

## 1,3-Diazido-2-(azidomethyl)-2-propylammonium Salts

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New energetic inorganic materials composed of 1,3-diazido-2-(azidomethyl)-2-propylammonium salts have been fully characterized by IR,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectroscopy and by elemental analyses, as well as single crystal X-ray diffraction. In addition, the heats of formation and detonation pressures and velocities were calculated.

### Introduction

Recently, considerable interest in organic azide compounds began with the use of azides for the synthesis of heterocycles such as triazoles and tetrazoles, as well as with their use as high energy density materials (HEDM) and as functional groups in pharmaceuticals.<sup>1</sup> Introduction of an azido group into an organic compound increases its energy by  $355 \text{ kJ mol}^{-1}$ ; therefore, its presence in energetic compounds is clearly favorable on thermodynamic grounds.<sup>2</sup> Azides as energetic additives were subjects of considerable research that was aimed at providing various binders and plasticizers for formulating solid propellants yielding greater energy.<sup>3</sup>

Many energetic polyazide compounds have been reported (Scheme 1). Especially spectacular is tetraazidomethane, ( $\text{CN}_{12}$ ), the highest nitrogen-containing (93.3%) binary C–N compound, which was isolated as an explosive colorless liquid from trichloroacetonitrile and excess sodium azide in a one step process.<sup>4</sup> Tri-,<sup>5</sup> tetra-,<sup>6</sup> hexa-<sup>6b</sup> and octaazide<sup>6b</sup> (2–5) were synthesized from the respective tosylate compounds, and sodium azide. Their large positive heats of formation, high thermal stabilities, low hydrolysis rate, and the ease of their preparation make 4 and 5 attractive as high energy plasticizers for oxygen-rich compounds.

Energetic salts which incorporate a nitro group<sup>7</sup> can substantially improve the oxygen balance of the corresponding compounds and eventually result in higher exothermicities of the combustion and detonation processes.<sup>8</sup> The synthesis and detonation properties of high energy density materials with ethylene- and trimethylene- bis(nitroiminotetrazolate) as anions and hydrazinium, aminoguanidinium, and tetrazolium as cations were reported in our laboratory.<sup>9</sup> These 5-nitroiminotetrazolate salts provided a new and straightforward approach to highly energetic salts with energetic amines or hydrazine. In this work, the syntheses of new energetic salts, based on 2-amino-1,3-diazido-2-(azidomethyl)propane (6)<sup>10</sup> with some of nitro-containing energetic acids, are of considerable interest because of their rather high densities, lower shock sensitivities, and high heats of formation.

### Results and Discussion

**Synthesis.** Amine, 6, which was synthesized from 2-amino-1,3-dichloro-2-(chloromethyl)propane and sodium azide in dimethyl sulfoxide, exhibits a low density ( $1.25 \text{ g cm}^{-3}$ ), an impact sensitivity of  $5 \text{ J}$ ,<sup>11</sup> calculated

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(11) (a) www.bam.de. (b) A portion of 20 mg of energetic compounds was subjected to a drop-hammer test using a 5 or 10 kg weight dropped. A range in impact sensitivities according to the UN Recommendations (Insensitive > 40 J; less sensitive  $\geq 35 \text{ J}$ ; sensitive  $\geq 4 \text{ J}$ ; very sensitive  $\leq 3 \text{ J}$ ).

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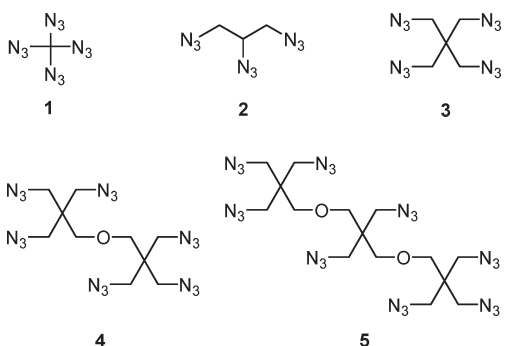
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Scheme 1. Polyazides

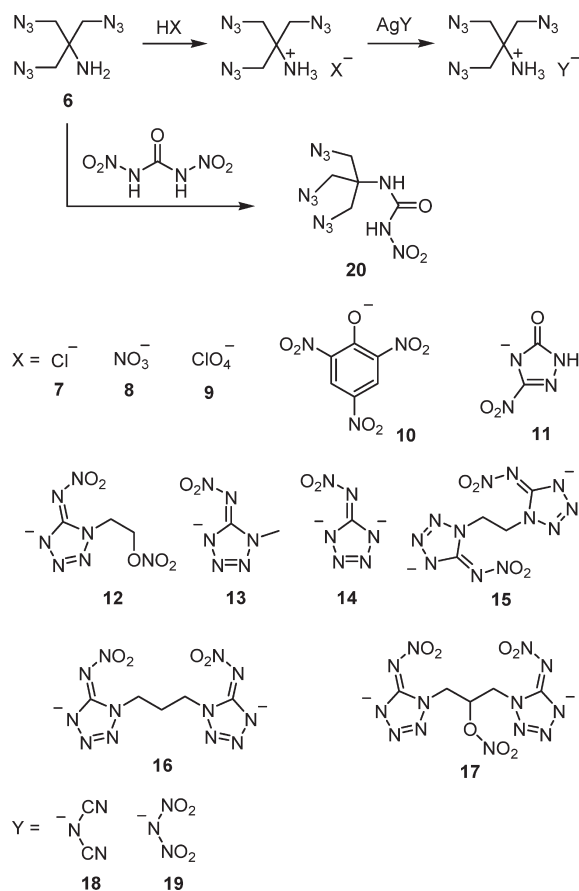


heat of formation of  $834 \text{ kJ mol}^{-1}$ ,<sup>12</sup> detonation pressure ( $P$ ) of  $15.21 \text{ GPa}$ , and detonation velocity ( $D$ ) of  $7134 \text{ m s}^{-1}$ .<sup>13</sup> New energetic materials containing energetic 1,3-diazido-2-(azidomethyl)-2-propylammonium cations and nitrate (**8**), perchlorate (**9**), picrate (**10**), 3-nitro-5-oxo-1,2,4-triazolide (**11**), and nitroiminotetrazolates (**12–17**) were synthesized by reacting equimolar quantities of the appropriate free bases and energetic acids (and HCl) in either water or acetonitrile (Scheme 2). On the other hand, reaction of silver dicyanamide or silver dinitramide with 1,3-diazido-2-(azidomethyl)-2-propylammonium chloride (**7**) yields the corresponding ammonium salts, **18** and **19**. The silver salts are obtained by the metathesis of sodium dicyanamide and potassium dinitramide<sup>14</sup> with silver nitrate in aqueous solution.

Surprisingly, the reaction of **6** and dinitrourea (DNU)<sup>15</sup> did not occur under the previous reaction conditions to make the ammonium dinitrourea salt. However, the nucleophilic amine group in **6** attacked the strongly electrophilic carbonyl carbon in DNU to displace nitramine and form the mononitro urea derivative, **20**, in good yield (Scheme 2).

**X-ray Crystal Structures.** Single crystals of compounds **8**, **10**, **15**, **18**, and **20** suitable for crystal structure analysis were obtained as described in the Experimental Section. All crystals were mounted on MiteGen MicroMesh using

Scheme 2. Synthesis of Energetic Salts



a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$ ). A MSC X-Stream low temperature device was used to keep the crystals at a constant 93(2), 173(2) or 293(2) K during data collection. Data collection was performed and the unit cell was initially refined using APEX2.<sup>16a</sup> Data reduction was performed using SAINT<sup>16b</sup> and XPREP.<sup>16c</sup> Corrections were applied for Lorentz, polarization, and absorption effects using SADABS.<sup>16d</sup> The structure was solved and refined with the aid of the programs in the SHELXTL-plus system of programs.<sup>16e</sup> The full-matrix least-squares refinement on  $F^2$  included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model (Figure 1).

