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Dense energetic salts of *N*,*N*′-dinitrourea (DNU)†

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The structure of dinitrourea (DNU) as determined by X-ray single-crystal diffraction is orthorhombic; space group: *Fdd*2; a = 12.0015(9), b = 17.6425(13), c = 4.5555(4); V = 964.57 Å^3, Z = 8, T = 90 K; D_c = 2.067 g cm^{-3}. The heat of formation ($\Delta_f H^\circ_{298}$) of DNU in the gas phase was calculated to be 24.88 kJ mol^{-1} by using the G3MP2 method based on isodesmic reactions. Eleven mono-organic salts of DNU were prepared in acetonitrile and characterized *via* NMR spectra, elemental analyses and DSC. Derivatives of 1,2,4-triazolium salts of DNU exhibit densities ranging from 1.75 to 1.86 g cm^{-3} and detonation properties comparable with those of RDX and HMX.

Introduction

As an important family of high energy density materials (HEDM), dinitrourea (DNU)[1–5] and its derivatives have attracted considerable interest due to their relatively high densities. For example, DNU has a density of 1.98 g cm^{-3}, while other high-explosive containing the dinitrourea fragment such as K-6,[6] K-56,[7] TNGU,[8] TNCB,[9] HHTDD[10] (Fig. 1) are very dense ranging from 1.93 to 2.07 g cm^{-3}. These materials were expected to exhibit superior detonation properties since density is a critical factor that, according to a semi-empirical equation suggested by Kamlet and Jacobs,[11] affects detonation performance, *viz*., detonation pressure (P) is dependent on the square of the density, and the detonation velocity (D) is proportional to the density.

DNU was also found to be a good precursor to nitroamine (H_2NNO_2)[12] and a facile starting material for preparation of K-6.[13,14] However, dinitrourea was initially reported to undergo decomposition at room temperature which could lead to spontaneous ignition.[1] Later, this drawback was overcome by washing with trifluoroacetic acid to remove the trace amount of acid contamination introduced during the manufacturing process.[3] Another hurdle for the practical utility of DNU is its instability to heat and friction which could be overcome by converting to an organic salt. Our previous experiences have demonstrated that when a strong N-acid was transformed into a corresponding organic salt, the thermal stability was improved by nearly 50 °C. For example, 5-nitroaminotetrazole decomposed at 128 °C, but 4-amino-1,2,4-triazolium-5-nitroaminotetrazolate was stable up to 184 °C.[15]

Most recently, ionic liquids/solids have been prepared and characterized as propellants where nitrate, perchlorate, dinitramide, azide, 3,5-dinitrotriazolate, 5-nitrotetrazolate, 5-nitroaminotetrazolate, 2,4,5-trinitroimidazolate, or azotetrazolate, *etc*. served as anion.[16–22] Considering that dinitrourea has a positive oxygen balance, its salts should release more energy *via* detonation resulting in better detonation properties. To date, knowledge about DNU is limited to its density, thermal behavior and reactions with formaldehyde[4] as well as its metal and ammonium salts.[5] No other energetic salts of DNU are available. In this paper, we report the crystal structure of DNU, its calculated detonation properties, and reactions with nitrogen heterocycles to form energetic salts (Scheme 1).

Discussion

Dinitrourea (DNU) (1) was synthesized according to the literature,[3] *i.e.*, after nitration of urea with mixed acid, the desired product precipitated, was washed with trifluoroacetic acid, and dried under vacuum. This colorless solid was readily soluble in CH_3CN, diethyl ether, ethyl acetate, benzene, THF, $CHCl_3$, CH_2Cl_2, *etc*. In contrast with a previous report,[3] we found that DNU was immediately decomposed in DMSO with concomitant gas evolution, and it gradually decomposed in water. In CD_3CN as solvent, the proton NMR spectrum contains a broad peak at 11.0 ppm which corresponds to a typical N-acid proton. The mass spectrum (MS-EI solid

