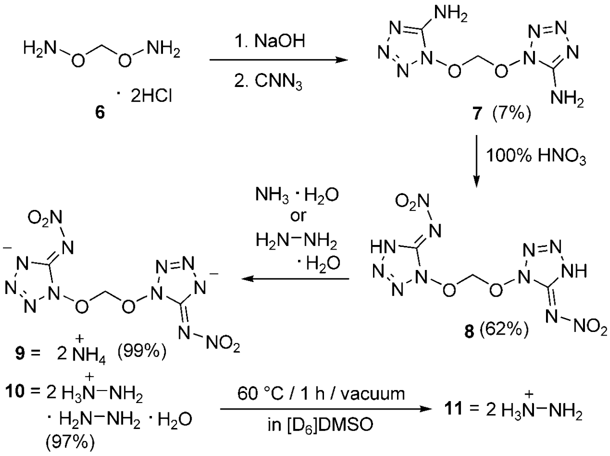


Figure 1. a) Single-crystal X-ray structure and photograph of a crystal of **3**. The ruler scale is in mm. b) Single-crystal X-ray structure of **9**·2 H_2O.

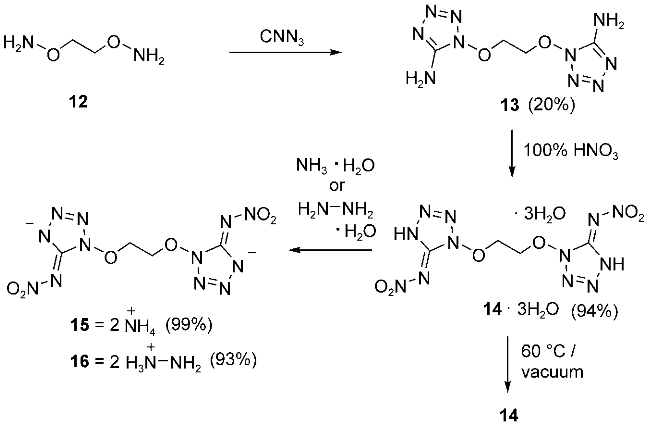
interested in utilizing our well-established 5-aminotetrazole synthesis methodology with the highly sterically hindered diaminomethane.[14] Unfortunately, addition of the methylene diamine to cyanogen azide failed. However, it was possible to prepare **7** by the analogous reaction of cyanogen azide with the less sterically hindered methylene bis(oxyamine)[15] (Scheme 2), and to investigate energetic ionic liquids based on this bisoxyamine.[16] Nitration of **7** with 100% nitric acid led to the extremely sensitive **8** (I-9: Idaho) that can be converted to the more stable salts **9** and **10**.



Scheme 2. Synthesis of **8** and its salts.

The structures of **8**, **9**, and **10** are supported by IR, and ^1H, ^{13}C, and ^{15}N NMR spectroscopic data as well as elemental analysis. Structural confirmation of **9**·2 H_2O by single-crystal X-ray diffraction analyses is given in Figure 1 b.[13] Compounds **8** and **9** decomposed slowly in [D_6]DMSO during NMR measurements. While elemental analyses were successfully carried out for salts **9** and **10**, an attempted elemental analysis for neutral **8** resulted in a violent detonation in the apparatus during the measurement. Although attempts to remove the hydrazine and water molecules in the crystal of **10** to give **11** at 60 °C under high vacuum were unsuccessful, it was possible to remove these species under the same conditions from a solution in [D_6]DMSO.

Next similar successful attempts were made to prepare **13** and **14** (I-10: Idaho) in good yield.[17] The energetic salts **15** and **16** were generally obtained by acid–base reactions with **14**·3 H_2O and energetic bases (Scheme 3). Elemental analyses attempted for neutral alkoxy-5-nitroiminotetrazoles **14**·3 H_2O and **14** resulted in violent detonations in the apparatus during measurement.



Scheme 3. Synthesis of **14** and its salts.