The azido-containing nitrogen rich ammonium cations employed in this study are all the subject of many X-ray studies and are therefore structurally well characterized. Compounds **8**, **10**, **15**, and **18** crystallize in a variety of crystal systems, and the space groups are  $P2_1/c$  for **8**,  $P1$  for

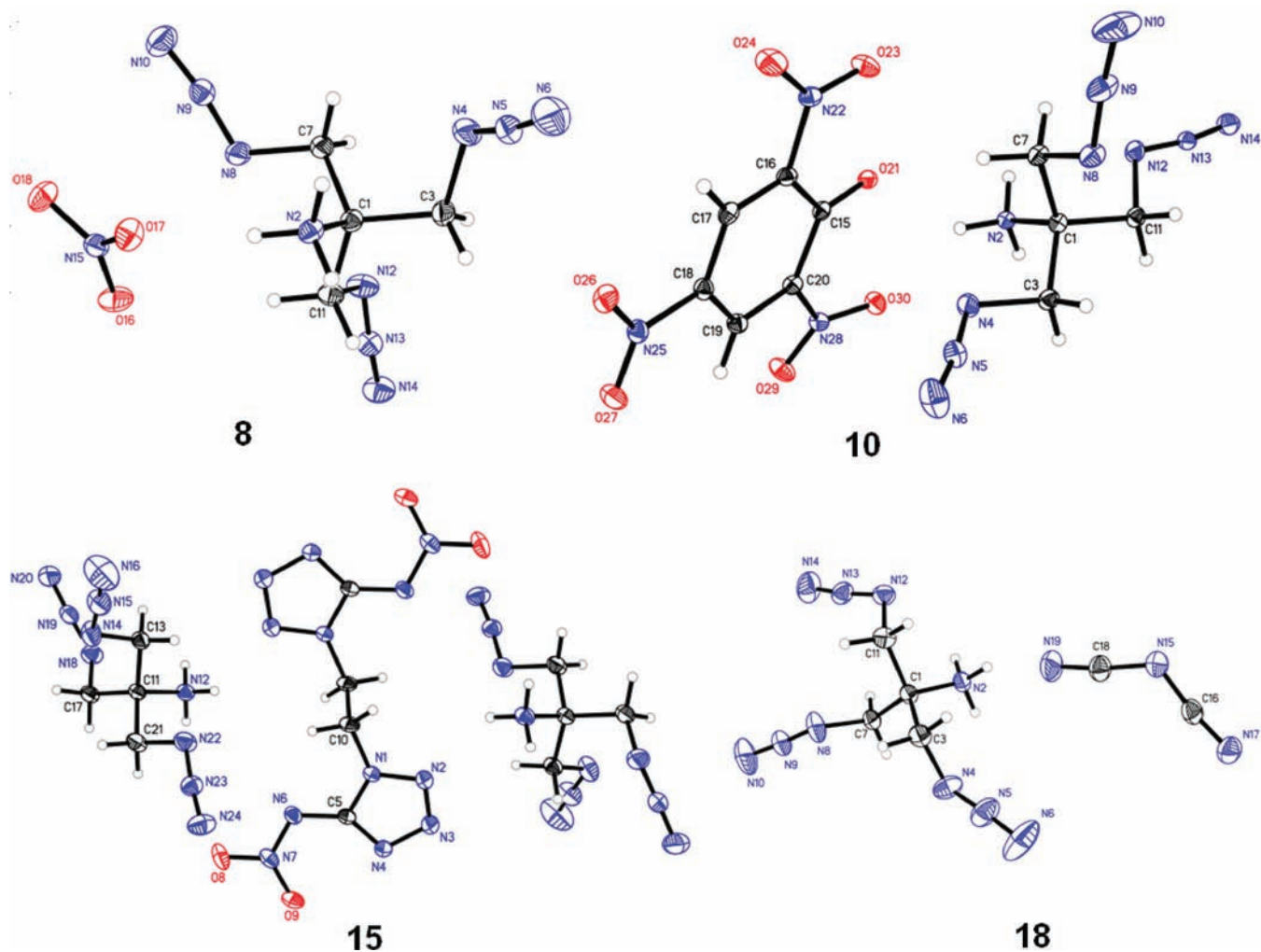
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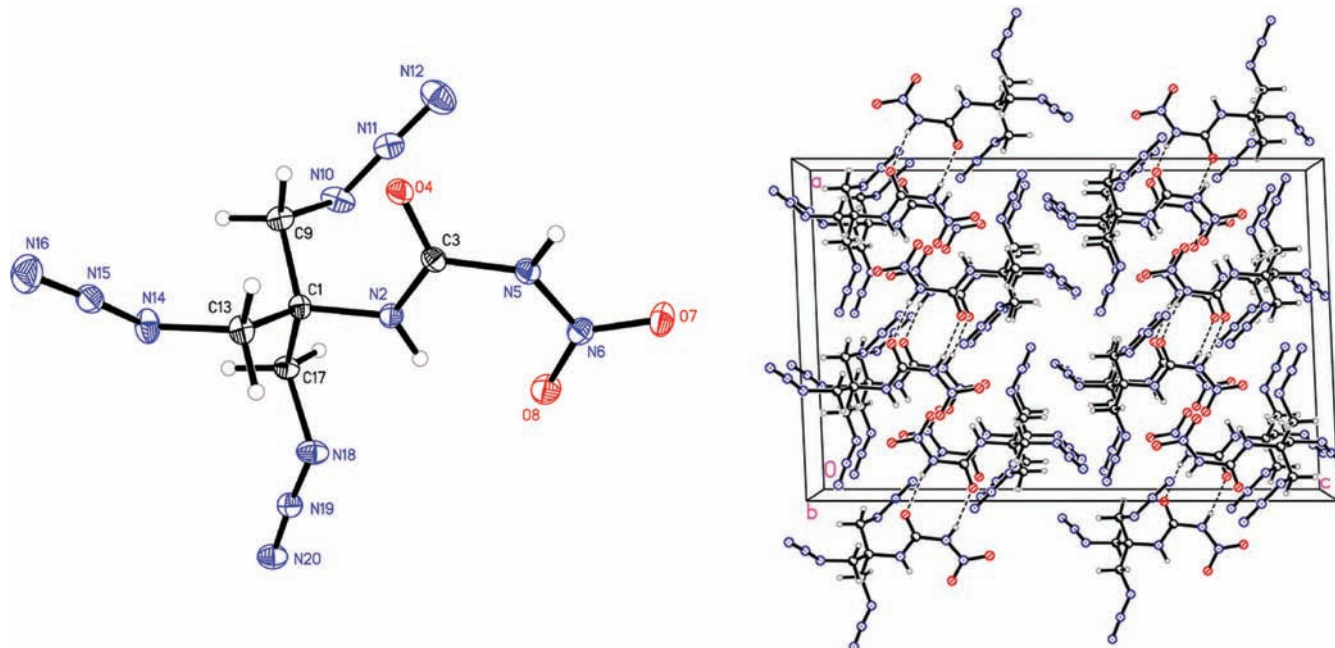


**Figure 1.** Molecular structures of ammonium salts **8**, **10**, **15**, and **18**. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å]: **8**: C1–N2 1.5036(11), C1–C3 1.5365(12), C3–N4 1.4776(13), N4–N5 1.2344(12), N5–N6 1.1296(13), N15–O16 1.2308(11), N15–O17 1.2518(10), N15–O18 1.2762(10); **10**: C1–N2 1.5012(13), C1–C3 1.5283(14), C3–N4 1.4762(14), N4–N5 1.2325(14), N5–N6 1.1283(15), C15–O21 1.2569(13), C15–C16 1.4505(15), C16–N22 1.4686(13), N22–O23 1.2275(12), N22–O24 1.2279(13); **15**: N1–N2 1.3491(13), N1–C5 1.3510(13), N1–C10 1.4541(13), N2–N3 1.2926(14), N3–N4 1.3650(14), N4–C5 1.3339(14), C5–N6 1.3655(14), N6–N7 1.3181(13), N7–O8 1.2486, N7–O9 1.2630(13), C11–N12 1.4985(14), C11–C13 1.5272(14), C13–N14 1.4785(14), N14–N15 1.2335(16), N15–N16 1.1245(18); **18**: C1–N2 1.4957(14), C1–C3 1.5288(16), C3–N4 1.4723, N4–N5 1.2161, N5–N6 1.124(2), N15–C16 1.294, C16–N17 1.1498(18).

