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$[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}$: A New High-Nitrogen High-Energetic Material

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The reaction of $[N_2H_5]^+{}_2[SO_4]^{2-}$ with barium 5,5′-azotetrazolate gave new high-energy-density materials (HEDM) based on the 5,5′-azotetrazolate dianion. The dihydrazinium salt of $[N_4C{-}N{=}N{-}CN_4]^{2-}$ **1**, its dihydrate **2**, and its dihydrazinate **3** were prepared in high yield. Synthesis in water afforded yellow needles of $[N_2H_5]_2{}^+[N_4C{-}N{=}N{-}CN_4]^{2-}\cdot 2H_2O$ (**2**): monoclinic, $P2/c$, $a = 8.958(2)$ Å, $b = 3.6596(7)$ Å, $c = 16.200(3)$ Å, $\beta = 96.834(3)°$, $V = 527.3(2)$ Å^3, $Z = 2$; synthesis in anhydrous hydrazine gave yellow $[N_2H_5]_2{}^+[N_4C{-}N{=}N{-}CN_4]^{2-}\cdot 2N_2H_4$ (**3**): triclinic, $P\bar{1}$, $a = 4.6208(6)$ Å, $b = 8.585(1)$ Å, $c = 9.271(1)$ Å, $\alpha = 108.486(2)°$, $\beta = 95.290(2)°$, $\gamma = 102.991(2)°$, $V = 334.51(8)$ Å^3, $Z = 1$. The compounds were characterized by elemental analysis and vibrational (IR, Raman) and multinuclear NMR spectroscopy (^1H, ^{13}C, ^{14}N, ^{15}N). The new compounds represent new high-nitrogen HEDMs with one of the highest nitrogen contents reported to date ($[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}$ 85.2%; $[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}\cdot 2H_2O$ 73.3%; $[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}\cdot 2N_2H_4$ 85.7%). The standard heat of formation of the solvate-free compound **1** was computed at the MP2(FULL)/6-311+G(d,p) level of theory to be $\Delta H°_f = 264$ kcal mol^{-1}, which translates to 1147 kcal kg^{-1} and is one of the highest ever reported. The compounds are stable at room temperature, almost insensitive to friction and impact, but detonate violently when the explosion is initiated, e.g., by rapid heating over the decomposition temperature or by using an initiator.

Introduction

The synthesis of energetic, nonnuclear materials has been a long-term goal in our research group.[1−3] Modern high-energy-density materials (HEDM) derive most of their energy either (i) from oxidation of the carbon backbone, as with traditional energetic materials,[4,5] or (ii) from their very high positive heat of formation. Examples of the first class are traditional explosives such as TNT, RDX, and HMX.[6] Modern nitro compounds such as CL-20[2,7] or the recently reported hepta- and octanitrocubanes[8] possess very high densities and enhance the energies utilizing substantial cage strain. The most recent and most exciting member of the second class of compounds is 3,3′-azobis(6-amino-1,2,4,5-tetrazine),[9] which shows the desired remarkable insensitivity to electrostatic discharge, friction, and impact while having a very high heat of formation of $\Delta H°_f = 206$ kcal mol^{-1} (936.7 kcal kg^{-1}). In this paper we report on the synthesis and characterization of $[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}$ (**1**), $[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}\cdot 2H_2O$ (**2**), and $[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}\cdot 2N_2H_4$ (**3**), which are new members of the second family, which derive most of their energy from their very high positive heats of formation.

After the first synthesis of 5,5′-azotetrazolate salts by Thiele, who investigated some alkali, alkaline earth, and heavy metal salts as well as the $[NH_4]^+$, $[N_2H_6]^{2+}$, and $[NH_3OH]^+$ salts,[10,11] the 5,5′-azotetrazolate dianion has often been considered for practical use. The heavy metal salts of 5,5′-azotetrazolate,[12,13] particularly lead 5,5′-azotetrazolate dihydroxide,[14−16] have been investigated for use as initiators.

Among others, the guanidinium, methylammonium, and semicarbazide salts of 5,5′-azotetrazolate were tested as gas generators in combination with the oxidizers KNO_3 and $KClO_4$.[17,18] The ammonium, guanidinium, and triamminoguanidinium salts of 5,5′-azotetrazolate were found to be powerful yet smokeless gas generators.[19] Compared to HMX in composite propellants, these compounds gave comparable performance and

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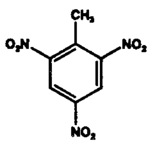
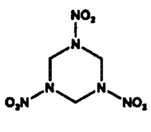
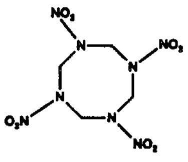


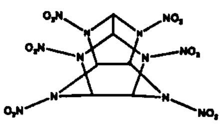
TNT



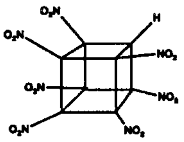
RDX



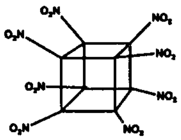
HMX



CL-20

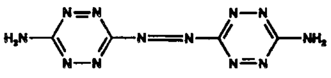


hepta-

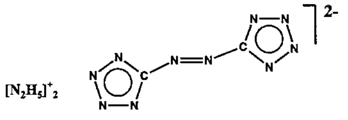


octa-

nitrocubane



3,3'-azobis(6-amino-1,2,4,5-tetrazine)



cooler, less reactive, and less visible gases. 5,5′-Azotetrazolate decomposes in acidic medium under nitrogen evolution to 1-hydrazinotetrazole.[20,21] We therefore replaced the more acidic $[N_2H_6]^{2+}$ ion with the more basic $[N_2H_5]^+$ ion.