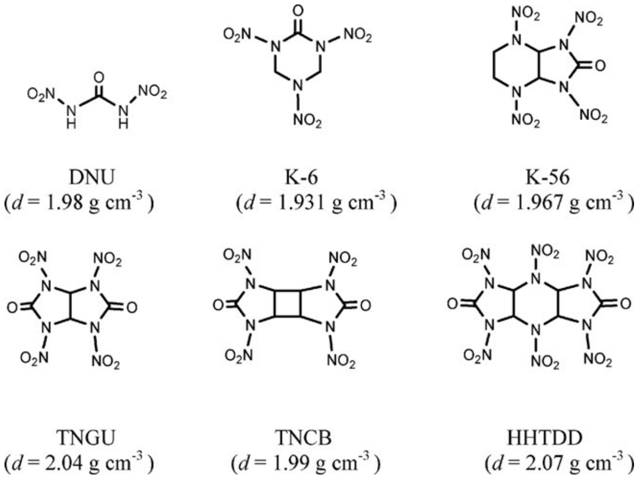

Fig. 1 Structures of some explosive candidates containing a DNU fragment.

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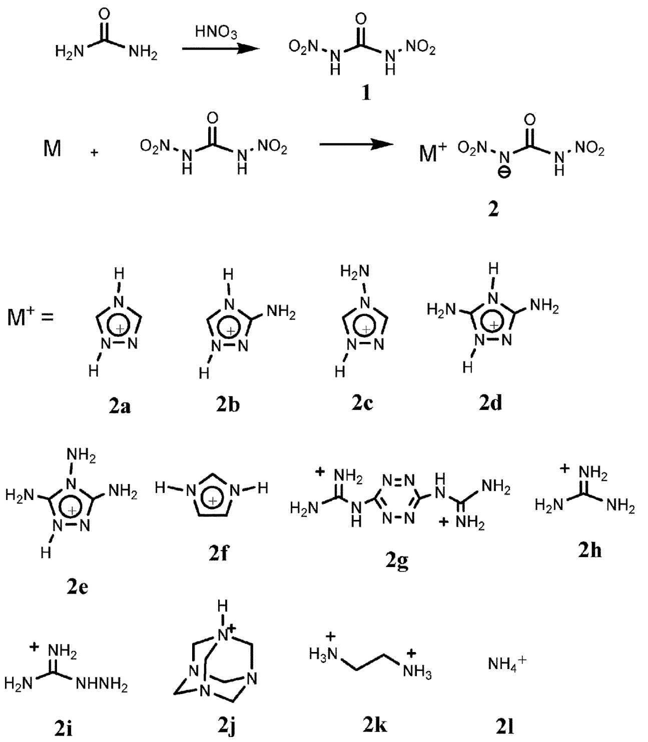


Scheme 1 Synthesis of DNU salts.

probe) clearly supports the existence of the molecule with a molecular ion peak 150 (M^+, 0.1), and reasonable fragments such as 107 ($(NO_2)_2NH$, 0.2), 89 ($M^+ - NHNO_2$, 0.4), 62 (NO_2NH_2, 3.2), 46 (NO_2^+, 100).

DNU was crystallized from a diethyl ether–hexane mixture yielding clear colorless needles suitable for crystallographic analysis (Table 1). The complete molecule, symmetry generated in the chiral orthorhombic space group *Fdd*2, is shown in Fig. 2(a). The absolute configuration could not be determined reliably. There is a spiral twist to the molecule and the torsion angle O1–N1–N2–C1 is −11.2°. There are relatively few structurally determined congeners, however, K-6,[6] K-56,[7a] DNDAGU,[7b] 1,3-dinitro-1,3-diazacyclopentanone[7c] and a few derivatives[7d] of the latter are known. These all display structural features similar to the DNU framework although the bond lengths in K-56 are surprisingly asymmetric compared to DNU. The packing of DNU displays stacks of hydrogen bonded units (*via* the amino N–H···OC ketone synthon) parallel to the *c*-axis. The packing is efficient and results in a high density of 2.067 g cm^{-3} at 90 K.

