Energetic Materials

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Energetic Mono-, Di-, and Trisubstituted Nitroiminotetrazoles**

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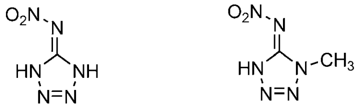
Over the last decade, the synthesis of energetic heterocyclic compounds has attracted considerable interest.[1–3] Environmental contamination by nitro compounds is associated principally with the explosives industry and military testing of explosives.[2] Compounds with a high nitrogen-atom content are potential candidates for the replacement trinitrotoluene (TNT) and other common explosives, such as 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), 2,4,6,8,10,12-(hexanitrohexaaza)cyclododecane (CL-20), 1,3,3-trinitroazetidine (TNAZ), and 1,1-diamino-2,2-dinitroethene (FOX-7), which have high densities and energies because of substantial cage strain, or for use in propellants when combined with a suitable oxidizer.[2,3] The combination of a tetrazole ring with energetic groups containing oxygen atoms, such as nitro groups, nitrate esters, or nitramines, is of particular interest.[1d,4] To meet the continuing need for improved energetic materials, the synthesis of energetic heterocyclic compounds has attracted considerable interest as a result of their rather large densities, good oxygen balance, and high heats of formation.[1,2]

Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials. Much attention has been focused on azoles, and in particular tetrazoles, as energetic compounds.[1,2] Energetic materials based on tetrazoles show the desirable properties of high N-atom content and thermal stability (due to aromaticity).[5] Tetrazole compounds containing nitroimino groups have been investigated intensively as energetic materials both theoretically and experimentally, as the nitroimino group can offer improved density and oxygen balance, and a high heat of formation.[4] Additionally, the decomposition of these compounds results in the generation of nitrogen gas. Therefore, they are very promising candidates for applications requiring environmentally friendly energetic materials.[1b] The high energetic density materials (HEDMs) with the best performance (RDX, HMX) belong to the class of typical organic cyclic and cage molecules.

Nitroiminotetrazoles are of special interest because they combine both the oxidizer and energetic nitrogen-rich backbone in one molecule. The simple 5-(nitroimino)tetrazole system was prepared nearly 60 years ago by treatment of nitroaminoguanidine with KNO_2 and concentrated HCl.[6a,b] In 1957, the synthesis of a 1-alkyl-substituted 5-nitroiminotetrazole was investigated extensively by two different methods:[6c] 1) the direct nitration of 1-methyl-5-aminotetrazole with nitric acid, and 2) the reaction of potassium methylnitramine with cyanogen bromide to form methylnitrocyanamide. When methylnitrocyanamide was treated with hydrazoic acid, 1-methyl-5-nitroiminotetrazole was isolated.

More recently, the complete characterization of nitroiminotetrazole and its salts as HEDMs was reported (Scheme 1).[4] The heat of formation was determined for each nitroiminotetrazole compound by bomb calorimetric measurements, and the density in the crystalline state was determined by single-crystal X-ray diffraction.[4a] Furthermore, a complex of copper nitroiminotetrazole, which was formed in high yield by the reaction of 1-methyl-5-nitroiminotetrazole with copper(II) nitrate in aqueous solution, was synthesized and investigated as a new primary explosive.[4c]



Scheme 1. Simplest nitroiminotetrazoles.

Our research group recently reported the preparation of mono-, di-, and trisubstituted 5-aminotetrazole compounds by a convenient method based on the reaction of cyanogen azide[7] with primary amines[8a] or hydrazines.[8b] The nitration of these aminotetrazoles with 100 % nitric acid without a solvent has now been shown to give mono-, di-, and trisubstituted nitroiminotetrazole derivatives (Scheme 2). The treatment of aminotetrazole compounds, which were synthesized from primary amines and cyanogen azide, with excess 100 % nitric acid[9] led to nitroiminotetrazoles **1**–**9** in good yields (**1**: 88 %, **2**: 89 %, **3**: 84 %, **4**: 67 %, **5**: 64 %, **6**: 88 %, **7**: 67 %, **8**: 74 %, **9**: 72 %).[10] When the reaction was complete, the reaction mixture was poured into ice water and stirred for 1–3 h to give a white solid. In the case of compounds **1**, **2**, and **3**, the white solid did not precipitate from ice water, but was obtained when the mixture was dried with air. Compounds **1** and **2** were formed as a mixture and separated by crystallization from water. The structures of **2**, **4**, and **9** are supported by IR, ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR spectroscopic data as well as elemental analysis (Table 1).

