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Synthesis and Characterization of New Energetic Nitroformate Salts

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New energetic nitroformate salts that contain high-nitrogen cations were synthesized by taking advantage of the relatively high acidity of nitroform. All of the new salts have been characterized by elemental, spectral, and thermal analyses. Single-crystal X-ray analysis of **2** shows that it is a co-crystal of a neutral 4-amino-1,2,4-triazole molecule with the 4-amino-1,2,4-triazolium nitroformate ion pair. The presence of the neutral molecule appears to lend stability to the salt. The structure of 3,6-diguanidino-1,2,4,5-tetrazinium nitroformate (**10**) was also confirmed by single-crystal X-ray analysis. Theoretical performance calculations indicate that these materials have properties which compare favorably with hydrazinium nitroformate, TNT and Tetryl suggesting potential applications as eco-friendly oxidizers.

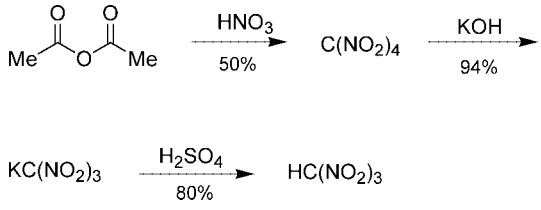
Introduction

On the basis of their special properties such as lower vapor pressures and higher densities than their atomically similar non-ionic analogues, the synthesis of energetic salts as a unique class of high energetic materials has attracted considerable interest over the past decade.[1] Recently, the syntheses of new members of heterocyclic-based energetic, low-melting salts were reported.[2] Some of them display attractive energetic properties including high positive heats of formation and high density, e.g., the salt of 3-amino-6-(nitroamino)tetrazine (ANAT) with 3,6-diguanidinotetrazine exhibits a heat of formation of +1089 kJ mol^{-1}.[2a] Due to its high oxygen content and labile hydrogen atom which facilitates the preparation of nitroformate derivatives, nitroform (trinitromethane) is a very valuable compound for use in the preparation of ingredients with good explosive and propellant properties. A number of nitroform derivatives including those with potassium, silver, pyridinium, piperidinium, ammonium, guanidinium, aminoguanidinium, diaminoguanidinium, triaminoguanidinium, and hydrazinium cations have been reported.[3] Among them, hydrazinium nitroformate (HNF) has received considerable attention as an effective oxidizer.[4]

High-energy solid oxygen oxidizers which possess useful propellant properties such as high density, good thermal stability and high impact resistance continue to be sought. Ammonium nitrate (AN) and ammonium perchlorate (AP) are two oxidizers widely used in military and civilian applications. HNF has a higher heat of formation than AP (ΔH_f = –71 kJ mol^{-1} compared to –292.88 kJ mol^{-1}), is relatively dense (1.86 g cm^{-3}) and is more environmentally friendly making it a suitable substitute. Because of its rather high thermal stability (T_d = 123 °C),[4c] HNF is in the minority relative to most nitroform salts which often decompose rapidly at ≤25 °C. However, hydrazine hydrate, the precursor to HNF, is a probable human carcinogen. Therefore, it was worthwhile to attempt to design benign energetic salts with trinitromethanide as the anion. With respect to this need, we have prepared several high-nitrogen energetic salts with the highly oxidizing trinitromethanide anion, two of which appear to exhibit considerable promise.

Results and Discussion

The key synthon, nitroform (NF), was prepared from acetic anhydride through a three-step process in 38% overall yield (Scheme 1)[5] (m.p. 22 °C; reported m.p. 15–26 °C mainly due to the degree of purity of the product)[4c,6] (see Supporting Information).



Scheme 1.

Due to the high acidity of nitroform (pK_a = 0),[4c] which is comparable to mineral acids, a series of nitrogen-rich compounds were protonated in methanol or water at 25 °C or below (Scheme 2). All of the nitroform salts **1**, **3**–**11** are formed in nearly quantitative yields and in high purity.