**Table 1.** Crystallographic Data for **8**, **10**, **15**, **18**, and **20**

	<b>8</b>	<b>10</b>	<b>15</b>	<b>18</b>	<b>20</b>
formula	C <sub>4</sub> H <sub>9</sub> N <sub>11</sub> O <sub>3</sub>	C <sub>10</sub> H <sub>11</sub> N <sub>13</sub> O <sub>7</sub>	C <sub>12</sub> H <sub>22</sub> N <sub>32</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>9</sub> N <sub>13</sub>	C <sub>5</sub> H <sub>8</sub> N <sub>12</sub> O <sub>3</sub>
fw	259.22	425.32	678.52	263.26	284.23
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	8.7297(16)	7.4766(8)	7.7636(7)	11.4871(5)	15.6078(18)
<i>b</i> (Å)	9.0361(17)	10.7765(11)	25.836(2)	8.5229(3)	6.2557(7)
<i>c</i> (Å)	13.415(3)	12.0355(12)	8.0569(7)	12.8121(5)	24.224(5)
$\alpha$ (deg)	90	113.0670(10)	90	90	90
$\beta$ (deg)	93.330(2)	96.2560(10)	118.4650	95.3950(10)	92.481(2)
$\gamma$ (deg)	90	101.730(2)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1056.4(3)	854.19(15)	1420.7(2)	1248.79(9)	2362.9(5)
<i>Z</i>	4	2	2	4	8
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	173(2)	93(2)	173(2)	293(2)	93(2)
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.630	1.654	1.586	1.400	1.598
$\mu$ (mm <sup>-1</sup> )	0.138	0.141	0.128	0.106	0.134
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0324	0.0328	0.0361	0.0471	0.0306
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0869	0.0865	0.0895	0.1286	0.0790

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$



**Figure 2.** Molecular structure of **20**. Thermal ellipsoids represent 50% probability. Selected bond lengths [ $\text{\AA}$ ]: C1–N2 1.4720(12), N2–C3 1.3321(12), C3–O4 1.2320(12), C3–N5 1.4093(12), N5–N6 1.3689(12), N6–O7 1.2242(11), N6–O8 1.2300(11), C1–C9 1.5411(13), C9–N10 1.4800(14), N10–N11 1.2386(13), N11–N12 1.1293(14).

**10**,  $P2_1/c$  for **15**, and  $P2_1/n$  for **18** (Table 1). Within the limits of structure measurement, the azido-containing ammonium cation of all compounds show very similar bond lengths and angles for the pentaerythryl tetraazide **2**.<sup>6c</sup>

The azide moiety in all ammonium cations (**8**, **10**, **15**, **18**) consists of longer N(4)–N(5) [in the case of **15**: N(14)–N(15)] than N(5)–N(6) [in the case of **15**: N(15)–N(16)], and the angle N(4)–N(5)–N(6) [in the case of **15**: N(14)–N(15)–N(16)] is slightly bent. For the nitrate,<sup>16f</sup> picrate,<sup>16g</sup> and nitroiminotetrazolate,<sup>9b</sup> it is also evident that the energetic anion has the similar geometry, as were identified in previous structure determinations.

The molecular structure of the nitrourea derivative **20** is shown in Figure 2. It crystallizes in the monoclinic space group  $P2_1/c$  with eight molecules in the unit cell. The calculated density is  $1.598 \text{ g cm}^{-3}$  at 93(2) K (Table 1). The geometry is comparable to those found for other dinitrourea compounds.<sup>15b</sup> The packing of the atoms of compound **20** is dominated by a three-dimensional (3D) network in which single planes are connected by strong intermolecular hydrogen bonding (N5 $\cdots$ O4\_#1 2.7655(11)  $\text{\AA}$ ; symmetry transformation used to generate equivalent atoms: #1 =  $-x, y, -z + 1/2$ ). A view of the hydrogen bonds of one plane and the unit cell along the  $b$  axis is shown in Figure 2.

**<sup>15</sup>N NMR Spectroscopy.** The <sup>15</sup>N NMR spectra of **12**, **15**, and **18** were measured in CD<sub>3</sub>CN or DMSO-*d*<sub>6</sub>. The chemical shifts are given with respect to CH<sub>3</sub>NO<sub>2</sub> as external standard. Azides in which the N<sub>3</sub> group is directly bonded to an alkyl group (electron-donating)

show signals in their <sup>15</sup>N NMR spectra with increasing  $\delta$  values in the order N $\alpha$ , N $\gamma$ , N $\beta$  (Figure 3).<sup>17a</sup>

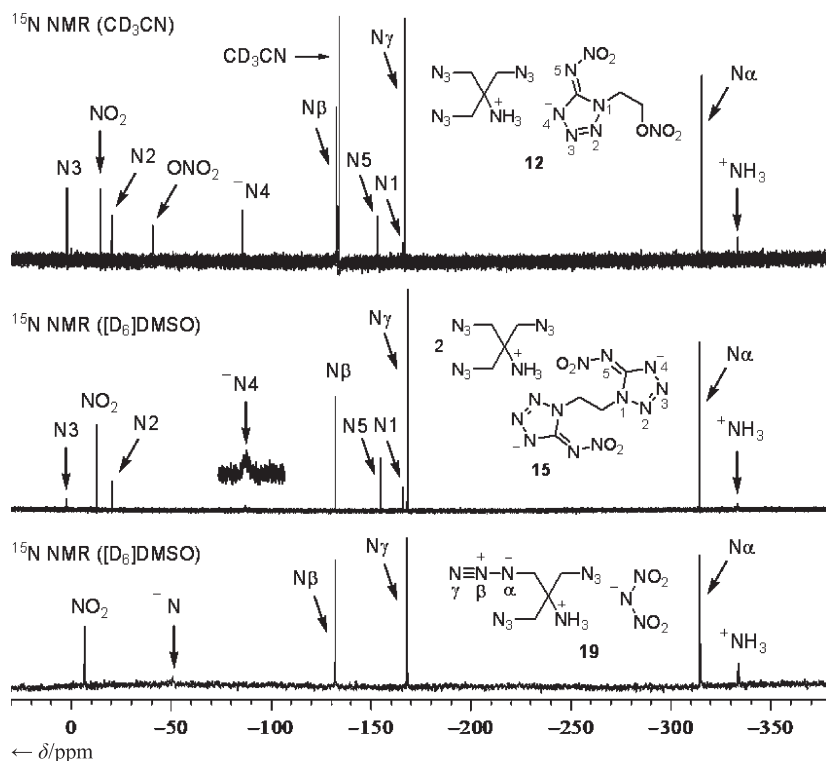
In the case of azide linked to an electron-withdrawing unit, the order N $\alpha$ , N $\beta$ , N $\gamma$  was found instead, as is typical for simple alkyl and aryl azides.<sup>4,17</sup> The signals for the N $\alpha$  (–310 and –316 ppm) and ammonium cation appear at the highest field. N $\beta$  and N $\gamma$  lie between –127 and –133 ppm, and –163 and –170 ppm, respectively (Table 2). Comparison of the resonances observed for the 1-substituted 5-nitroiminotetrazolate anion with those of the compounds in this study shows expected shifts.<sup>9b</sup> The resonance of N4 in **12** and **15** is comparable with neutral 5-nitroiminotetrazole derivatives, which was about 50–60 ppm higher field.<sup>9</sup> The assignments are given based on the literature values of the chemical shift of the 5-nitroiminotetrazolate anion.<sup>9</sup> The remainder of the <sup>14</sup>N or <sup>15</sup>N NMR spectra for all compounds are available in the Supporting Information.