As expected and found in several structures of oxy-5-nitroiminotetrazoles and their salts discussed here, the five-membered ring is nearly planar, building an aromatic system, which can be seen by the torsion angle N1-N2-N3-N4 of between 0.09(10)° and 0.10(17)°. The ring moieties of **3** and **9**·2H_2O are in agreement with the geometry observed for 5-nitroiminotetrazoles and their salts.[5,8,9,12,18]

The tetrazole ring of **3** is nearly planar and four similar bond lengths are observed (N1-N2 1.356 Å, N3-N4 1.364 Å, N1-C5 1.351 Å, N4-C5 1.342 Å) (Figure 1 a). These distances are considerably longer than N2=N3 double bonds (1.279 Å) but significantly shorter than the O6−C7 single bond (1.466 Å). The nitroimine unit lies in the plane of the tetrazole ring as clearly shown by the C5-N8-N9-O10 torsion angle of −0.27(13)° and C5-N8-N9-O11 torsion angle of 179.41(8)°, in which the oxygen atoms O10 and O11 are slightly twisted out of the plane. The methoxy unit does not lie in the plane of the tetrazole ring [torsion angle C5-N1-O6-C7 of 91.45(11)°]. The packing structure of **3** is strongly influenced by strong hydrogen bonds. These extensive hydrogen bonding interactions between oxygen atom O11 from nitro group and N4 [N4···O11 2.792(12)], can be seen in Figure 1 a) along the *a* axis.

The unit cell of **9**·2 H_2O, which crystallizes with a calculated density [1.610 g cm^{-3}, 296(2) K] in the monoclinic space group $P2_1/n$, contains four formula moieties. Between the oxy nitroiminotetrazole, a torsion angle N1-O10-C11-O12 of 78.73(13)° is observed. (Figure 1 b). The packing of **9**·2 H_2O is also characterized by a three-dimensional network (Supporting Information), whereby several strong hydrogen bonds are formed between the nitrogen atom of the ammonium cation and the nitrogen atom of the tetrazolate anion N4 and N16.

The ^{15}N NMR spectra of alkoxy nitroiminotetrazole and its salts were measured in [D$_6$]DMSO and chemical shifts are given with respect to CH_3NO_2 as external standard. In Figure 2, selected ^{15}N NMR spectra of **4**, **11**, and **14** are shown. The spectrum of **14** (bottom) is depicted with six signals at −154.7 (N5), −124.3 (N4), −117.0 (N1), −24.5 (N3), −17.8 (N6), and −10.6 ppm (N2). The signals for N1, which has oxygen as a neighbor in the tetrazole ring appear as expected at lower field (117.0 ppm) compared with the N1 position (170.6 ppm) of 1,1′-ethylenebis(5-nitroiminotetrazole).[12] The assignments are based on the literature values of the remainder of the peaks which are essentially unchanged for the nitroiminotetrazole group. The ammonium or hydrazinium nitrogen atoms of salts **4** or **11** are observed as an intense signal at $\delta = -350.9$ or -324.1 ppm, respectively, similar to other salts.[18]

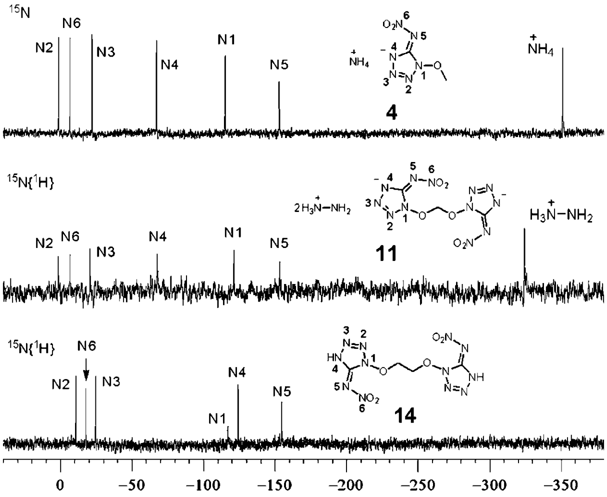


Figure 2. ^{15}N NMR spectra of oxy-5-nitroiminotetrazole and selected salts.

In Table 1 it is shown that all alkoxy nitroiminotetrazoles and their salts are highly endothermic compounds. The enthalpies of energetic materials depend on the molecular structure of the compounds. Consequently, heterocycles with higher nitrogen content, especially tetrazole, show higher heats of formation (see Supporting Information). All of the compounds exhibit positive heats of formation with **8** having the highest value of 3.58 kJ g^{-1}. Compound **15** in spite of the lower nitrogen content has a high positive heat of formation with a value of 2.24 kJ g^{-1}.