Results and Discussion

Synthesis and Properties of Dihydrazinium 5,5′-Azotetrazolate Salts. The reaction of barium azotetazolate with $[N_2H_5]^+{}_2[SO_4]^{2-}$, generated from commercially available $[N_2H_6]^{2+}[SO_4]^{2-}$ [22] with $N_2H_4{\cdot}H_2O$ in water, gave a yellow solution. After filtration, water was allowed to evaporate. Yellow needles of dihydrazinium 5,5′-azotetrazolate dihydrate (**2**) were isolated. By heating **2** to 100 °C in vacuo for 2 days, the water was removed to form dihydrazinium 5,5′-azotetrazolate **1**. Reaction of $[N_2H_6]^{2+}[SO_4]^{2-}$ with barium 5,5′-azotetrazolate carried out in anhydrous hydrazine gave, after filtration, a yellow solution that was concentrated in vacuo and was allowed to crystallize at low temperature. Yellow needles of dihydrazinium 5,5′-azotetrazolate dihydrazinate (**3**) were isolated. The quality of all elemental analyses suffers because of the difficulty of obtaining correct values for compounds with extremely high nitrogen content.[9]

Due to a large number of observed frequencies, including combination modes, only the most intensive bands in the vibrational spectra were assigned. The IR spectra display an asymmetric $C-N_3$ stretching vibration at 1390 cm^{-1} and an asymmetric $C-N_2$ stretching mode of the azo group at 735 cm^{-1}. The Raman spectra are dominated by the vibrations of the azotetrazolate ion, especially by the symmetric $C-N_{azo}$ stretching vibration observed at 1384 cm^{-1} and the N−N stretching vibration of the azo group at 1480 cm^{-1}. A table with calculated vibrational frequencies is included in the Supporting Information.

The ^1H NMR spectra show one singlet for **1** at $\delta = 6.94$, for **2** at $\delta = 6.74$, and for **3** at $\delta = 5.86$, including the signals of the hydrazine and water protons. The ^{13}C resonance of the tetrazolate carbon atom for all compounds is found at $\delta = 173$. The ^{14}N NMR spectra show only one broad resonance for all compounds at $\delta = -335$ (**1**), $\delta = -333$ (**2**), and $\delta = -331$ (**3**) for all hydrazine nitrogen atoms. Other signals were not observed due to the high quadrupolar moment of ^{14}N. The ^{15}N NMR spectrum of **3** also displays only one peak for the hydrazine nitrogen atoms at $\delta = -331.7$ (hydrazine, hydrazinium), indicating a fast proton exchange in solution with respect to the NMR time scale. The ^{15}N NMR resonances for the tetrazolate nitrogen atoms in **3** were observed at $\delta = -67.3$ (N_α) and $\delta = 13.3$ (N_β). The nitrogen atoms of the diazo group have a ^{15}N NMR chemical shift of $\delta = 102.2$.

Sensitivity. All compounds **1**−**3** showed poor sensitivity toward shock or friction. No detonation was observed in the drop hammer test (5 kg, 50 cm).[23] Also no detonation was observed when grinding the compounds forcefully in a mortar. All compounds were insensitive to an electric discharge of about 20 kV.

Decomposition Products. For the determination of the explosion products, 100 mg of substance was loaded in a 150 mL evacuated steel vessel. The explosion was initiated by rapid electrical resistance heating of a Pt wire in the steel bomb. The gaseous products were analyzed by mass spectrometry and IR spectroscopy. For all compounds no solid or liquid residues were found in the steel bomb after the explosion. All compounds produced dinitrogen besides dihydrogen as well as small amounts of ammonia. Carbon was found to be present as methane. Water was also found in the decomposition products of **2**.

Description of Crystal Structures. The bond lengths and angles of the tetrazolate rings in **2** and **3** are in good agreement with the 5,5′-azotetrazolate dianion in bis[hydroxolead(II)] 5,5′-azotetrazolate.[24] The N=N bond lengths of the diazo group for **2** and **3** (1.25 and 1.26 Å, respectively**)** are longer than the reported bond length of 1.20 Å for bis[hydroxolead(II)] 5,5′-azotetrazolate.[24] The bond lengths and angles of hydrazinium ions of **2** and **3** are in good agreement with the hydrazinium ions of bis(hydrazinium) 4-hydroxy-1-oxo-2*H*-phthalazine-6,7-dicarboxylate.[25] Both compounds exhibit strong hydrogen bonds. Every hydrogen atom in **2** and **3** is involved in hydrogen bonding. The bonding parameters obtained from the calculation of the azotetrazolate ion are in good agreement with the observed values from X-ray diffraction (a table with bonding parameters is included in the Supporting Information).