On the basis of our calculations, heats of formation are one of the important characteristics for energetic salts which are directly related to the number of nitrogen–nitrogen bonds in the ionic species.<sup>18</sup> The lattice energies were estimated according to Jenkins et al.<sup>18a</sup> The heats of formation for azide compounds **3** and **6–20** were calculated with Gaussian 03<sup>12</sup> and are summarized in Table 3. These values were computed by using the method of isodesmic reactions (see Supporting Information). The enthalpy of an isodesmic reaction ( $\Delta H_{r298}$ ) is obtained by combining the MP2/6-311 + + G\*\* energy difference for the reaction, the scaled zero point energies, and other thermal factors. Atomization energies were calculated by the G2 method.<sup>19</sup> All of the optimized structures were

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**Figure 3.** Selected  $^{15}\text{N}$  NMR spectra of ammonium salts **12**, **15**, and **19**.

**Table 2.**  $^{15}\text{N}$  NMR Chemical Shift for Azide of Energetic Salts and Polyazides<sup>a</sup>

compd	$\text{N}\alpha^b$	$\text{N}\beta^{b,c}$	$\text{N}\gamma^b$
<b>3</b> <sup>d</sup>	-314.5	-131.2 (2.9 Hz)	-167.8
<b>4</b> <sup>e</sup>	-314.3	-130.8 (3.1 Hz)	-168.3
<b>5</b> <sup>e</sup>	-314.2, -313.9	-130.8 (3.1 Hz), -130.4 (3.2 Hz)	-168.5, -169.1
<b>6</b> <sup>f</sup>	-313.4	-131.0 (3.2 Hz)	-168.3
<b>7</b>	-314.6	-131.8	-168.5
<b>8</b>	-314.6	-132.5	-169.6
<b>9</b>	-315.9	-133.1 (3.2 Hz)	-166.1
<b>10</b>	-314.6	-132.0 (3.1 Hz)	-168.1
<b>11</b>	-314.0	-131.5	-169.1
<b>12</b>	-315.4	-132.7 (3.0 Hz)	-166.9
<b>13</b>	-314.6	-132.0	-168.2
<b>14</b>	-313.6	-131.1 (3.4 Hz)	-169.7
<b>15</b>	-314.6	-132.1 (3.2 Hz)	-168.2
<b>16</b>	-309.8	-127.3 (2.9 Hz)	-163.3
<b>17</b>	-315.0	-132.3 (3.1 Hz)	-167.4
<b>18</b>	-309.6	-127.0	-163.5
<b>19</b>	-314.7	-132.1 (3.1 Hz)	-168.0

<sup>a</sup> Measured with 50.7 MHz. <sup>b</sup> ppm. <sup>c</sup> With N,H coupling constant. <sup>d</sup> Ref 6. <sup>e</sup> Ref 6b. <sup>f</sup> Ref 10.

characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. All azido-containing ammonium salts were endothermic materials in the range of 2.39–4.59  $\text{kJ g}^{-1}$ ; salts **14** and **18** have the highest value at 4.59  $\text{kJ g}^{-1}$ . The ethylene bridged nitroiminotetrazolate salt **15** (4.31  $\text{kJ g}^{-1}$ ) resulted in a slightly higher value than the neutral azido-containing amine (**6**) (4.25  $\text{kJ g}^{-1}$ ) (Table 3).

Differential scanning calorimetry (DSC) was used to assess the thermal stability of the new azide containing ammonium salts **7–19** as well as polyazides **3–6**, **20**. The decomposition temperatures of compounds **8** and **9** are higher than 200 °C. Eight compounds (**3**, **7**, **10**, **11**, **13**, **14**,

**15**, **18**, and **20**) have melting points and the remainder **4–6**, **8**, **9**, **12**, **16**, **17**, and **19** decomposed between 171–210 °C without melting, with **9** having the highest thermal stability being stable up to 210 °C (Table 3). These decomposition temperatures are generally lower than the starting material of **6**. Impact testing was carried out using a BAM Fallhammer.<sup>11</sup> In Table 3, there is a range of impact sensitivities. All of the azide compounds (5–30 J) are less sensitive than or equally sensitive to **6** (5 J); except for the non-sensitive picrate salt (**10**: 40 J). The detonation pressures ( $P$ ) and detonation velocities ( $D$ ), calculated with the Cheetah 5.0 program using the experimentally determined densities (from gas pycnometer 25 °C), and the calculated values of the heats of formation of **3** and **6–20**, based on traditional Chapman–Jouget thermodynamic detonation theory (Table 3).

Among the investigated energetic salts, **8–19** show higher detonation parameters than **6** ( $P = 15.21$  GPa,  $D = 7134$   $\text{m s}^{-1}$ ). The calculated detonation pressures of **8–19** lie in the range between 18.84 and 26.45 GPa. The highest detonation pressure is found for **15** (26.45 GPa) which is comparable to the known explosives such as TNT (19.53 GPa) or TATB (31.15 GPa).<sup>20</sup> The detonation velocities of energetic salts **8–19** were calculated to be in the range of 7642–8429  $\text{m s}^{-1}$ . They exceed the detonation velocity of TNT (6881  $\text{m s}^{-1}$ ).<sup>20</sup> The detonation pressure of the propyl bridged nitroiminotetrazolate of salts **16** (22.68 GPa) and **17** (22.51 GPa) have similar values and slightly lower than other nitroiminotetrazolate salts **12** (24.49 GPa), **13** (24.22 GPa), **14** (24.64 GPa), and **15** (26.45 GPa).