Table 1: Physical properties of oxy nitroiminotetrazoles, and their salts compared with RDX and HMX.

Compd	$T_{dec.}$[a] [°C]	d[b] [g cm^{-3}]	ΔH_f°[c] [kJ g^{-1}]	P[d] [GPa]	D[e] [m s^{-1}]	IS[f] [J]	OB[g] [%]
3	116	1.66	3.15[h]	31.5	8660	5	−30
4	184	1.55	2.40	27.7	8448	1.5	−41
5	156	1.63	2.98	32.3	9036	4	−42
8	157	1.90	3.58[h]	46.7	9867	1	−11
9	167	1.71	2.38	33.9	8984	1	−24
14	134	1.81	3.47[h]	38.4	9200	1.5	−25
15	202	1.72	2.24	33.3	9014	2	−36
16	169	1.73	2.92	35.5	9305	1.5	−38
RDX[i]	230	1.82	0.42	35.2	8977	7.4	−22
HMX[i]	287	1.91	0.35	39.6	9320	7.4	−22

[a] Thermal decomposition temperature under nitrogen gas (DSC, 5 °C min^{-1}); no melting points are observed. [b] From gas pycnometer (25 °C). [c] Heat of formation (calculated with Gaussian 03). [d] Calculated detonation pressure (Cheetah 5.0). [e] Calculated detonation velocity (Cheetah 5.0). [f] Impact sensitivity (BAM drophammer). [g] OB = Oxygen balance (%) for $C_aH_bO_cN_d$: $1600\times(c-2a-b/2)/M_w$ (M_w = molecular weight of salt). [h] Solid state. [i] Ref. [19].

Impact sensitivity measurements were made using standard BAM Fallhammer techniques.[20] Listed in Table 1 are impact sensitivities ranging from those of the relatively less sensitive **3** and **5** to the very sensitive compounds **4**, **8**, **9**, and **14**–**16** between 1 J and 3 J. Thermal stabilities of the energetic compounds were studied with differential scanning calorimetry (DSC). All oxy nitroiminotetrazoles decomposed between 116 and 202 °C without melting. In the case of ammonium salt **15**, decomposition occurred at the highest temperature at 202 °C, while $T_{dec} = 134$ °C is observed for neutral **14** as the least thermally stable species.

By using the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer values, 25 °C) of the new highly energetic oxy nitroiminotetrazoles, and their salts, the detonation pressures (P) and detonation velocities (D) were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using Cheetah 5.0 (Table 1).[21] The calculated detonation pressures of oxy nitroiminotetrazoles and their salts lie in the range between $P = 27.7$ and $P = 46.7$ GPa (comparable to RDX 35.2 GPa and HMX 39.6 GPa). Detonation velocities lie between $D = 8448$ and $D = 9867$ m s^{-1} (comparable to RDX 8977 m s^{-1}, HMX 9320 m s^{-1}). These properties coupled with the rather high thermal and hydrolytic stabilities make these high-nitrogen materials attractive candidates for energetic applications. The relatively good oxygen balances of **8**, **9**, and **14** are −11 %, −24 %, and −25 %, respectively, which are comparable with those of RDX (−22 %) and HMX (−22 %).

In summary, compounds **8**, **14**, and **16** exhibit good physical and detonation properties, such as moderate thermal stabilities, high densities, highly endothermic, good detonation pressures and good detonation velocities. Calculated detonation values of these compounds are comparable to those of explosives such as HMX ($P = 39.63$ GPa, $D = 9320$ m s^{-1}). However, they are very impact sensitive with values between 1 and 1.5 J. The impact sensitivity of these compounds could be reduced by combination with a less sensitive oxidizer, e.g., ammonium nitrate.

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[13] CCDC 782054 (**3**), 782055 (**5**), and 782056 (**9**·2 H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[20] a) www.bam.de. b) A portion of 20 mg of alkoxy nitroiminotetrazole and their salts was subjected to a drop-hammer test using a 5 or 10 kg weight dropped. The range in impact sensitivities according to the UN Recommendations is: insensitive >40 J; less sensitive ≥ 35 J; sensitive ≥ 4 J; very sensitive ≤ 3 J.

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