In **2** every hydrazinium ion is involved in hydrogen bonding to the azotetrazolate units, to another hydrazinium ion, and to a water molecule. Hydrogen bonds formed by the NH_3^+ group are shorter than those of the NH_2 group of the hydrazine. The azotetrazolate dianion of **2** has hydrogen bonds only to the ring nitrogen atoms. Three nitrogen atoms are connected to hydrazinium ions, and the fourth nitrogen atom is involved in hydrogen bonding with a water molecule. Water molecules are connected to two hydrazinium ions (2.84 Å); moreover, there are other N−H···O interactions. Their lone pairs are involved in hydrogen bonding with two $[N_2H_5]^+$ ions. The hydrazinium···water hydrogen bond compares well with the hydrazinium··

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·water hydrogen bond in 5-dinitromethyltetrazole dihydrazine monohydrate (2.86 Å)[26] and the shortest water···hydrazine hydrogen bond in hydrazine hydrate (2.79 Å).[27]

In **3** every hydrogen atom participates in hydrogen bonding. The bonds are in general longer than in **2**. Some distances suggest that some of the hydrogen atoms participate in two hydrogen bonds. The nitrogen atoms of the diazo group are connected to hydrazinium ions that have another hydrogen bond to the N(2) ring nitrogen atom. The N(3) ring nitrogen is involved in two hydrogen bonds to the NH_2-nitrogen of a hydrazinium ion. N(4) and N(5) each form hydrogen bonds to a hydrazine molecule with equal distances to both ring nitrogens (N···N distances 3.37 and 3.34 Å, respectively). There are also two hydrogen-bridged interactions between hydrazinium and hydrazine molecules with N···N contact distances of 2.84 and 3.15 Å. These are shorter than the contact distances in hydrazine (shortest N···N contact distance 3.19 Å)[28] because of the charge of the hydrazinium ion but compare well with a substance with similar $[N_2H_5]^+{-}N_2H_4$ interactions, $[N_2H_5]^+[Fe(N_2H_4)(S_2\text{-}C_6H_4)_2]^-\cdot 1.33N_2H_4$, that has reported NH···N distances of about 3 Å.[29]

Thermal Analysis. Simultaneous DTA/TGA measurements were performed under atmospheric conditions using a heating rate of 5 K/min and samples of about 12 mg in open aluminum crucibles. The first mass loss after the evaporation of water in **2** and hydrazine in **3** is detected at about 120 °C followed by explosion at 163 and 174 °C (figures are included in the Supporting Information). These dynamic explosion temperatures depend on several parameters (mainly heating rate and sample amount), and in any case they are far above temperatures for safe storage of large amounts of the explosives. The water content of **2** was found to correspond formally to about 4 mol, but only 0.8 mol shows the typical behavior of a hydrate (a DTA peak and a TG step between 80 and 100 °C). The dihydrazinate **3**, however, agrees well with the formula, and a separation of both moles is visible as a small DTA minimum at 90 °C.

To avoid explosion, heating rates below 0.5 K/min are necessary. This indicates a good ignitibility comparable to nitrocellulose based propellants or CL 20. The primary reaction step of **1** corresponds to about 43% mass loss and the maximum rate temperatures of the strongly exothermic reaction (about 1450 J/g).

To establish reaction kinetics of the first step, three isothermal TGA measurements were performed using larger samples (about 34 mg) and closing the crucibles slightly with a lid to achieve favorable conditions for gas-phase autocatalysis (see Supporting Information).

Indeed—as usual for explosives—the decomposition was found to be moderately autocatalytic with maximum rates close to the end of the reaction (inflection points of the TGA curves or tops of the peaks in the derivated DTGA curves).

Up to 40% mass loss the decomposition is well described by a zero-order reaction with autocatalysis (optimal parameter values in parentheses; fit see Figure 5):

$$M = M_e(\exp(atAe)^{-E/RT} - 1)/a \qquad (1)$$

where M = mass loss [%], M_e = mass loss when reaction is complete [%] (= 45.53), t = reaction time [s], T = reaction temperature [K], a = acceleration factor (= 5.908), E = activation energy [kJ/mol] (= 169.29), A = frequency factor [s^{-1}] (= 2.1028×10^{17}), K = gas constant (= 0.0083143 kJ/(mol·K)).

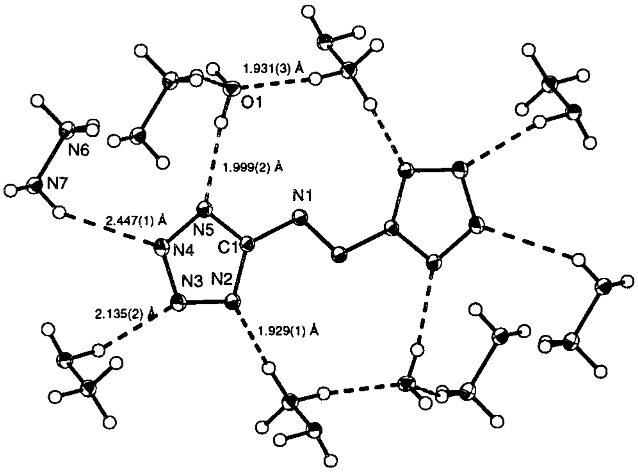

Figure 1. Hydrogen bonds to the azotetrazolate dianion of **2** as an ORTEP plot (thermal ellipsoids represent 25% probability).