Table 1 Crystal data for **1** and **2a**

Empirical formula	$CH_2N_4O_5$	$C_3H_5N_7O_5$
M_r	150.07	219.14
Crystal system	Orthorhombic	Monoclinic
Space group	*Fdd*2	$P2_1$
a/Å	12.0015(9)	7.6156(3)
b/Å	17.6425(13)	4.9837(2)
c/Å	4.5555(4)	10.3119(4)
β/°	90	95.530(1)
V/Å^3	964.57(13)	389.55(3)
Z	8	2
T/K	90(2)	90(2)
D_c/Mg m^{-3}	2.067	1.868
μ/mm^{-1}	0.210	0.173
θ Range for data collection/°	4.11–30.03	1.98–29.00
Reflections collected	3712	5716
Indep. reflections (R_{int})	389 (0.0191)	1151 (0.0196)
Data/restraints/parameters	389/1/47	1151/1/136
GOF	1.097	1.091
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0236	0.0255
$wR_2{}^a$ ([$I > 2\sigma(I)$])	0.0617	0.0655

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

DNU is a fairly strong N-acid, which readily reacts with organic bases. In a previous report,[5] its alkali and alkaline earth metal salts were successfully prepared in water. Reactions of DNU with hydrazine or hydroxylamine give a substitution product rather than simple salts. Ethanol is not recommended as a solvent for DNU since the reaction may form *N*-nitrocarbamates. In our hands, acetonitrile was the most suitable solvent for reactions of DNU to form organic salts. Although some organic bases, *e.g.* 3,4,5-triamino-1,2,4-triazole, are slightly soluble in CH_3CN, reaction of DNU in CH_3CN solution for an extended time normally gave the desired mono salt as a precipitate with good purity based on elemental analysis. Although, under all conditions tried, we were not successful in synthesizing bianionic salts even when a two-fold excess of base was used, this work is continuing. Some of the mono salts can be prepared in water, but in lower yields than in CH_3CN as a solvent. For example, when DNU and 1,2,4-triazole or 3-amino-2,4-triazole were mixed in 1 : 1 or 1 : 2 ratio in water, the mono salts were immediately crystallized. The structure of **2a** (triazolium dinitrourea) is shown in Fig. 3(a). This compound is also chiral and again the absolute configuration could not be determined reliably. The deprotonation of the DNU has led to an asymmetry in the bond lengths with a contraction of N8–N9 to 1.321 (2) Å (1.394(2) Å in neutral DNU) and a 0.02–0.05 Å lengthening of the N–O bonds indicating delocalization of the anionic charge. The addition of the cation leads to significant hydrogen bonding in the extended structure shown in Fig. 3(b) (N2–H2...O11 synthon, N4–H4...O6 synthon N12–H12···O6 synthon as well as cation–cation interactions *e.g.*, N2–H2···N1). This leads to a structure that is almost as closely packed as the neutral DNU with a relatively high density 1.868 g cm^{-3} at 90 K.

Physical properties of DNU salts

As observed previously, DNU itself began to lose weight at about 90 °C, and completely decomposes at 110 °C.[3] After forming salts, the thermal stability was greatly improved. For example, the DNU salts of **2e** and **2g** were thermally stable to 180 °C. Density is one of the most important properties of energetic materials. From Table 2, it can be seen that triazolium based DNU salts exhibit higher densities than other species. Normally, when a dense compound acts as an anion, the density of the corresponding salt will decrease by 0.2 g cm^{-3} or more. Most recently, we established volume parameters to predict the density of energetic salts.[23] Based on these parameters, the volume of DNU anion was estimated at 137 Å^3. The predicted densities are also listed in Table 2 which are reasonably close to the experimental values providing that

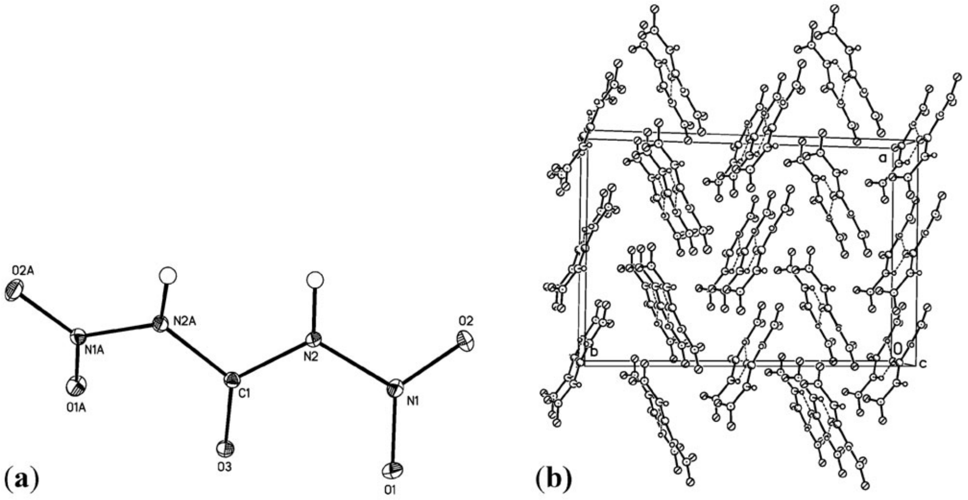


Fig. 2 (a) Displacement ellipsoid (30%) plot of DNU (**1**) with hydrogen atoms (arbitrary spheres) shown. (b) Ball-and-stick packing diagram showing alternating hydrogen bonded stacks parallel to the *c* axis indicated by dashed lines.