The physical data for **1**, **3**, **5**·H_2O, **5**, **6**·H_2O, **6**, **7**·2H_2O, **7**, and **8** are summarized in the Supporting Information. The ^{15}N NMR spectra of **6** and **8** could not be recorded owing to the poor solubility of these compounds in dimethyl sulfoxide

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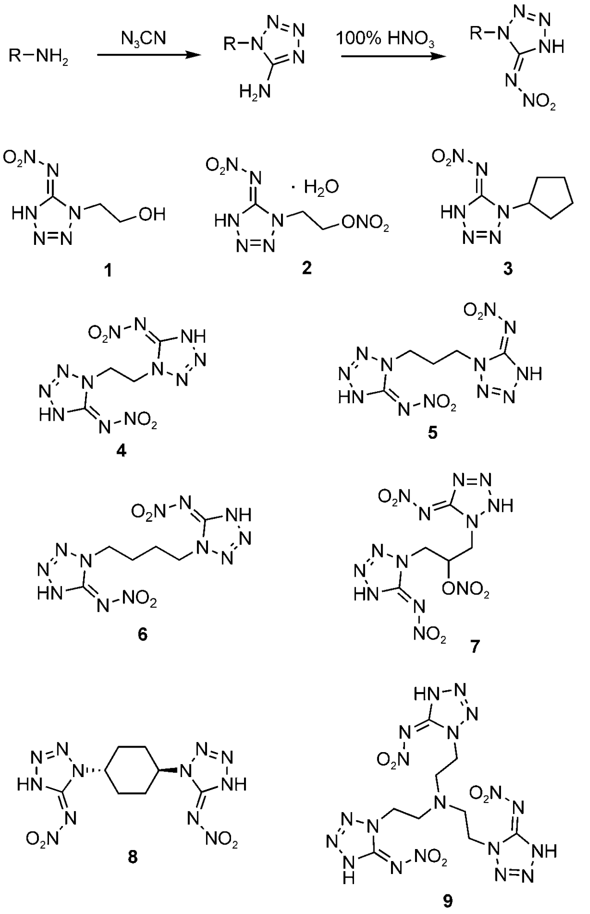

Scheme 2. Synthesis of nitroiminotetrazoles.

Table 1: Selected physical data of nitroiminotetrazole derivatives **2**, **4**, and **9**.[a]

2: colorless crystal; IR (KBr): $\tilde{\nu}=3545$, 3446, 3019, 2980, 2851, 2739, 2641, 2581, 2478, 1642, 1583, 1493, 1451, 1414, 1350, 1314, 1291, 1259, 1059, 897, 853 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO): $\delta=4.57$–4.60 (m, 2H), 4.88–4.92 (m, 2H), 7.02 ppm (br s, 3H); ^{13}C NMR ([D$_6$]DMSO): $\delta=44.2$, 69.5, 150.7 ppm; ^{15}N NMR ([D$_6$]DMSO): $\delta=-171.3$ (m, N1), −155.4, −153.1, −40.2 (t, $^{3}J_{N,H}=3.3$ Hz, N7), −25.0 (t, $^{3}J_{N,H}=2.0$ Hz, N2), −23.7 (N3), −15.4 ppm (NO$_2$).

4: colorless crystal; IR (KBr): $\tilde{\nu}=3430$, 3196, 3107, 3031, 1581, 1489, 1308, 1261, 1025 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO): $\delta=4.66$ (s, 4H), 11.65 ppm (br s, 2H); ^{13}C NMR ([D$_6$]DMSO): $\delta=44.6$, 150.9 ppm; ^{15}N NMR ([D$_6$]DMSO, 55 °C): $\delta=-170.6$, −156.8, −154.3, −24.7, −20.1, −15.5 ppm.