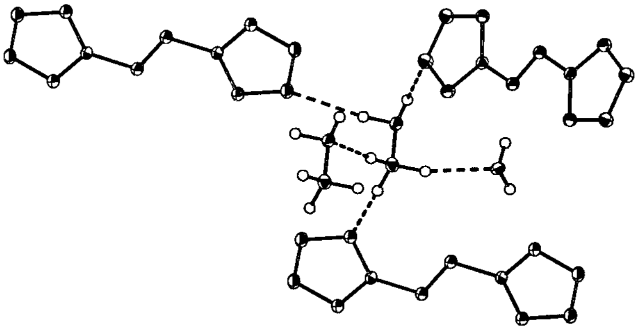

Figure 2. Hydrogen bonds of the hydrazinium ion of **2** as an ORTEP plot (thermal ellipsoids represent 25% probability).

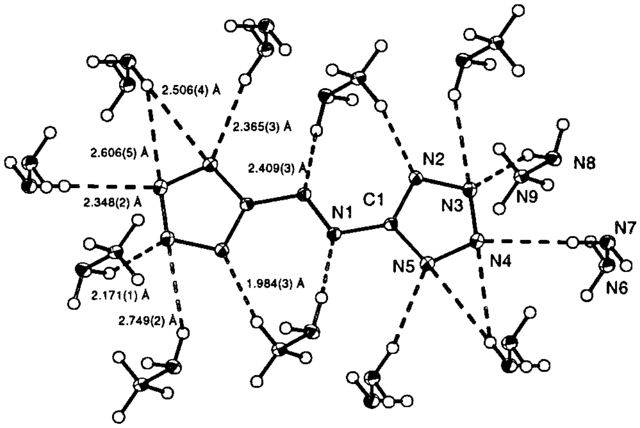

Figure 3. Hydrogen bonds to the azotetrazolate dianion of **3** as an ORTEP plot (thermal ellipsoids represent 25% probability).

Assuming a mass loss of 1% to be uncritical for most applications, the shelf life (= time to reach this reaction degree) of **1** can be calculated for different storage temperatures (Table 4).

The results predict sufficient stability to pass the hardest test used for military ammunition (71 °C for 30 days) and to survive the usually demanded 10 years shelf life because the effective storage temperature will be considerably below 48 °C.

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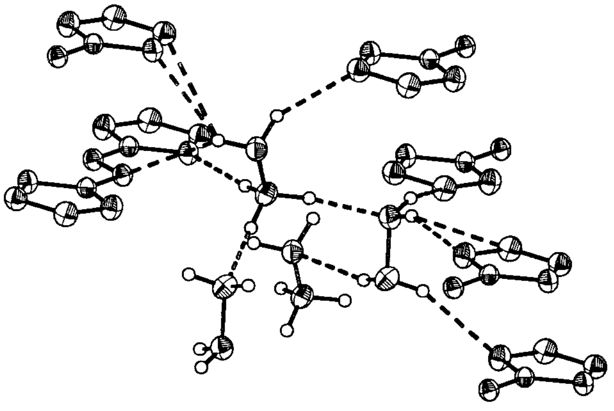

Figure 4. Hydrogen bonds of the hydrazinium and hydrazine units of **3** as an ORTEP plot (thermal ellipsoids represent 25% probability). Some tetrazolate atoms were omitted for clarity.

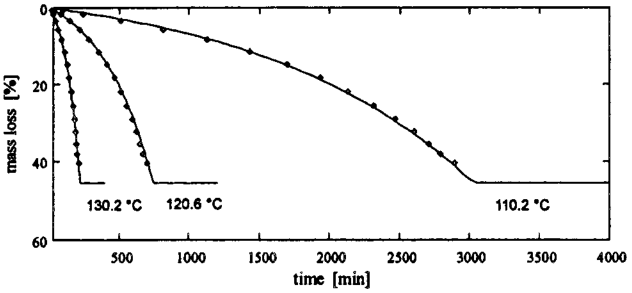

Figure 5. Decomposition of **1** (— calculated, ◇◇◇◇ measured).

Thermodynamic Aspects. To obtain information on the heat of formation of $[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}$ (**1**), we initially calculated the lattice energy (U_L)[30,31] and the corresponding lattice enthalpy (ΔH_L) for **1** for the process indicated in eq 2.

$$[N_2H_5]^+{}_2[N_4C{-}N{=}N{-}CN_4]^{2-}(s) \rightarrow 2[N_2H_5]^+(g) + [N_4C{-}N{=}N{-}CN_4]^{2-}(g) \quad (2)$$

The recently published relationship by Jenkins et al.[32,33] (eq 3) provides an excellent way to determine the lattice energy for 1:1, 1:2, and 2:1 salts. The experimentally determined molecular volume (V_M = 334.5 Å^3 = 0.3345 nm^3) was used together with the empirical α (165.3 kJ mol^{-1}) and β (−29.8 kJ mol^{-1}) parameters which have been suggested in the original publication for 2:1 salts.[32]

$$U_L = |z_+||z_-|\nu[(\alpha/V_M{}^{-0.33}) + \beta] \quad (3)$$

($|z_+|$ and $|z_-|$ are the charges of the cations and anions; ν is the number of ions per molecule).