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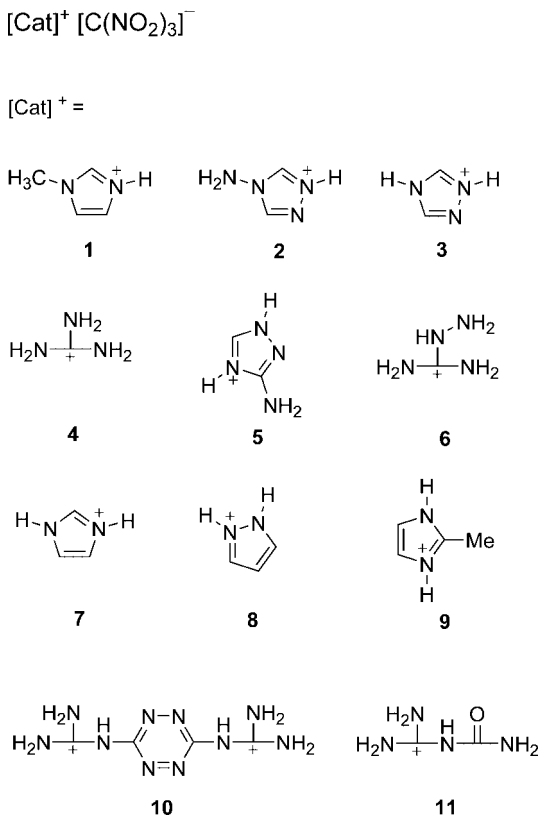
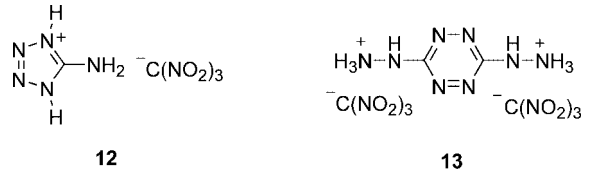


Scheme 2.

While attempting to synthesize 4-amino-1,2,4-triazolium nitroformate, the product which was obtained after recrystallization from methanol and diethyl ether was found to be molecular 4-amino-1,2,4-triazole combined with the 4-amino-1,2,4-triazolium nitroformate in a novel co-crystal **2**. The same product was obtained even after a prolonged reaction time (36 h) or by increasing the equivalent ratio of nitroform from 1 to 5 and reaction temperature from 25 °C to 50 °C. Using water as solvent did not affect the results. However, the expected 1:1 salt **5** was obtained when the 3-amino isomer, 3-amino-1,2,4-triazole, and nitroform were reacted. Guanylurea nitroformate (**11**) was synthesized by reaction of guanylurea carbonate with nitroform in methanol. Meanwhile, all attempts to isolate the corresponding nitroformate salts with 5-amino-1*H*-tetrazole (**12**) and 3,6-dihydrazinotetrazine (**13**) were unsuccessful due to their extremely low thermal stability. The reaction mixture foamed dramatically even at 0 °C which suggested that the desired product decomposed immediately (Scheme 3).



Scheme 3.

All the new salts, namely, 1-methylimidazolium, 3-amino-1,2,4-triazolium, 1,2,4-triazolium, guanidinium, 4-amino-1,2,4-triazolium, aminoguanidinium, imidazolium, pyrazolium, 2-methylimidazolium, 3,6-diguanidino-1,2,4,5-tetrazinium and *N*-guanylurea nitroformate (**1**–**11**) were characterized by IR, and ^{1}H and ^{13}C NMR spectral and elemental analyses. The IR spectra of these salts exhibit absorption bands in the range 1510–1590 cm^{-1} which are attributed to the presence of nitro groups. The several main absorption bands in the range 3100–3430 cm^{-1} can be assigned to the N–H bonds. It was not possible to locate the ^{13}C NMR signal of the nitroformate anion in **1**–**11**.

Crystals suitable for single-crystal X-ray analysis were obtained by crystallization from methanol and diethyl ether for **2** and water for **10**. The structure of **2** (Figure 1) consists of a co-crystal of a neutral 4-amino-1,2,4-triazole with the 4-amino-1,2,4-triazolium nitroformate ion pair. The tetrahedral geometry and bond length [1.412(1) Å] of the amino group of the triazolium cation indicates little interaction by the N1 lone pair and the triazolium ring pi system, similar to other triazolium species.[2b,7] However, there are many strong hydrogen bonds which stabilize this structure and assist with charge delocalization. The extended structure of