9: white solid; IR (KBr): $\tilde{\nu}=3431$, 3258, 3075, 2843, 1583, 1492, 1449, 1308, 1256, 1040, 719 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO): $\delta=2.99$ (t, $^{3}J=5.2$ Hz, 6H), 4.12 (t, $^{3}J=5.2$ Hz, 6H), 12.71 ppm (br s, 3H); ^{13}C NMR ([D$_6$]DMSO): $\delta=44.7$, 49.5, 149.8 ppm; ^{15}N NMR ([D$_6$]DMSO): $\delta=-351.7$, −168.9, −156.3, −155.1, −26.1, −25.0, −15.1 ppm.

[a] ^{1}H, ^{13}C, and ^{15}N NMR (external standard: CH$_3$NO$_2$) spectra were recorded at 300.1, 75.5, and 50.7 MHz, respectively. The data for **1**, **3**, **5**·H$_2$O, **5**, **6**·H$_2$O, **6**, **7**·2H$_2$O, **7**, and **8** are summarized in the Supporting Information.

(DMSO). Single crystals suitable for X-ray crystal-structure determination were obtained from aqueous solution. X-ray crystal structures of 4,5-dihydro-1-(2-hydroxyethyl)-5-nitroimino-1*H*-tetrazole (**1**) and 1,2-bis(4,5-dihydro-5-nitroimino-1*H*-tetrazol-1-yl)ethane (**4**; I-8: Idaho) are shown in Figure 1.[11] Structural details are given in the Supporting Information. The colorless crystals are stable at room temperature and not hygroscopic.

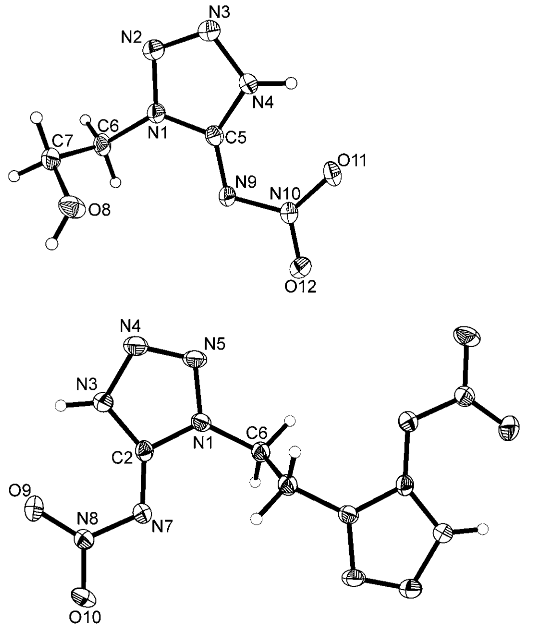

Figure 1. Molecular structures (hydrogen atoms shown as spheres of arbitrary radius, and thermal displacement set at 50% probability) of **1** (top) and **4** (bottom).

Figure 2 shows the ^{15}N NMR spectra of **7** (with six signals at $\delta=-173.8$, −155.2, −150.6, −44.3, −25.3, and −15.4 ppm) and **9** (with seven signals at $\delta=-351.7$, −168.9, −156.3, −155.1, −26.1, −25.0 and −15.1 ppm). The signals for the tertiary amine group in compound **9** appear as expected at

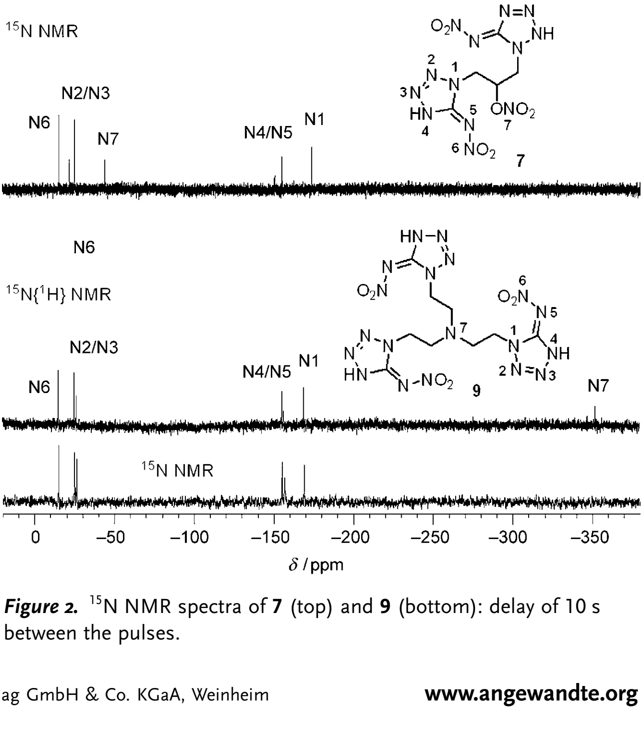

Figure 2. ^{15}N NMR spectra of **7** (top) and **9** (bottom): delay of 10 s between the pulses.