The so obtained lattice energy for compound **1** of $U_L(\mathbf{1})$ = 1250 kJ mol^{-1} (299 kcal mol^{-1}) was converted into the lattice enthalpy (ΔH_L) by means of the general relationship (eq 3) for M_pX_q salts where n_M and n_X are equal to 3 for monatomic ions, 5 for linearpolyatomic ions, and 6 for polyatomic nonlinear ions as in this case.[34] This equation simply assumes that the vibrational degrees of freedom are equally excited in both the crystal and the gaseous ions while applying corrections for rotational degrees of freedom possessed by the product gaseous ions.

$$U_L(M_pX_q) = \Delta H_L(M_pX_q) - \{p[(n_M/2) - 2] + q[(n_x/2) - 2]\} \quad (4)$$

This leads to a lattice enthalpy for compound **1** of $\Delta H_L(\mathbf{1})$ = 1257 kJ mol^{-1} (301 kcal mol^{-1}).

In the next step the total energies of all compounds involved in eq 5 were computed ab initio at the HF/6-31G(d,p) and MP2-(FULL)/6-311G(d,p) levels of theory (Table 4). These data were used to calculate the energy of reaction 5, which after zero-point energy correction ($\Delta zpe^{MP2}(4) = -169$ kJ mol^{-1} = −40.4 kcal mol^{-1}, see Table 1)[35] and corrections for the translational ($\Delta U^{tr}(4) = (21/2)RT$) and rotational term ($\Delta U^{rot}(4) = (13/2)RT$) and for the work term ($p\Delta V = 7RT$) was converted into the reaction enthalpy ($\Delta H°(4)$) at 298 K (Table 1).[35] This results in a reaction enthalpy of $\Delta H^{\circ MP2}(4) = -2506$ kJ mol^{-1} (−599 kcal mol^{-1}).

$$2N_2H_5{}^+(g) + N_4C{-}N{=}N{-}CN_4{}^{2-}(g) \rightarrow 2CH_4(g) + H_2(g) + 7N_2(g) \quad (5)$$

The standard heat of formation of methane is well known from the literature ($\Delta H°_f(CH_4,g) = -74.9$ kJ mol^{-1} = −17.9 kcal mol^{-1}),[36] and therefore the heat of formation of compound **1** in the solid state can be calculated as $\Delta H°_f(\mathbf{1},s) = +1105$ kJ mol^{-1} (264 kcal mol^{-1}), which gives with a molecular weight of $M(\mathbf{1})$ = 230.2 g mol^{-1} finally a heat of formation of $\Delta H°_f(\mathbf{1})$ = 4800 kJ kg^{-1} = 1147 kcal kg^{-1}. This value is substantially higher than that of any presently used explosive[4] and exceeds even that of 1,1′-dimethyl-5,5′-azotetrazole (189 kcal mol^{-1})[15] and the recently published 3,3′-azobis(6-amino-1,2,4,5-tetrazine),[9] which has a reported heat of formation of $\Delta H°_f$ = 862 kJ mol^{-1} = 206 kcal mol^{-1}, which translates (M = 220.2 g mol^{-1}) to $\Delta H°_f$ = 3919 kJ kg^{-1} = 937 kcal kg^{-1}.

We also determined the heat of combustion of compound **1**, which was then converted into the experimental heat of formation of compound **1**: $\Delta H°_f(\mathbf{1})_{exp}$ = 205 kcal mol^{-1}. This value is somewhat lower than the calculated heat of formation of compound **1** of $\Delta H°_f(\mathbf{1})$ = 264 kcal mol^{-1}. The difference between the calculated and measured heat of formation can be attributed to the fact that the estimated lattice energy is slightly too low due to strong hydrogen bridges in the solid state. Assuming that all the other computed gas-phase values are reliable, the experimental-based lattice enthalpy of compound **1** can now be back-calculated to be $\Delta H_L(\mathbf{1})_{exp}$ = +388 kcal mol^{-1}, which is slightly higher than the calculated value of $\Delta H_L(\mathbf{1})_{exp}$ = +301 kcal mol^{-1}.