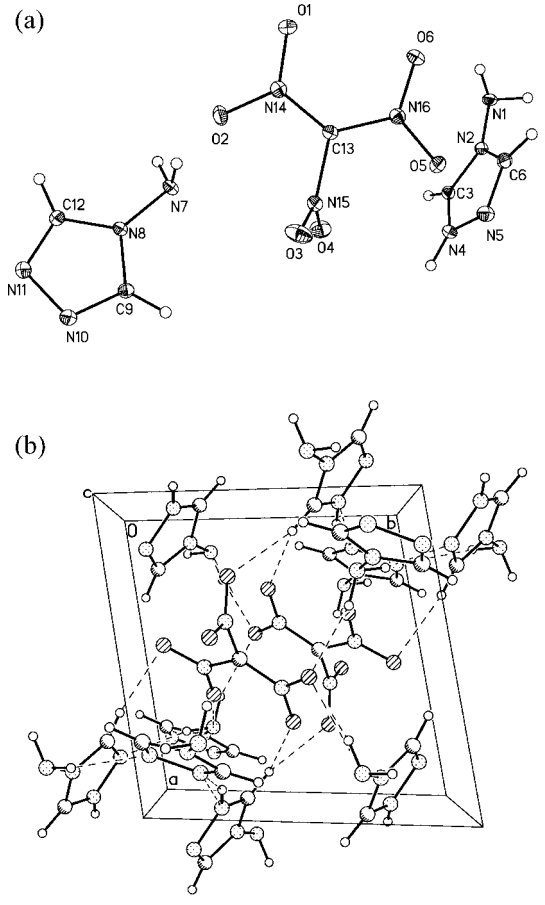


Figure 1. (a) Thermal ellipsoid plot (30%) and labeling scheme for 4-amino-1,2,4-triazolium nitroformate (**2**). Hydrogen atoms included but are unlabelled for clarity. (b) Ball and stick packing diagram of **2** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonding.

2 (Figure 1, b) shows some of these strong hydrogen bonds and indicates the layer structure formed by alternating nitroformate anions and cationic triazolium/neutral triazole. The triazolium/neutral triazole pair hydrogen bond into an oblique square which stacks to form a four-sided channel with an approximate diameter of 3.8 Å. Although an anhydrous salt of **10** could be obtained by dehydration in vacuo at room temperature (confirmed by elemental analyses), the structure of **10** (Figure 2) is a dihydrate and consists of a 3,6-diguanidino-1,2,4,5-tetrazinium dication with two nitroformate anions.

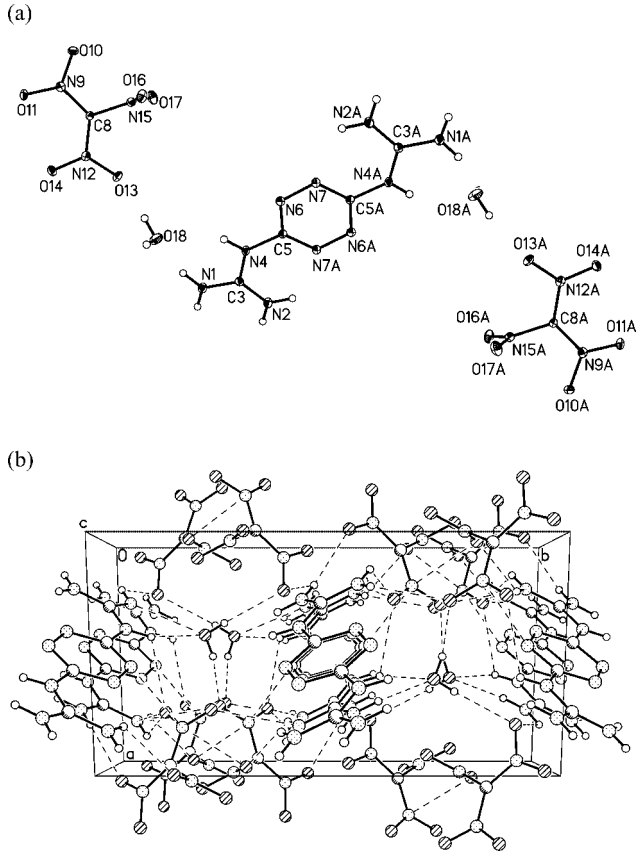


Figure 2. (a) Thermal ellipsoid plot (30%) and labeling scheme for 3,6-diguanidino-1,2,4,5-tetrazinium nitroformate (**10**). Hydrogen atoms included but are unlabelled for clarity. (b) Ball and stick packing diagram of **10** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonding.

In this structure, the guanidine moieties are planar with an 8.7° dihedral angle to the central tetrazinium ring. This indicates a stabilization of the cation via delocalization of the charge over the entire diguanidino tetrazinium moiety. The extended structure also forms a strongly hydrogen-bonded network with alternating anionic nitroformate/water and cationic tetrazinium layers parallel to the *a* axis (Figure 2, b). There are few known nitroformate structures.[7a,8] In **2** and **10**, one nitro group is ca. 73° and 85° degrees, respectively, to the main plane of the anion. This angle varies in the other published structures from planar[8b] to 90°.[8d]