the volumes of triazolium salts were corrected by −8 Å^3 to account for strong hydrogen bonds. Normally materials with strong hydrogen bonds have low solubility in common solvents; this is also true for DNU salts. As a matter of fact, most of the DNU salts are slightly soluble in water due to strong hydrogen bonding. As demonstrated, some triazolium salts did have unexpectedly high densities, but very few imidazolium salt or guanidinium salts would have much higher densities than the predicted values based on our volume parameters. In other words, triazolium could be the candidate cation of choice to form high density salts with oxygen-rich anions.

Heats of formation ($\Delta_f H^\circ_{298}$) of DNU and DNU anions were computed using the G3MP2 method[24] in the Gaussian03 program suite,[25] based on the isodesmic reactions below (Scheme 2):

Gas phase heats of formation ($\Delta_f H^\circ_{298}$) for the reference molecules, *e.g.*, urea, HNO_2, NH_2NH_2 and NH_3, NH_2^- are -235.5 ± 1.2 kJ mol^{-1}, -76.73 kJ mol^{-1}, 95.35 kJ mol^{-1}, -45.94 ± 0.35 kJ mol^{-1}, 111.78 ± 0.42 kJ mol^{-1}, which are taken from NIST webbook.[26] Accordingly, $\Delta_f H^\circ_{298}$ of DNU, DNU$^-$ and DNU^{2-} in the gas phase were calculated to be 24.88, −198.46 and 31.38 kJ mol^{-1}, respectively. Using 20 kcal mol^{-1} as the widely-accepted heat of sublimation for DNU, the estimated $\Delta_f H^\circ_{298}$ of DNU in the solid state is −58.8 kJ mol^{-1}. The detonation pressure and detonation velocity of DNU was thus calculated using Cheetah 4.0 as 36.1 GPa and 8861 m s^{-1}, which compare favorably with RDX (P = 34.4 GPa, D = 8750 m s^{-1}).

The heats of formation of the triazolium cations were also computed with isodesmic reactions using G3 [27] or G3MP2 method with 1,2,4-triazolium as reference whose heat of formation in the gas phase is known as 836.78 kJ mol^{-1}.

The heats of formation of 3-amino-1,2,4-triazolium, 4-amino-1,2,4-triazolium, 3,5-diamino-1,2,4-triazolium and 3,4,5-triamino-1,2,4-triazolium were calculated to be 799.41, 942.70, 763.99, 877.55 kJ mol^{-1}, respectively. The incremental contribution of each additional N–NH_2 is 110 kJ mol^{-1}, while