high field in the H-decoupled ^{15}N NMR spectrum. The N1, N4, and N5 signals for both compounds were observed at δ values between −151 and −174 ppm. The signals were assigned on the basis of literature values for the chemical shifts of substituted nitroiminotetrazoles.[4a]

Density is one of the most important physical properties of all energetic materials. As is shown in Table 2, the densities of the new nitroiminotetrazoles range from 1.454 to 1.858 g cm^{-3} (RDX: 1.816; HMX: 1.910 g cm^{-3}). The decomposition temperatures (without melting) fall between 117 and 233 °C. (Compounds **4**, **5**, **8**, and **9** explode at their decomposition temperatures (as determined by differential scanning calorimetry (DSC)).

Table 2: Physical properties of nitroiminotetrazoles **1**–**9** and comparison with those of RDX and HMX.

Compound	T_d[a] [°C]	Density[b] [g cm^{-3}]	$\Delta_f H^{\circ}_{298}$[c] [kJ mol^{-1} (kJ g^{-1})]	P[d] [GPa]	νD[e] [m s^{-1}]	IS[f] [J]	OB[g] [%]
1	158	1.722	258.7 (1.49)	28.23	8465	20	−55.2
2	117	1.712	350.1 (1.60)	30.88	8496	> 40	−23.6
3	124	1.454	398.8 (2.01)	17.70[h]	7358[h]	20	−121
4	194	1.858	1038.3 (3.63)	38.19	9329	10	−39.1
5	173	1.658	1032.0 (3.44)	28.06	8374	10	−53.3
6	145	1.579	989.6 (3.15)	24.71	7963	15	−66.2
7	139	1.759	922.5 (2.55)	33.02	8741	3	−28.8
8	233	1.564	1022.2 (3.00)	23.61	7667	15	−84.6
9	182	1.616	1649.7 (3.40)	25.96	8185	10	−64.3
RDX[i]	230	1.816	92.6 (0.42)	35.17	8977	7.4	−21.6
HMX[i]	287	1.910	104.8 (0.35)	39.63	9320	7.4	−21.6

[a] Temperature of thermal decomposition under nitrogen gas (DSC, 10 °C min^{-1}). [b] The density at 25 °C was determined by using a gas pycnometer. [c] Heat of formation calculated by using Gaussian 03 (with 83.68 kJ mol^{-1} as the enthalpy of sublimation for each compound). [d] Calculated detonation pressure. [e] Calculated detonation velocity. [f] Impact sensitivity (determined by a BAM drop-hammer test). [g] Oxygen balance (%) for $C_aH_bO_cN_d$: $1600\times(c-2a-b/2)/M_w$; M_w = molecular weight of the nitroiminotetrazole. [h] Values were determined by using Cheetah 4.0. [i] Data from reference [2].

The remaining task was to determine the heats of formation of the substituted nitroiminotetrazoles **1**–**9**. These values were computed by using the method of isodesmic reactions (see the Supporting Information). Calculations were carried out by using the Gaussian 03 suite of programs.[12] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G** basis set, and zero-point energies were calculated at the MP2/6-311++G** level. All 1-substituted nitroiminotetrazoles exhibited positive heats of formation, with the highest calculated for **4**, **5**, and **9** (3.63, 3.44, and 3.40 kJ g^{-1}, respectively; RDX: 0.417; HMX: 0.354 kJ g^{-1}).