Densities and thermochemical data for **1**–**11** are summarized in Table 1. DSC and TGA were used to evaluate the relative thermal stabilities of **1**–**11** and are measured under comparable conditions. In the DSC thermograms, most of the salts (**1**, **3**–**11**) decomposed at their melting points except for **2** which melted sharply at 92 °C. The results from DSC are consistent with those obtained using TGA. The decomposition temperatures of **1**–**11** occur over the range of 74–167 °C with **2** displaying the highest decomposition temperature (167 °C). The results indicate that the neutral 4-amino-1,2,4-triazole contained in the 4-amino-1,2,4-triazolium nitroformate crystal may have a stabilizing effect on the product. Comparison of guanylurea nitroformate (**11**) with guanylurea dinitramide (FOX-12),[9] showed that the stability of **11** is slightly lower than FOX-12 (T_d = 153 °C vs. 216 °C), but they have essentially the same density, detonation pressure and detonation velocity (Table 2). The low decomposition temperature of nitroform salts **1**, **3**–**11** and HNF (T_d = 120–153 °C) confirmed further that the thermal stability of compounds with the trinitromethanide anion is low.

Table 1. Densities and thermochemical results for nitroformate salts at 298.15 K.

Compd.	d[a]	T_d[b]	OB[c]	$\Delta_f H_m$[d]	I_{sp}[e]	P[f]	D[g]
1	1.60	83	–51.48	–91.7	222.1	22.1	7399
2	1.62	167	–17.01	163.5	267.6	26.6	8079
3	1.70	90	–14.54	47.6	262.3	28.3	8261
4	1.79	126	–7.62	–233.7	251.5	32.4	8984
5	1.74	74	–17.01	24.4	255.2	28.6	8365
6	1.80	107	–10.66	–124.5	257.0	33.9	9145
7	1.77	104	–32.86	–81.8	240.5	27.5	7977
8	1.63	86	–32.86	40.5	253.9	23.9	7582
9	1.53	98	–51.48	–120.1	218.9	19.6	7117
10	1.79	100	–16.06	207.6	256.6	31.0	8660
11	1.74	153	–15.80	–421.9	228.5	26.0	8174

[a] Density [g cm^{-3}]. [b] Decomposition temperature (°C). [c] OB = Oxygen balance (%) for $C_aH_bO_cN_d$: 1600 ($c - 2a - b/2$)/MW, MW = molecular weight of salt. [d] Heat of formation [kJ mol^{-1}]. [e] Specific impulse (s). [f] Detonation pressure (GPa). [g] Detonation velocity (m s^{-1}).

Table 2. Comparison of salts **2** and **10** with conventional explosives.[a]

Compound	MW	OB [%]	D [m/s]	P [GPa]	d [g/cm^3]
HNF	183	+13.1	8902	46.9	1.86
RDX	222	–21.61	8800	36.5	1.77
TNT	227	–73.96	6660	19.3	1.66
Tetryl	287	–47.35	7770	27.3	1.75
FOX-12	209	–19.1	8210	25.7	1.75
2	235	–17.01	8079	26.6	1.69
10	498	–16.06	8660	31.0	1.79

[a] Ref.[4c], ref.[9] for FOX-12.

As one of the important physical properties of energetic salts, the densities of **1**–**10** were measured by using helium displacement methods to yield results shown in Table 1. All of the compounds had densities > 1.50 g/cm^3 with **10** exhibiting a density of 1.79 g/cm^3 which is comparable with HNF (1.86 g/cm^3). The performance of a high explosive is

measured by its detonation velocity, vD (m/s), detonation pressure, P (Gpa), and specific impulse I_{sp} (s).[10] These parameters are directly related to oxygen balance (OB), density, and heat of formation. The detonation pressure and velocity (based on traditional Chapman–Jouget thermodynamic detonation theory) and specific impulse (I_{sp}) were obtained by using Cheetah 4.0 (Table 1).[11]

For the compounds **1**–**11** the calculated detonation pressures lie in the range between P = 19.6 GPa (**9**) and P = 33.9 GPa (**6**). Detonation velocities are distributed from D = 7230 m s^{-1} (**8**) to D = 9145 m s^{-1} (**6**). Substituents on the nitrogen-containing heterocycle lower the density and detonation performance of the corresponding nitroform salts (**2** to **3**, **1** to **7**). Aminoguanidinium nitroformate (**6**) has the highest density and best performance among these salts; however, it decomposes within 36 h at 25 °C with loss of color. The salts **2** and **10** show the best stability being storable at 25 °C for several weeks. In addition, the performance potential of salts **2** and **10** are superior to the conventional explosives TNT and Tetryl as shown in Table 2.