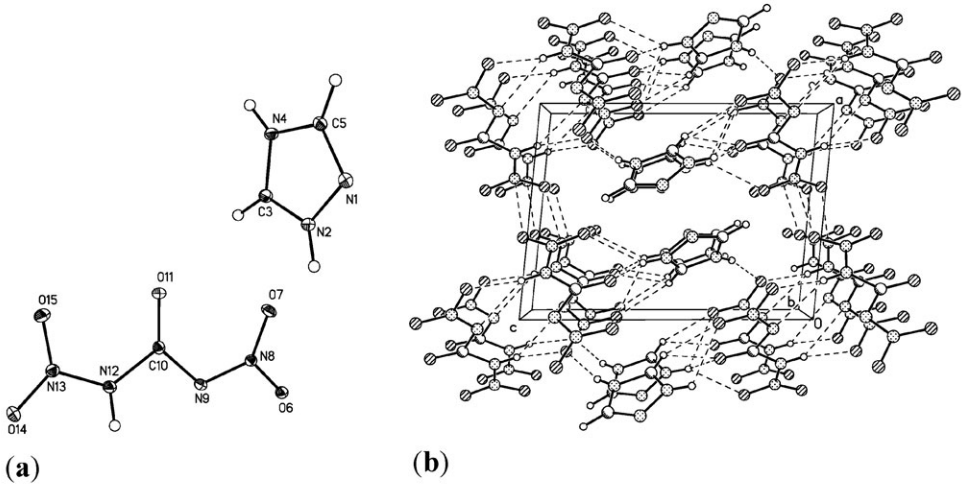


Fig. 3 (a) Displacement ellipsoid plot of **2a** with hydrogen atoms shown. (b) Ball and stick packing diagram of **2a** viewed down the *b* axis. Hydrogen bonding indicated by dashed lines.

Table 2 Melting points, densities, heat of formation ($\Delta_f H^\circ_{298}$) and detonation properties of DNU salts[a,b,c]

Compd	Mp/°C	Density/g cm^{-3} Exptl.	Density/g cm^{-3} Calc.	$\Delta_f H^\circ_{298}$ (cation)	$\Delta_f H^\circ_{298}$ (anion)	ΔH_L	$\Delta_f H^\circ_{298}$	P/GPa	D/m s^{-1}
1	90	1.98	1.98	—	—	—	−58.8	36.1	8861
2a	122	1.83	1.80[d]	836.78[e]	−198.46	510.72	127.6	33.8	8648
2b	148	1.80	1.79[d]	799.41[f]	−198.46	499.78	101.17	32.2	8568
2c	110	1.86	1.81[d]	942.70[f]	−198.46	504.08	240.16	36.4	8905
2d	157	1.85	1.78[d]	763.99[f]	−198.46	495.28	70.25	35.1	8881
2e	182	1.75	1.79[d]	877.55[g]	−198.46	480.85	198.24	31.0	8609
2f	105	1.68	1.68	720.18[e]	−198.46	500.01	21.71	23.8	7681
2g	179	1.73	1.73	1903.55[h]	−198.46	1398.48	108.15	28.2	8244
2h	148	1.67	1.69	563.74[f]	−198.46	510.30	−145.02	26.2	8240
2i	128	1.73	1.71	660.31[f]	−198.46	506.24	−44.39	29.8	8676
2j	151	1.65	1.68	799.10[i]	−198.46	462.35	138.29	21.3	7715
2k	110	1.73	1.71	1630.5[f]	−198.46	1514.11	−280.53	28.85	8507
2l	105	1.75[j]	1.76	630.54[e]	−198.46	542.24	−110.16	32.3	9051
2m[k]	135	1.70[j]	1.61	630.54[e]	31.38	1585.77	−293.31	31.1	9016

[a] $\Delta_f H^\circ_{298}$, ΔH_L (lattice energy) kJ mol^{-1}. [b] Lattice energy (ΔH_L)—estimated according to ref. 27. [c] Detonation pressure (P), detonation velocity (D)—calculated using Cheetah 4.0. [d] Volume of the salts were corrected by −8 Å, for strong hydrogen bonds, see ref. 23. [e] NIST web book, ref. 26. [f] Calculated value using G3 method. [g] Calculated value using G3MP2 method. [h] From ref. 18*k*. [i] From ref. 18*i*. [j] From ref. 5. [k] $(NH_4^+)_2DNU^{2-}$.

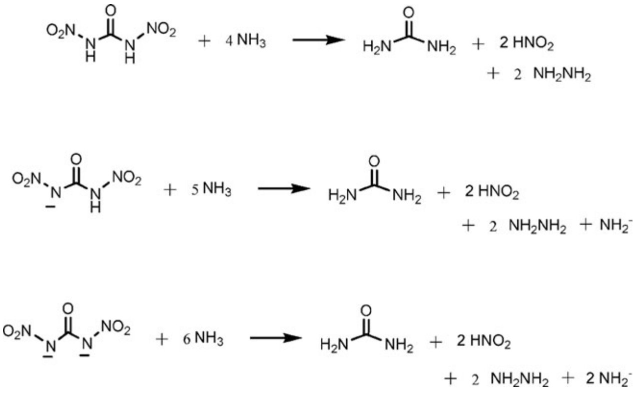
each additional C–NH_2 accounts for a decrease in heat of formation by 36 kJ mol^{-1}. Salts **2c** and **2d** show detonation properties similar to those of DNU. It is notable that the mono ammonium salt of DNU (**2l**) (9051 m s^{-1}) exhibits the highest detonation velocity among the current salts tested, which is similar to that of HMX (9100 m s^{-1}). This is similar to the bis-ammonium salt of DNU (**2m**), although **2m** has a lower heat of formation and a more negative oxygen balance. This apparently benefits from its higher density than predicted (Scheme 3).