**Table 3.** Physical Properties of Energetic Ammonium Salts **8–19** Compared with Polyazides

compd	lattice energy <sup>a</sup> [kJ mol <sup>-1</sup> ]	$\Delta H_f^\circ$ cation <sup>a</sup> [kJ mol <sup>-1</sup> ]	$\Delta H_f^\circ$ anion <sup>a</sup> [kJ mol <sup>-1</sup> ]	$\Delta H_f^\circ$ <sup>a</sup> [kJ mol <sup>-1</sup> , kJ g <sup>-1</sup> ]	m.p. <sup>b</sup> [°C]	density <sup>c</sup> [g cm <sup>-3</sup> ]	$P^d$ [GPa]	$\nu D^e$ [m s <sup>-1</sup> ]	IS <sup>f</sup> [J]
<b>3</b> <sup>i</sup>				1132.0 <sup>g</sup> (4.79)	46	1.44	20.97	7964	7.5
<b>4</b> <sup>j</sup>					205 (dec.)	1.28			10
<b>5</b> <sup>j</sup>					204 (dec.)	1.29			10
<b>6</b> <sup>k</sup>				833.9 <sup>g</sup> (4.25)	245 (dec.)	1.25	15.21	7134	5
<b>7</b>	475.7	1541.9	-230.3	835.9 (3.59)	150	1.48	20.90	7686	5
<b>8</b>	470.7	1541.9	-307.9	763.3 (2.94)	204 (dec.)	1.58	25.47	8241	5
<b>9</b>	448.8	1541.9	-277.8	815.3 (2.75)	210 (dec.)	1.50	22.64	7571	10
<b>10</b>	415.8	1541.9	-108.5	1017.6 (2.39)	168	1.58	23.34	7741	40
<b>11</b>	438.2	1541.9	63.9	1167.6 (3.58)	172	1.50	22.91	8000	20
<b>12</b>	409.1	1541.9	188.1	1320.9 (3.18)	171 (dec.)	1.45	24.59	7737	30
<b>13</b>	436.0	1541.9	306.7	1412.6 (4.15)	98	1.53	24.22	8160	7.5
<b>14</b>	1027.0	1541.9	338.7	2395.5 (4.59)	111	1.53	24.64	8246	10
<b>15</b>	944.4	1541.9	783.0	2922.4 (4.31)	186	1.60	26.45	8429	5
<b>16</b>	904.3	1541.9	721.8	2901.3 (4.19)	191 (dec.)	1.47	22.68	8101	7
<b>17</b>	867.6	1541.9	643.3	2859.4 (3.79)	181 (dec.)	1.47	22.51	7942	7.5
<b>18</b>	448.0	1541.9	113.4	1207.2 (4.59)	150	1.40 <sup>h</sup>	18.84	7642	17.5
<b>19</b>	445.7	1541.9	-156.2	939.9 (3.10)	178 (dec.)	1.49	25.03	7917	20
<b>20</b>				706.4 <sup>g</sup> (2.49)	79	1.54	22.25	7881	30

<sup>a</sup> Calculated via Gaussian 03. <sup>b</sup> Thermal decomposition temperature under nitrogen gas (DSC, 10 °C min<sup>-1</sup>). <sup>c</sup> Gas pycnometer (25 °C). <sup>d</sup> Calculated detonation pressure (Cheetah 5.0). <sup>e</sup> Calculated detonation velocity (Cheetah 5.0). <sup>f</sup> Impact sensitivity (BAM drophammer). <sup>g</sup> Solid state. <sup>h</sup> Density from X-ray measurement (20 °C). <sup>i</sup> Ref 6. <sup>j</sup> Ref 6b. <sup>k</sup> Ref 10.

In this paper, we have synthesized new energetic materials **8–19** based on the 1,3-diazido-2-(azidomethyl)-2-propylammonium cation and anions such as nitrate, perchlorate, picrate, 3-nitro-5-oxo-1,2,4-triazolide, and 5-nitroiminotetrazolate as well as dicyanamide and dinitramide which can be obtained by metathesis. The new energetic salts and polyazides have been fully characterized, including IR, <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N NMR, elemental analysis, and single crystal structure analysis. In addition, we determined the energetic properties of all new materials, which include calculated heats of formation, and detonation pressure and velocity. In particular, compound **15** ( $\Delta H_f^\circ = 4.31$  kJ g<sup>-1</sup>,  $P = 26.45$  GPa,  $D = 8429$  m s<sup>-1</sup>) exhibits good thermal and hydrolytic stability, moderate density, and a heat of formation which gives remarkable enhancement of the detonation pressure and velocity when compared to **6**:  $\Delta H_f^\circ = 4.25$  kJ g<sup>-1</sup>,  $P = 15.21$  GPa,  $D = 7134$  m s<sup>-1</sup>.

## Experimental Section

**Safety Precautions.** *Caution!* While we have experienced no difficulties with the shock instability of the 1,3-diazido-2-(azidomethyl)-2-propylammonium salts **7–19**, they must be synthesized only in 2–3 mmol amounts. For safety, large amounts of polyazides **3–6** should be stored in dichloromethane below 4 °C. Manipulations must be carried out in a hood behind a safety shield. Leather gloves must be worn.

**General Methods.** <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300 for <sup>1</sup>H and <sup>13</sup>C NMR) and 500 MHz (Bruker AVANCE 500 for <sup>15</sup>N NMR) operating at 300.1, 75.5, and 50.7 MHz, respectively, by using [D<sub>6</sub>]DMSO, CD<sub>3</sub>CN, or CDCl<sub>3</sub> as solvent and locking solvent unless otherwise stated. The melting and decomposition points were obtained on a Differential Scanning Calorimeter (TA Instruments Company, Model: Q10) at a scan rate of 10 °C min<sup>-1</sup>. IR spectra were recorded using KBr pellets for solids on BIORAD model 3000 FTS spectrometer. Densities of the energetic compounds were obtained at room temperature by employing a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were determined using an Exeter CE-440 elemental analyzer. Details of the single crystal X-ray diffraction analysis of compounds **8**, **10**, **15**, **18**, and **20** are provided in Supporting Information. Data were collected on a Bruker

three-circle platform diffractometer equipped with a SMART APEX II CCD detector. CCDC-731771 (**8**), CCDC-731773 (**10**), CCDC-731770 (**15**), CCDC-731774 (**18**), and CCDC-731772 (**20**) 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.

**1,3-Diazido-2,2-bis-[[3-azido-2,2-bis(azidomethyl)propoxy]methyl]propane (5):**<sup>6b</sup>. Colorless liquid; IR (KBr)  $\tilde{\nu}$  2934, 2873, 2104 (N<sub>3</sub>), 1298 (N<sub>3</sub>), 1149, 1106; <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO)  $\delta$  3.33 (s, 12 H), 3.32 (s, 8H), 3.29 (s, 4H); <sup>13</sup>C NMR (75.5 MHz, [D<sub>6</sub>]DMSO)  $\delta$  70.2, 70.0, 51.8, 51.6, 45.2, 44.7; <sup>15</sup>N NMR (50.7 MHz, CDCl<sub>3</sub>):  $\delta$  -130.4 (t, <sup>3</sup>J(N,H) = 3.2 Hz; N $\beta$ ), 130.8 (t, <sup>3</sup>J(N,H) = 3.1 Hz; N $\beta$ ), -168.5 (N $\gamma$ ), -169.1 (N $\gamma$ ), -313.9 (N $\alpha$ ), -314.2 (N $\alpha$ ); Anal. Calcd for C<sub>15</sub>H<sub>24</sub>N<sub>24</sub>O<sub>2</sub> (572.51): C, 31.47; H, 4.23; N, 58.72; found C, 31.97; H, 4.35; N, 56.37.

**2-Amino-1,3-diazido-2-(azidomethyl)propane (6):**<sup>10</sup>. To a solution of 12.0 g (0.0680 mol) 2-amino-1,3-dichloro-2-(chloromethyl)propane<sup>10</sup> in 100 mL dimethyl sulfoxide was added 22.0 g (0.338 mol) sodium azide. The suspension was stirred for 24 h at 90–100 °C. The reaction mixture was cooled, and then poured into saturated sodium chloride. The aqueous layer was extracted three times with diethyl ether (3  $\times$  250 mL). The combined organic extracts were washed six times (6  $\times$  200 mL) with saturated sodium chloride and finally one time with water (300 mL). The ether layer was dried with magnesium sulfate. After removal of the solvent in air, the light yellow liquid **6** (12.3 g, 0.0628 mol, 92%) was obtained.