By using the experimental values for the densities of nitroiminotetrazoles **1**–**9**, we calculated the detonation pressures (P) and velocities (D) on the basis of traditional Chapman–Jouget thermodynamic detonation theory by using Cheetah 4.0 and 5.0.[13] For compounds **1**–**9**, the calculated detonation pressures lie in the range between 17.70 and 38.19 GPa (RDX: 35.17; HMX: 39.63 GPa). The detonation velocities lie in the range between 7358 and 9329 m s^{-1} (RDX: 8977; HMX: 9320 m s^{-1}).

For initial safety testing, the impact sensitivity was tested according to BAM methods (BAM Fallhammer).[14] A range of impact sensitivities was found, from the insensitive compound **2** (40 J) to the sensitive nitroiminotetrazoles (**1**, **3**–**6**, **8**, and **9**: 10–20 J) and the very sensitive compound **7** (3 J; Table 2). HMX and RDX have an impact sensitivity of 7.4 J.[2]

The physical values for the decomposition temperature, density, oxygen balance, heat of formation (in kJ g^{-1}), and detonation properties of **4**, **5**, and **6** decrease as the number of methylene groups increases, although their shock sensitivity is essentially constant at 10–15 J.

Safety precautions: Although we have experienced no difficulties with the shock instability of nitroiminotetrazoles **1**–**9**, these compounds must be synthesized only in 2–3 mmol amounts, and extreme care is absolutely necessary, particularly with compound **7**. Manipulations must be carried out in a fume hood behind a safety shield. Leather gloves must be worn.

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Keywords: energetic materials · explosives · heats of formation · nitrogen heterocycles · tetrazoles

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[9] An alternate method with 70% HNO_3 was also used for the synthesis of nitroiminotetrazoles **4** and **5**. The reaction mixture was stirred for 3 days and then dried in air, and the white solid product was recrystallized from water. However, the products were obtained by this method in just 30–34% yield.

[10] The 1-substituted aminotetrazole (2 mmol) was added in small portions to 100% HNO_3 (10 mL) at 0°C. The reaction mixture was stirred at ambient temperature for 18 h and then poured into ice water (20 g) and stirred for a further 3 h. The product was precipitated, filtered, washed with water, and dried in air at room temperature.

[11] Crystallographic data for **1**: $C_3H_6N_6O_3$: $M_r = 174.14$; crystal size: $0.88 \times 0.48 \times 0.34$ mm^3; triclinic, $P\bar{1}$, $a = 7.1095(13)$, $b = 7.1116(13)$, $c = 7.8928(15)$ Å, $\alpha = 89.235(2)$, $\beta = 66.303(2)$, $\gamma = 66.804(2)°$, $V = 330.86(11)$ Å^3, $Z = 2$, $2\theta_{max} = 56.6°$, $\rho_{calcd} = 1.748$ mg m^{-3}, $\mu = 0.153$ mm^{-1}, $F(000) = 180$, $R_1 = 0.0393$ for 1475 observed ($I > 2\sigma I$) reflections and 0.0419 for all 1616 reflections, goodness-of-fit = 1.065, 110 parameters. Crystallographic data for **4**: $C_4H_6N_{12}O_4$: $M_r = 286.21$; crystal size: $0.25 \times 0.12 \times 0.11$ mm^3; monoclinic, $P2_1/n$, $a = 8.182(3)$, $b = 6.614(2)$, $c = 10.463(3)$ Å, $\alpha = 90$, $\beta = 112.380(4)$, $\gamma = 90°$, $V = 523.6(3)$ Å^3, $Z = 2$, $2\theta_{max} = 56.6°$, $\rho_{calcd} = 1.815$ mg m^{-3}, $\mu = 0.159$ mm^{-1}, $F(000) = 292$, $R_1 = 0.0808$ for 1124 observed ($I > 2\sigma I$) reflections and 0.0868 for all 1265 reflections, goodness-of-fit = 1.228, 91 parameters. CCDC 703780 (**1**) and CCDC 703781 (**4**) 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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[14] a) www.bam.de. b) A portion of nitroiminotetrazoles **1–9** (20 mg) was subjected to a drop-hammer test, in which a 5 or 10 kg weight was dropped. For the categorization of impact sensitivities (insensitive: > 40 J; less sensitive: ≥ 35 J; sensitive: ≥ 4 J; very sensitive: ≤ 3 J), see: J. C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Loehnwitz, P. Mayer, H. Noeth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 4237 – 4253.