Experimental

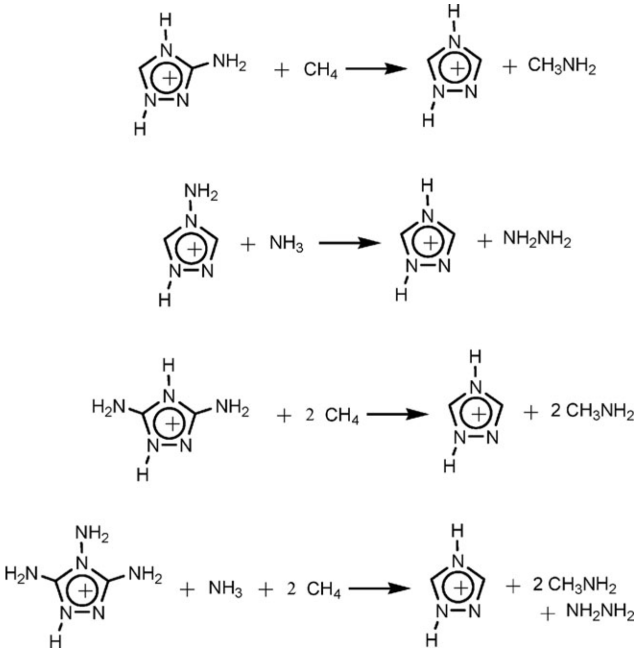
CAUTION: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged!

General methods

^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, using DMSO-d_6 as solvent unless otherwise indicated. Chemical shifts are reported relative to Me_4Si. The melting and decomposition points were obtained on a differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of 10 °C min^{-1}, respectively. Densities of solid salts were obtained at room temperature by employing a Micromeritics Accupyc1330 gas pycnometer. Elemental analyses were determined using an Exeter CE-440 elemental analyzer.



Scheme 2 Isodesmic reactions for DNU and DNU anions.



Scheme 3 Isodesmic reactions for triazolium cations.

X-Ray crystallography

Crystals of compounds DNU, **1**, (**2a**) were removed from the flask, a suitable crystal was selected and attached to a glass fiber, and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device.

Data were measured using omega scans 0.5(0.3)° per frame for 30 s for both. A total of 1464 (2400) frames were collected with a final resolution of 0.71 (0.83) Å. Cell parameters were retrieved using APEX2 (SMART) software[28] and refined using the INTEGRATE module (SAINT Plus)[29] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINT Plus software. Absorption corrections were applied using multi-scan absorption correction in the SCALE module in APEX2 (SADABS).[30] The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.[31] Structure were solved in the space group *Fdd*2 for **1** and $P2_1$ for **2a** by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of the polar axis to be determined and Friedel reflections were then merged for the final refinement. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1.

CCDC reference numbers 654504 and 654505.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712417a

Synthesis of dinitrourea (DNU, 1)

DNU was synthesized according to the literature.[3] Urea (3.0 g) was added in portions to a mixture of 6 mL H_2SO_4 (98%) and 8 mL HNO_3 (100%, prepared from H_2SO_4 and $NaNO_3$). After stirring for 3 h at room temperature, a white precipitate was collected and washed with trifluoroacetic acid (20 mL × 4), and dried under vacuum. 2.5 g, yield 40%. ^{1}H NMR (CD_3CN) δ: 11.48 (br s, 2H). ^{13}C NMR (CD_3CN) δ 142.3. MS (EI-solid probe): 150 (M^+).

General synthesis procedure for DNU salts

To a DNU (1.2 mmol) solution in 5 mL CH_3CN, was added 1 mmol of triazole, 3-aminotriazole, 4-aminotriazole, 3,5-diaminotriazole, 3,4,5-triaminotriazole, imidazole, guanidinium bicarbonate or hexamethylenetetrazine or 0.5 mmol of 3,6-diguanidine-1,2,4,5-tetrazine, aminoguanidinium carbonate, or ethylenediamine (0.5 mmol), respectively. After stirring at room temperature for 3–12 h, the white precipitate was filtered off and washed with CH_3CN (3 mL × 3), diethyl ether (3 mL × 3) and dried under vacuum.