Light yellow liquid; IR (KBr)  $\tilde{\nu}$  3374, 2930, 2865, 2103 (N<sub>3</sub>), 1447, 1289 (N<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.30 (s, 6H; CH<sub>2</sub>), 1.34 (br. s, 2H; NH<sub>2</sub>); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  56.0, 55.6; <sup>15</sup>N NMR (50.7 MHz, CDCl<sub>3</sub>):  $\delta$  -131.0 (t, <sup>3</sup>J(N,H) = 3.2 Hz; N $\beta$ ), -168.3 (N $\gamma$ ), -313.4 (N $\alpha$ ), -344.4 (NH<sub>2</sub>).

**1,3-Diazido-2-(azidomethyl)-2-propylammonium Chloride (7).** The reaction of 470 mg (2.40 mmol) of **6** with 300  $\mu$ L 36% hydrochloric acid in 10 mL diethyl ether at 4 °C gave a white solid, **7**, (540 mg, 2.32 mmol, 97%) after filtration which could be recrystallized from water.

Colorless crystals; IR (KBr)  $\tilde{\nu}$  3407, 2986, 2851, 2625, 2552, 2124 (N<sub>3</sub>), 1605, 1518, 1500, 1452, 1302, 1261; <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO)  $\delta$  8.97 (s, 3H; <sup>+</sup>NH<sub>3</sub>), 3.72 (s, 6H; CH<sub>2</sub>); <sup>13</sup>C NMR (75.5 MHz, [D<sub>6</sub>]DMSO)  $\delta$  57.6, 51.3; <sup>15</sup>N NMR (50.7 MHz, [D<sub>6</sub>]DMSO)  $\delta$  -131.8 (N $\beta$ ), -168.5 (N $\gamma$ ), -314.6 (N $\alpha$ ),

–330.1 ( $^+NH_3$ ); Anal. Calcd for  $C_4H_9ClN_{10}$  (232.63): C, 20.65; H, 3.90; N, 60.21; found C, 20.74; H, 3.84; N, 59.76.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium Nitrate (8).** The reaction of 300 mg (1.53 mmol) of **6** with 100  $\mu$ L 70% nitric acid in 10 mL diethyl ether at 4 °C gave a white solid, **8**, (350 mg, 1.35 mmol, 88%) which after filtration could be recrystallized from water. Colorless crystals; IR (KBr)  $\tilde{\nu}$  3420, 3017, 2934, 2793, 2644, 2567, 2114 ( $N_3$ ), 1604, 1536, 1451, 1416, 1385, 1306, 1182;  $^1H$  NMR (300 MHz,  $[D_6]DMSO$ )  $\delta$  8.50 (br. s, 3H;  $^+NH_3$ ), 3.67 (s, 6H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $[D_6]DMSO$ )  $\delta$  57.5, 51.5;  $^{14}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  –1.0 (s;  $NO_3^-$ ), –132.5 (br. s;  $N\beta$ ), –169.6 (br. s;  $N\gamma$ ), –337.3 (br. s;  $^+NH_3$ );  $^{15}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  –131.9 (t,  $^3J(N, H) = 3.2$  Hz;  $N\beta$ ), –168.4 ( $N\gamma$ ), –314.6 ( $N\alpha$ ), –334.4 ( $^+NH_3$ ); Anal. Calcd for  $C_4H_9N_{11}O_3$ : C, 18.54; H, 3.50; N, 59.45; found: C, 18.57; H, 3.33; N, 59.27; during elemental analysis the compound exploded.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium Perchlorate (9).** The reaction of 300 mg (1.53 mmol) of **6** with 100  $\mu$ L 69%  $HClO_4$  in 10 mL of diethyl ether at 4 °C gave a two layer colorless liquid. The organic layer was removed, and product **9** (310 mg, 1.05 mmol, 68%) was washed with ether.

Colorless liquid; IR (KBr)  $\tilde{\nu}$  3346, 2929, 2102 ( $N_3$ ), 1120, 1078;  $^1H$  NMR (300 MHz,  $CD_3CN$ )  $\delta$  6.04 (s, 3H;  $^+NH_3$ ), 3.68 (s, 6H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $CD_3CN$ )  $\delta$  60.6, 52.0;  $^{15}N$  NMR (50.7 MHz,  $CD_3CN$ )  $\delta$  –133.1 (t,  $^3J(N, H) = 3.2$  Hz,  $N\beta$ ), –166.1 ( $N\gamma$ ), –315.9 ( $N\alpha$ ), –335.4 ( $^+NH_3$ ); Anal. Calcd for  $C_4H_9ClN_{10}O_4$  (296.63): C, 16.20; H, 3.06; N, 47.22; found C, 16.65; H, 3.24; N, 47.98.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium Picrate (10).** The reaction of 400 mg (2.04 mmol) of **6** with 460 mg (2.01 mmol) of picric acid in 10 mL of  $CH_3CN$  at reflux for 10 min gave yellow crystals of **10** (840 mg, 1.98 mmol, 98%) after air drying. Yellow crystals; IR (KBr)  $\tilde{\nu}$  3399, 3211, 3090, 2859, 2780, 2557, 2492, 2119 ( $N_3$ ), 1610, 1572, 1535, 1493, 1445, 1419, 1358, 1331, 1265, 1082, 907, 793, 712;  $^1H$  NMR (300 MHz,  $[D_6]DMSO$ )  $\delta$  8.61 (s, 2H), 8.48 (br. s, 3H;  $^+NH_3$ ), 3.66 (s, 6H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $[D_6]DMSO$ )  $\delta$  161.0, 141.8, 125.3, 124.7, 57.6, 51.5;  $^{15}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  –7.5 ( $NO_2$ ), –10.9 ( $NO_2$ ), –132.0 (t,  $^3J(N, H) = 3.1$  Hz,  $N\beta$ ), –168.1 ( $N\gamma$ ), –314.6 ( $N\alpha$ ), –334.1 (br. s;  $^+NH_3$ ); Anal. Calcd for  $C_{10}H_{11}N_{13}O_7$ : C, 28.24; H, 2.61; N, 42.82; found: C, 28.05; H, 2.54; N, 42.96.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium 3-Nitro-5-oxo-1,2,4-triazolide (11).** The reaction of 400 mg (2.04 mmol) of **6** with 260 mg (2.00 mmol) of 3-nitro-1,2,4-triazol-5-one (NTO)<sup>21</sup> in 10 mL of  $CH_3CN$  under reflux for 30 min gave yellow crystals of **11** (620 mg, 1.90 mmol, 95%) after air drying and washing with ether. Yellow crystals; IR (KBr)  $\tilde{\nu}$  3398, 3011, 2779, 2506, 2111 ( $N_3$ ), 1598, 1509, 1447, 1400, 1377, 1301, 1038, 776;  $^1H$  NMR (300 MHz,  $[D_6]DMSO$ )  $\delta$  9.14 (br. s, 4H), 3.61 (s, 6H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $[D_6]DMSO$ )  $\delta$  162.4, 157.0, 57.7, 52.6;  $^{15}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  –19.6 ( $NO_2$ ), –109.0 ( $N_2$ ), –131.5 ( $N\beta$ ), –169.1 ( $N\gamma$ ), –194.6 (br. s;  $N_3$ ), –196.1 ( $N_1$ ), –314.0 ( $N\alpha$ ), –336.1 (br. s;  $^+NH_3$ ); Anal. Calcd for  $C_6H_{10}N_{14}O_3$  (326.24): C, 22.09; H, 3.09; N, 60.11; found C, 21.82; H, 2.93; N, 60.00; during elemental analysis the compound exploded.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium 4-(2-Nitratooethyl)-5-nitroiminotetrazolate (12).** The reaction of 400 mg (2.04 mmol) of **6** with 474 mg (2.00 mmol) of 1-(2-nitratooethyl)-5-nitroiminotetrazole<sup>9a</sup> in 5 mL of  $H_2O$  at ambient temperature gave white gum semisolid **12** (810 mg, 1.95 mmol, 98%) after washing with ether and air drying. White gummy semisolid; IR (KBr)  $\tilde{\nu}$  3381, 2936, 2556, 2115 ( $N_3$ ), 1641, 1504, 1455, 1369, 1311, 1282;  $^1H$  NMR (300 MHz,  $CD_3CN$ )  $\delta$  7.24 (br. s, 3H;  $^+NH_3$ ), 4.85–4.82 (m, 2H;  $CH_2$ ), 4.51–4.54 (m, 2H;  $CH_2$ ), 3.81 (s, 6H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $CD_3CN$ )  $\delta$  157.1, 71.0, 60.1, 52.4,