Whereas compound **1** has a significantly higher heat of formation compared with 3,3′-azobis(6-amino-1,2,4,5-tetrazine),[9] the measured density of $\mathbf{1}\cdot 2N_2H_4$ (**3**) (1.461 g cm^{-3}) is somewhat lower than the reported density for [3,3′-azobis(6-amino-1,2,4,5-tetrazine)]·2DMSO, which is 1.526 g mol^{-1}.[9]

To assess more quantitatively the expected detonation properties of compound **1**, we calculated the expected detonation pressure (P) and detonation velocity (D) using the semiempirical

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Table 1. Selected Bond Lengths [Å] and Angles [deg] of **2** and **3**

	2	**3**		**2**	**3**
N(1)−N(1A)	1.257(4)	1.265(3)	N(1)−C(1)	1.409(3)	1.402(2)
N(2)−N(3)	1.336(3)	1.336(2)	N(2)−C(1)	1.337(3)	1.340(2)
N(3)−N(4)	1.329(3)	1.329(2)	N(4)−N(5)	1.337(3)	1.343(2)
N(5)−C(1)	1.330(3)	1.336(2)	N(6)−N(7)	1.453(3)	1.443(2)
N(8)−N(9)		1.450(2)			
N(1A)-N(1)−C(1)	113.1(3)	113.5(2)	N(3)−N(2)−C(1)	104.0(2)	104.4(1)
N(4)−N(3)−N(2)	109.7(2)	109.7(1)	N(3)−N(4)−N(5)	109.2(2)	109.1(1)
C(1)−N(5)−N(4)	104.5(2)	104.7(1)	N(5)−C(1)−N(2)	112.6(2)	112.0(1)
N(5)−C(1)−N(1)	119.0(2)	119.8(1)	N(2)−C(1)−N(1)	128.4(2)	128.1(2)

Table 2. Intermolecular NN and NO Distances [Å] and Angles [deg] of H Atoms Involved in Hydrogen Bonds in **2**

O(1)−H(11)··N(5)	2.807(3)	169(4)	N(6)−H(63)··O(1)	2.838(3)	159(3)
N(6)−H(61)··N(7)	2.869(4)	175(3)	N(7)−H(71)··N(3)	3.012(3)	154(4)
N(6)−H(62)··N(2)	2.866(3)	169(3)	N(7)−H(72)··N(4)	3.178(3)	149(3)

Table 3. Intermolecular NN Distances [Å] and Angles [deg] of H Atoms Involved in Hydrogen Bonds in **3**

N(6)−H(61)··N(8)	3.153(3)	160(2)	N(8)−H(82)··N(1)	3.175(2)	145(2)
N(6)−H(62)··N(5)	3.212(3)	158(2)	N(9)−H(91)··N(6)	3.390(3)	140(2)
N(7)−H(71)··N(4)	3.176(3)	151(2)	N(9)−H(91)··N(7)	2.839(3)	167(2)
N(7)−H(72)··N(4)	3.375(3)	146(2)	N(9)−H(92)··N(2)	2.879(3)	164(2)
N(7)−H(72)··N(5)	3.335(3)	157(2)	N(9)−H(93)··N(6)	2.815(3)	164(2)
N(8)−H(81)··N(3)	3.031(3)	151(2)			

Table 4. Calculation of Shelf Life of **1**

storage temp [°C]	shelf life
71	56 days
60	1.1 year
50	7.2 years
48	10 years
40	54 years

equations suggested by Kamlet and Jacobs (eqs 6 and 7).[37−41]

$$P\,[\text{kbar}] = K\rho^2\varphi \tag{6}$$

where $K = 15.58$ and ρ is density in g cm^{-3}; $\varphi = NM^{0.5}Q^{0.5}$ with N = moles of gas per g of explosive, M = g of gas per mol of gas, and Q = estimated or guessed heat of detonation (cf. eq 4).

$$D\,[\text{mm}\ \mu\text{s}^{-1}] = A\varphi(1 + B) \tag{7}$$

with $A = 1.01$; $B = 1.30$.

For compound **1** we calculated a detonation pressure of P = 247 kbar and a detonation velocity of 6.33 mm μs^{-1} (6330 ms^{-1}).

To enhance the detonation properties, we are currently evaluating (i) the oxidation of **1** and **3** with oxygen-transfer reagents[42] and (ii) the possibility of preparing other polymorphs of **1** and **3** with higher densities.

Ab Initio Computations. The Gaussian G98W program was used for all structure and frequency calculations.[43] Hartree−Fock (HF)[44−46] and Møller−Plesset (MP2)[47−49] computations were carried out employing 6-31G(d,p) and 6-311+G(d,p) basis sets, respectively.[50,51] Whereas the CCSD(T) method has generally been shown to be reliable for covalently bound nonmetal compounds,[52,53] often the less expensive MP2 method in combination with a triple-ζ basis set gives very good structural, vibrational, and energetic results.[52] Since the contribution of the core orbitals to the binding energy is structure-dependent,[54] the frozen core approximation was assumed not to allow sufficient variational freedom in the calculations in order to correctly determine the energies for the compounds studied in this paper. Therefore, we applied the more expensive MP2(FULL) method where all electrons are included in a correlation calculation. The DFT variant B3-LYP, which is a HF/DFT hybrid functional constructed from Becke's three-parameter exchange functional[55] and the Lee, Yang, Parr correlation functional,[56] was used for calculating the vibrational frequencies.

Experimental Section

Caution! Although all materials studied in this work are almost insensitive to electrostatic discharge, friction, and impact, all HEDMs should be treated with respect and appropriate safety precautions should be taken at all times.