2a. ^{1}H NMR δ: 9.24 (s, 2H). ^{13}C NMR δ 143.7, 153.2. Calc. for $C_3H_5N_7O_5$: C, 16.44; H, 2.30; N, 44.75. Found: C, 16.33; H, 2.16; N, 44.37%.

2b. ^{1}H NMR δ: 8.23 (s, 1H). ^{13}C NMR δ 139.6, 151.1, 153.9. Calc. for $C_3H_6N_8O_5$: C, 15.39; H, 2.58; N, 47.86. Found: C, 15.41; H, 2.38; N, 47.76%.

2c. ^{1}H NMR δ: 9.46 (s, 2H). ^{13}C NMR δ 144.1, 153.4. Calc. for $C_3H_6N_8O_5$: C, 15.39; H, 2.58; N, 47.86. Found: C, 15.62; H, 2.36; N, 48.05%.

2d. ^{13}C NMR δ 144.1, 151.5, 154.0. Calc. for $C_3H_7N_9O_5$: C, 14.46; H, 2.83; N, 50.60. Found: C, 14.40; H, 2.60; N, 50.45%.

2e. ^{1}H NMR δ: 5.55 (s, 2H), 7.00 (s, 4H). ^{13}C NMR δ 150.0, 153.9. Calc. for $C_3H_8N_{10}O_5$: C, 13.64; H, 3.05; N, 53.02. Found: C, 13.79; H, 2.88; N, 52.42%.

2f. ^{1}H NMR δ: 9.02 (s, 1H), 7.63 (s, 2H). ^{13}C NMR δ 119.5, 134.5, 154.0. Calc. for $C_4H_6N_6O_5$: C, 22.03; H, 2.77; N, 38.53. Found: C, 22.09; H, 2.56; N, 38.25%.

2g. ^{1}H NMR δ: 8.15 (s). ^{13}C NMR δ 153.7, 154.2, 158.5. Calc. for $C_6H_{12}N_{18}O_{10}$: C, 14.52; H, 2.44; N, 50.80. Found: C, 14.79; H, 2.26; N, 50.31%.

2h. ^{1}H NMR δ: 7.00 (s). ^{13}C NMR δ 156.7, 158.2. Calc. for $C_2H_7N_7O_5$: C, 11.49; H, 3.37; N, 46.89. Found: C, 11.76; H, 3.30; N, 46.71%.

2i. ^{1}H NMR δ: 5.54 (br s, 2 H), 6.76 (br s, 2 H), 7.14 (br s, 2 H), 8.55 (br s, 1 H), ^{13}C NMR δ 154.1, 158.9. Calc. for $C_2H_8N_8O_5$: C, 10.72; H, 3.60; N, 49.99. Found: C, 10.84; H, 3.53; N, 49.33%.

2j. ^{1}H NMR δ: 4.81 (s, 12H). ^{13}C NMR δ 71.4, 153.9. Calc. for $C_7H_{14}N_8O_5 \cdot 0.5H_2O$: C, 28.10; H, 5.05; N, 37.45. Found: C, 28.04; H, 4.66; N, 37.50%.

2k. ^{1}H NMR δ: 3.06 (s, 4H), 9.16 (br s, 6H). ^{13}C NMR δ 36.7, 154.1. Calc. for $C_4H_{12}N_{10}O_{10}$: C, 13.34; H, 3.36; N, 38.89. Found: C, 13.33; H, 3.25; N, 39.13%.

Conclusions

In conclusion, a variety of new energetic salts of DNU were synthesized and characterized. The structure of DNU was established using X-ray single-crystal diffraction. DNU and derivatives of 1,2,4-triazolium show high density (1.75–1.86 g cm^{-3}) as result of strong hydrogen bonding. Most of the DNU salts exhibit detonation pressures (>30 GPa) and detonation velocities comparable to RDX. To design salts with the most attractive energetic properties, the cation and anion should be carefully selected to deliberately form strong inter- and/or intra-molecular hydrogen bonds which in turn enhances the density and concomitantly the detonation characteristics.

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