44.6;  $^{15}N$  NMR (50.7 MHz,  $CD_3CN$ )  $\delta$  2.2 ( $N_3$ ), –14.3 ( $NO_2$ ), –20.1 (s;  $N_2$ ), –44.7 (t,  $^3J(N, H) = 3.4$  Hz;  $ONO_2$ ), –85.7 ( $N_4$ ), –132.7 (t,  $^3J(N, H) = 3.0$  Hz;  $N\beta$ ), –153.2 ( $N_5$ ), –166.0 (br. s;  $N_1$ ), –166.9 ( $N\gamma$ ), –315.4 ( $N\alpha$ ), –333.2 (br. s;  $^+NH_3$ ); Anal. Calcd for  $C_7H_{13}N_{17}O_5$ : C, 20.24; H, 3.16; N, 57.34; found: C, 19.97; H, 3.08; N, 54.41.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium 4-Methyl-5-nitroiminotetrazolate (13).** The reaction of 980 mg (5 mmol) of **6** with 720 mg (4.44 mmol) of 1-methyl-5-nitroiminotetrazole monohydrate<sup>9a,22</sup> in 20 mL of  $CH_3CN$  at ambient temperature gave white solid **13** (1.46 g, 4.29 mmol, 97%) after air drying and washing with ether. **13** could be recrystallized with  $CH_3CN$ . Colorless crystals; IR (KBr)  $\tilde{\nu}$  3418, 3001, 2934, 2868, 2643, 2576, 2119 ( $N_3$ ), 1607, 1548, 1508, 1459, 1312, 1289;  $^1H$  NMR (300 MHz,  $[D_6]DMSO$ )  $\delta$  3.68 (s, 9H;  $CH_2$  and  $CH_3$  overlap), 8.39 (br. s, 3H;  $^+NH_3$ );  $^{13}C$  NMR (75.5 MHz,  $[D_6]DMSO$ )  $\delta$  156.8, 57.6, 51.5, 32.5;  $^{14}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  –11.4 (s;  $NO_2$ ), –131.7 (br. s;  $N\beta$ );  $^{15}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  6.1, –11.4 ( $NO_2$ ), –15.6, –73.2, –132.0 ( $N\beta$ ), –153.7, –166.4, –168.2 ( $N\gamma$ ), –314.6 ( $N\alpha$ ), –333.7 ( $^+NH_3$ ); Anal. Calcd for  $C_6H_{12}N_{16}O_2$  (340.27): C, 21.18; H, 3.55; N, 65.86; found C, 21.40; H, 3.56; N, 65.60.

**Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium] 5-Nitroiminotetrazolate (14).** The reaction of 400 mg (2.04 mmol) of **6** with 130 mg (0.878 mmol) of 5-nitroiminotetrazole monohydrate<sup>22</sup> in 10 mL of  $CH_3CN$  at ambient temperature gave colorless crystals of **14** (450 mg, 0.861 mmol, 98%) after air drying. **14** could be recrystallized with  $CH_3CN$ . Colorless crystals; IR (KBr)  $\tilde{\nu}$  3422, 2920, 2859, 2766, 2571, 2118 ( $N_3$ ), 1561, 1447, 1398, 1377, 1295, 1017;  $^1H$  NMR (300 MHz,  $[D_6]DMSO$ )  $\delta$  7.12 (br. s, 6H;  $^+NH_3$ ), 3.48 (s, 12H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $[D_6]DMSO$ )  $\delta$  157.8, 57.3, 53.3;  $^{15}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  –8.2 (s;  $N_2$  and  $N_3$ ), –12.1 ( $NO_2$ ), –120.3 ( $N_1$  and  $N_4$ ), –131.1 (t,  $^3J(N, H) = 3.4$  Hz;  $N\beta$ ), –147.4 ( $N_5$ ), –169.7 ( $N\gamma$ ), –313.6 ( $N\alpha$ ), –338.4 ( $^+NH_3$ ); Anal. Calcd for  $C_9H_{18}N_{26}O_2$  (522.41): C, 20.69; H, 3.47; N, 69.71; found C, 20.80; H, 3.39; N, 71.61.

**Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium] Ethylene Bis(5-nitroiminotetrazolate) (15).** The reaction of 400 mg (2.04 mmol) of **6** with 286 mg (1.00 mmol) of ethylene bis-(5-nitroiminotetrazole)<sup>9a</sup> in 20 mL of  $CH_3CN$  at ambient temperature gave colorless crystals of **15** (640 mg, 0.943 mmol, 94%) after air drying. Colorless crystals; IR (KBr)  $\tilde{\nu}$  3429, 3224, 3092, 3016, 2941, 2536, 2490, 2118 ( $N_3$ ), 1587, 1525, 1459, 1391, 1344, 1304, 1103, 1032;  $^1H$  NMR (300 MHz,  $[D_6]DMSO$ )  $\delta$  8.51 (br. s, 6H;  $^+NH_3$ ), 4.49 (s, 4H;  $CH_2$ ), 3.68 (s, 12H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $[D_6]DMSO$ )  $\delta$  155.6, 57.6, 51.5, 43.9;  $^{15}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  2.3 ( $N_3$ ), –12.8 ( $NO_2$ ), –20.3 ( $N_2$ ), –87.0 (br. s;  $N_4$ ), –132.1 (t,  $^3J(N, H) = 3.2$  Hz;  $N\beta$ ), –154.9 ( $N_5$ ), –165.9 ( $N_1$ ), –168.2 ( $N\gamma$ ), –314.6 ( $N\alpha$ ), –333.5 (br. s;  $^+NH_3$ ); Anal. Calcd for  $C_{12}H_{22}N_{32}O_4$ : C, 21.24; H, 3.27; N, 66.06; found: C, 21.29; H, 3.20; N, 66.23.

**Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium] Trimethylene Bis(5-nitroiminotetrazolate) (16).** The reaction of 500 mg (2.55 mmol) of **6** with 471 mg (1.48 mmol) of trimethylene bis-(5-nitroiminotetrazole)<sup>22</sup> in 10 mL of  $CH_3CN$  at ambient temperature gave white gum semisolid **16** (960 mg, 1.39 mmol, 94%) after air drying and washing with ether. White gummy semisolid; IR (KBr)  $\tilde{\nu}$  3426, 2940, 2878, 2560, 2113 ( $N_3$ ), 1502, 1455, 1310;  $^1H$  NMR (300 MHz,  $[D_6]DMSO$ )  $\delta$  8.07 (br. s, 6H;  $^+NH_3$ ), 4.14 (t,  $^3J(H, H) = 7.0$  Hz, 4H;  $CH_2$ ), 3.70 (s, 12H;  $CH_2$ ), 2.28 (quin,  $^3J(H, H) = 7.0$  Hz, 2H;  $CH_2$ );  $^{13}C$  NMR (75.5 MHz,  $[D_6]DMSO$ )  $\delta$  156.2, 58.1, 51.7, 43.5, 27.8;  $^{15}N$  NMR (50.7 MHz,  $[D_6]DMSO$ )  $\delta$  8.9 ( $N_3$ ), –7.5 ( $NO_2$ ), –14.4 ( $N_2$ ), –75.9 (br. s;  $N_4$ ), –127.3 (t,  $^3J(N, H) = 2.9$  Hz;  $N\beta$ ), –149.6 ( $N_5$ ), –155.3 ( $N_1$ ), –163.3 ( $N\gamma$ ),

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−309.8 (N $\alpha$ ), −328.7 (br. s;  $^+$ NH $_3$ ); Anal. Calcd for C $_{13}$ H $_{24}$ N $_{32}$ O $_4$  (692.54): C 22.55, H 3.49, N 64.72; found C 22.63, H 3.54, N 64.06.

**Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium] 4,4'-(2-Nitratopropan-1,3-diyl)-bis(5-nitroiminotetrazolate) (17).** The reaction of 430 mg (2.19 mmol) of **6** with 361 mg (1.00 mmol) of 2-nitratopropan-1,3-bis(5-nitroiminotetrazol-1-yl)propane<sup>9a</sup> in 10 mL of CH $_3$ CN at ambient temperature gave a colorless gum solid **17** (750 mg, 0.99 mmol, 99%) after washing with ether. White solid; IR (KBr)  $\tilde{\nu}$  3426, 2931, 2876, 2560, 2114 (N $_3$ ), 1653, 1505, 1453, 1370, 1305;  $^1$ H NMR (300 MHz, CD $_3$ CN)  $\delta$  7.61 (br. s, 6H;  $^+$ NH $_3$ ), 5.91 (m, 1H; CH), 4.45–4.64 (m, 4H; CH $_2$ ), 3.60 (s, 12H; CH $_2$ );  $^{13}$ C NMR (75.5 MHz, CD $_3$ CN)  $\delta$  157.5, 78.0, 57.4, 52.1, 44.8;  $^{15}$ N NMR (50.7 MHz, CD $_3$ CN)  $\delta$  4.5 (N $_3$ ), −14.3 (NO $_2$ ), −20.1 (m; N $_2$ ), −44.7 (d,  $^3J$ (N,H) = 3.5 Hz; ONO $_2$ ), −82.7 (N $_4$ ), −132.3 (t,  $^3J$ (N,H) = 3.1 Hz; N $\beta$ ), −153.3 (N $_5$ ), −167.4 (N $\gamma$ ), −168.3 (br. s; N $_1$ ), −315.0 (N $\alpha$ ), −334.7 (br. s;  $^+$ NH $_3$ ); Anal. Calcd for C $_{13}$ H $_{23}$ N $_{33}$ O $_7$ : C, 20.72; H, 3.08; N, 61.34; found: C, 21.06; H, 3.11; N, 61.75.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium Dicyanamide (18).** The reaction of 960 mg (4.13 mmol) of **7** with 800 mg (4.59 mmol) of silver dicyanamide<sup>23</sup> in 50 mL of H $_2$ O at ambient temperature gave colorless crystals of **18** (980 mg, 3.72 mmol, 90%) after filtration of silver chloride and air drying.

Colorless crystals: IR (KBr)  $\tilde{\nu}$  3551, 3402, 3026, 2882, 2830, 2739, 2639, 2575, 2277, 2213, 2141 (N $_3$ ), 1614, 1524, 1453, 1348, 1310, 1259;  $^1$ H NMR (300 MHz, [D $_6$ ]DMSO)  $\delta$  8.29 (br. s, 3H;  $^+$ NH $_3$ ), 3.62 (s, 6H; CH $_2$ );  $^{13}$ C NMR (75.5 MHz, [D $_6$ ]DMSO)  $\delta$  57.8, 51.7;  $^{15}$ N NMR (50.7 MHz, [D $_6$ ]DMSO)  $\delta$  −127.0 (N $\beta$ ), −163.5 (N $\gamma$ ), −205.3 (CN), −309.6 (N $\alpha$ ), −329.7 ( $^+$ NH $_3$ ), −360.9 (N); Anal. Calcd for C $_6$ H $_9$ N $_{13}$  (263.22): C, 27.38; H, 3.45; N, 69.18; found C, 26.92; H, 3.49; N, 68.26.

**1,3-Diazido-2-(azidomethyl)-2-propylammonium Dinitramide (19).** The reaction of 543 mg (2.34 mmol) of **7** with 500 mg

(2.34 mmol) of silver dinitramide<sup>14</sup> in 8 mL of H $_2$ O at ambient temperature gave colorless liquid **19** (680 mg, 2.24 mmol, 96%) after filtration of silver chloride and air drying.

Colorless liquid; IR (KBr)  $\tilde{\nu}$  3401, 2992, 2877, 2111 (N $_3$ ), 1596, 1535, 1499, 1432, 1299, 1260, 1205, 1028, 731;  $^1$ H NMR (300 MHz, [D $_6$ ]DMSO)  $\delta$  8.51 (br. s, 3H;  $^+$ NH $_3$ ), 3.66 (s, 6H; CH $_2$ );  $^{13}$ C NMR (75.5 MHz, [D $_6$ ]DMSO)  $\delta$  57.7, 51.5;  $^{14}$ N NMR (50.7 MHz, [D $_6$ ]DMSO)  $\delta$  −6.7 (NO $_2$ ), −50.8 (N $^-$ ), −132.0 (N $\beta$ ), 167.6 (N $\gamma$ ), 313.6 (N $\alpha$ ), 338.3 ( $^+$ NH $_3$ );  $^{15}$ N NMR (50.7 MHz, [D $_6$ ]DMSO)  $\delta$  −6.7 (NO $_2$ ), −50.8 (N $^-$ ), −132.1 (t,  $^3J$ (N,H) = 3.1 Hz; N $\beta$ ), −168.0 (N $\gamma$ ), −314.7 (N $\alpha$ ), −333.8 ( $^+$ NH $_3$ ); Anal. Calcd for C $_4$ H $_9$ N $_{13}$ O $_4$ : C, 15.85; H, 2.99; N, 60.06; found: C, 15.73; H, 2.86; N, 57.93.

**1-[1,3-Diazido-2-(azidomethyl)-2-propyl]-3-nitrourea (20).** The reaction of 400 mg (2.04 mmol) of **6** with 300 mg (2.00 mmol) of dinitrourea<sup>15</sup> in 10 mL of CH $_3$ CN at ambient temperature gave white solid **20** (350 mg, 1.23 mmol, 62%) after washing with ether and air drying (2  $\times$  2 mL). **20** was recrystallized from CH $_3$ CN.

Colorless crystals; IR (KBr)  $\tilde{\nu}$  3351, 3121, 3055, 2961, 2784, 2114 (N $_3$ ), 1687, 1601, 1536, 1450, 1286, 1205, 1076, 586;  $^1$ H NMR (300 MHz, [D $_6$ ]DMSO)  $\delta$  7.80 (br. s, 2H; NH), 3.58 (s, 6H; CH $_2$ );  $^{13}$ C NMR (75.5 MHz, [D $_6$ ]DMSO)  $\delta$  153.7, 57.5, 52.3; Anal. Calcd for C $_5$ H $_8$ N $_{12}$ O $_3$ : C, 21.13; H, 2.84; N, 59.14; found: C, 21.19; H, 2.75; N, 59.30.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for **8**, **10**, **15**, **18**, **20** and  $^{15}$ N NMR spectra of all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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