General Procedures. Manipulations of **3** were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques.

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Table 5. Ab Initio Computations

molecule	symmetry	electronic state	HF/ 6-31G(d,p) $-E$ (au) zpe (kcal mol^{-1})	MP2(FULL)/ 6-311+G(d,p) $-E$ (au) zpe (kcal mol^{-1})
H_2	D_{8h}	$^1\Sigma_g$	1.131334 6.6	1.160272 6.5
N_2	D_{8h}	$^1\Sigma_g$	108.943950 3.9	109.338888 3.1
CH_4	T_d	$^1A_1$	40.201705 29.8	40.398367 28.6
$[N_2H_5]^+$	C_s	$^1A'$	111.536342 46.0	111.973657 43.4
$[N_4C-N{=}N-CN_4]^{2-}$	C_{2h}	^1A_g	620.023105 41.2	622.438648 39.0

Table 6. Crystallographic Data for **2** and **3** and Details of Data Collection and Structural Refinement

	2	**3**
chemical formula	$C_{12}H_{12}N_{14}O_2$	$C_2H_{18}N_{18}$
fw [g mol^{-1}]	266.23	294.34
color, habit	yellow needle	yellow needle
temp [K]	193(2)	193(2)
cryst size [mm]	0.60 × 0.10 × 0.10	0.40 × 0.30 × 0.20
cryst syst	monoclinic	triclinic
space group	$P2/c$	$P\bar{1}$
a [Å]	8.958(2)	4.6208(6)
b [Å]	3.6596(7)	8.585(1)
c [Å]	16.200(3)	9.271(1)
α [deg]	90	108.486(2)
β [deg]	96.834(3)	95.290(2)
γ [deg]	90	102.991(2)
V [Å^3]	527.3(2)	334.51(8)
Z	2	1
ρ(calcd) [g cm^{-3}]	1.564	1.461
μ [mm^{-1}]	0.128	0.116
R1, wR2 [$I > 4\sigma(I)$]	0.0499, 0.1286	0.0354, 0.0949
R1, wR2 (all data)	0.0650, 0.1383	0.0417, 0.0989

Hydrazine was dried and degassed by standard methods.[57] Raman spectra were recorded on a Perkin-Elmer 2000 NIR FT-Raman spectrometer fitted with a Nd:YAG laser (1064 nm); infrared spectra, on a Nicolet 520 FT-IR spectrometer as pellet. The elemental analyses were performed with a C, H, N Analyzer Elementar Vario EL. NMR spectra were recorded on a JEOL EX400 instrument. Chemical shifts (δ scale) were recorded with respect to $(CH_3)_4Si$ (^1H, ^{13}C) and CH_3NO_2 ($^{14/15}N$). The ^{15}N NMR spectrum of **3** was recorded in [D$_6$]DMSO in a 10 mm probe with a sample amount of 2.5 g. The mass spectra were recorded with a Balzers QMG 420 instrument. For the determination of the melting points, samples were heated in capillaries in a Büchi B540 instrument. For thermal analysis a Netsch Simultaneous Thermal Analyser STA 429 was used.

$[N_2H_6]^{2+}[SO_4]^{2-}$ was used as provided by Merck, $N_2H_4{\cdot}H_2O$ was used as provided by Fluka, and barium 5,5′-azotetrazolate was prepared by literature methods.[10]

Crystallography. Crystals of **2** and **3** were mounted on glass fibers with small amounts of perfluoroether oil. Data (Table 6) were collected on a SIEMENS P4 diffractometer equipped with a Siemens CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97)[58] and refined by means of full-matrix least-squares procedures using SHELXL-97. Further information on the crystal-structure determinations has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 149898/149899.

Preparation of $[N_2H_5]^+_2[N_4C-N{=}N-CN_4]^{2-}$ (1). Water was removed from $[N_2H_5]^+_2[N_4C-N{=}N-CN_4]^{2-}{\cdot}2H_2O$ (**2**) by heating to 100 °C in vacuo for 2 days. IR (KBr): ν/cm^{-1} 3442 m, 3334 s, 3268 m, 3180 m, 3063−2650 s, 2198 m, 2081 m, 1640 m, 1590 m, 1544 m, 1503 w, 1454 w, 1396 s, 1279 w, 1193 m, 1159 m, 1123 s, 1085 s, 1044 m, 1037 m, 968 s, 774 m, 736 s, 619 m, 563 m, 476 m, 310 m. Raman (100 mW): ν/cm^{-1} 1477 m, 1418 w, 1380 vs, 1086 m, 1053 m, 1034 w, 922 w, 348 w. ^1H NMR ([D$_6$]DMSO): δ 6.94 ($N_2\mathit{H}_5$, H_2O). ^{13}C NMR ([D$_6$]DMSO) δ 173.6. ^{14}N NMR ([D$_6$]DMSO): δ −335 ($H_2\mathit{N}NH_3$). Anal. Calcd for $C_2H_{10}N_{14}$: 10.44% C, 4.38% H, 85.18% N. Found: 9.80% C, 4.89% H, 76.30% N. Explosion products: MS-(EI): m/z (%) 1(1), 2(27) [H_2], 14(12), 16(2) [CH_4], 27(1), 28(100) [N_2], 29(1). IR: ν/cm^{-1} 3334 m, 1626 m, 1150−800 [NH_3], 3017 w [CH_4], 2967 w, 2823 w [$N(CH_3)_xH_{2-x}$].

Preparation of $[N_2H_5]^+_2[N_4C-N{=}N-CN_4]^{2-}{\cdot}2H_2O$ (2). A mixture of 2.00 g (6.6 mmol) of barium 5,5′-azotetrazolate, 1.64 g (6.3 mmol) of $[N_2H_6]^{2+}[SO_4]^{2-}$, and 0.32 g (6.3 mmol) of hydrazinium hydrate was stirred in 50 mL of water for 30 min. The yellow solution was filtered and allowed to crystallize overnight. **2** was isolated as yellow needles. Yield: 1.45 g (87%). IR (KBr): ν/cm^{-1} 3280−2570 s, 2154 m, 2064 1651 m, 1612 m, 1532 m, 1455 m, 1405 s, 1332 w, 1309 w, 1286 w. 1190 m 1176 m, 1159 s, 1117 s, 1087 s, 1046 m, 1037 m, 970 s, 848 m, 770 m, 736 m, 725 m, 633 m, 620 m, 565 w, 533 w, 459 m, 318 m. Raman (100 mW): ν/cm^{-1} 3178 vw, 1478 s, 1430 w, 1387 vs, 1087 w, 1056 s, 966 w, 923 w, 155 w, 108w. ^1H NMR ([D$_6$]DMSO): δ 6.74 ($N_2\mathit{H}_5$, H_2O). ^{13}C NMR ([D$_6$]DMSO): δ 173.0. ^{14}N NMR ([D$_6$]DMSO): δ −333 ($H_2\mathit{N}NH_3$). Anal. Calcd for $C_2H_{14}N_{14}O_2$: 9.02% C, 5.30% H, 73.66% N. Found: 7.76% C, 4.57% H, 60.33% N. Explosion products: MS(EI): m/z (%) 1(1), 2(9) [H_2], 14(12), 16-(2) [CH_4], 17(1) [NH_3], 18(2) [H_2O], 19(1), 27(1), 28(100) [N_2], 29-(1). IR: ν/cm^{-1} 3650−3500 m [H_2O], 3360 w, 1626 w, 1150−800 [NH_3], 3015 [CH_4], 2960 w, 2820 w [$N(CH_3)_xH_{2-x}$].

Preparation of $[N_2H_5]^+_2[N_4C-N{=}N-CN_4]^{2-}{\cdot}2N_2H_4$ (3). A mixture of 2.00 g (6.6 mmol) of barium 5,5′-azotetrazolate and 1.64 g (6.3 mmol) of $[N_2H_6]^{2+}[SO_4]^{2-}$ was stirred in 30 mL of anhydrous hydrazine for 4 h. The resulting yellow solution was filtered, and most of the anhydrous hydrazine was removed in vacuo. After storing at 5 °C overnight, **3** was isolated as yellow crystals. Yield: 1.42 g (76%). IR (KBr): ν/cm^{-1} 3436 m, 3334 s, 3268−2667 s, 2258 m, 2198 m, 2081 m, 1640 s, 1591 s, 1445 s, 1396 s, 1356 m, 1193 m, 1159 s, 1125 s, 1078 s 1038 m, 1045 m, 967 s, 819 w, 773 m, 735 s, 619 s, 563 m, 478 m, 312 m. Raman (100 mW): ν/cm^{-1} 1478 s, 1412 w, 1374 vs, 1083 w, 1051 s, 1021 w, 921 w. ^1H NMR ([D$_6$]DMSO): δ 5.86 ($N_2\mathit{H}_5$, $N_2\mathit{H}_4$). ^{13}C NMR ([D$_6$]DMSO): δ 173.7. ^{14}N NMR ([D$_6$]DMSO): δ − 329 ($H_2\mathit{N}NH_3$). ^{15}N NMR ([D$_6$]DMSO): δ −331.7 ($H_2\mathit{N}NH_3$), −67.3(CN_β), 13.3 ($C\mathit{N}_\alpha$), 102.1($-\mathit{N}{=}\mathit{N}-$). Anal. Calcd for $C_2H_{18}N_{18}$: 8.16% C, 6.17% H, 85.67% N. Found: 7.48% C, 4.89% H, 76.30% N. Explosion products: MS(EI): m/z (%) 1(1), 2(13) [H_2], 14(11), 16-(2) [CH_4], 17(1) [NH_3], 28(100) [N_2], 29(1). IR: ν/cm^{-1} 3330 m, 1626 m, 1150−800 [NH_3], 3017 w [CH_4], 2960 w [$N(CH_3)_xH_{2-x}$].

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Supporting Information Available: X-ray crystallographic data for **2** and **3** in CIF format. DTA/TGA measurements at heating rates of 5 and 0.1 K/min as well as an isothermal TGA measurement of **1**. The vibrational and mutinuclear NMR spectra of **3** are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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