Conclusions

In conclusion, several energetic salts with the nitroformate anion have been synthesized and characterized. The neutral molecule contained in the crystalline salt **2** exhibits a stabilizing effect on the corresponding ion pair. This may offer a new way to stabilize energetic salts by designing co-crystals. In addition, thermal computations indicate that the performance potentials of **2** and **10** are better than the conventional explosives, TNT and Tetryl, which suggests their potential as eco-friendly oxidizers.

Experimental Section

Caution: Although none of the compounds described herein has exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices because their shock and impact sensitivities have not been determined. All nitroform salts should be stored at lower temperatures (–18 °C) to preclude decomposition.

General Methods: ^{1}H and ^{13}C NMR spectra were recorded with a 300-MHz NMR spectrometer operating at 300.13, and 75.48 MHz, respectively, using CD_3CN as solvent unless otherwise indicated. Chemical shifts were reported relative to Me_4Si. The melting and decomposition points were recorded with a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA) at a scan rate of 10 °C/min, respectively. IR spectra were recorded using KBr pellets for solids. Densities were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained by with a CE-440 elemental analyzer (EAI Exeter Analytical).

Computational Details: Computations were performed with the Gaussian03 (Revision D.01) suite of programs.[12] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses are carried out using B3-LYP functional with 6-31+G** basis set,[13] and single energy points were calculated at the MP_2(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

On the basis of Born–Haber energy cycles, the heat of formation of an ionic salt can be simplified by the formula:

$\Delta H_f°$(ionic salt, 298 K) = $\Delta H_f°$(cation, 298 K) + $\Delta H_f°$(anion, 298 K) – ΔH_L

where ΔH_L is the lattice energy of the ionic salts which could be predicted by the formula suggested by Jenkins et al.[14] as:

$\Delta H_L = U_{POT} + [p(nM/2 - 2) + q(nX/2 - 2)]RT$ (**A**)

where n_M and n_X depend on the nature of the ions M_p^+ and Xq^-, respectively, and are equal to **3** for monatomic ions, **5** for linear polyatomic ions, and **6** for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} (Equation **B**) has the form:

U_{POT}/kJ mol^{-1} = γ $(\rho_m/M_m)^{1/3}$ + δ (**B**)

where ρ_m/g cm^{-3} is the density, M_m is the chemical formula mass of the ionic material, values for g and the coefficients γ/kJ mol^{-1} cm and δ/kJ mol^{-1} were taken from ref.[14]

The remaining task is to determine the heat of formation of the cation, which is computed using the method of isodesmic reactions.[2c] The enthalpy of reaction ($\Delta H_r°_{298}$) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero point energies, and other thermal factors. Thus, the heat of formation of the cation being investigated can be readily extracted.

With the value of the heats of formation and density of energetic salts, the expected detonation pressures (P) and detonation velocities (D) were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory.[11a]

X-ray Analyses: Crystals of compound **2** (**10**) were removed from the flask, a suitable crystal selected, attached to a glass fiber, and data were collected at 90(2) K with a Bruker/Siemens SMART APEX instrument (Mo-K_α radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using omega scans 0.3° (0.5°) per frame for 5 (20) s, and a full sphere of data was collected. A total of 2400 (1065) frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[15] (APEX2)[16] software for **2** (**10**), and refined using SAINTPlus[17] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINTPlus software. Absorption corrections were applied using SADABS.[18] The structures were solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[19] Structure were solved in the space group $P\bar{1}$ and $P2_1/c$ for compounds **2** and **10**, respectively, by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined independently for the amino groups in **2**. No decomposition was observed during data collection. CCDC-628775 and -628776 contain the supplementary crystallographic data for **2** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Nitroform: The synthesis of nitroform is carried out as described in the literature (Supporting Information).[5]

General Procedure for the Preparation of Nitroformate Salts. 1-Methylimidazolium Nitroformate (1): A solution of nitroform (151 mg, 1.0 mmol) in methanol (2 mL) was slowly added to a solution of 1-methylimidazole (82 mg, 1.0 mmol) in methanol (2 mL) at 25 °C with stirring. After stirring for 3 h at room temperature,

the solvent was removed in vacuo to leave the desired product **1** (233 mg, 96%) as a yellow crystalline solid. IR (KBr): $\tilde{\nu}$ = 3415, 3150, 1584, 1535, 1484, 1277, 1153, 805 cm^{-1}. ^1H NMR: δ = 8.48 (s, 1 H), 7.39 (s, 2 H), 3.88 (s, 3 H) ppm. ^{13}C NMR: δ = 136.2, 124.2, 120.5, 36.6 ppm. $C_5H_7N_5O_6$ (233.14): calcd. C 25.76, H 3.03, N 30.04; found C 25.81, H 2.67, N 30.05.

4-Amino-1,2,4-triazolium Nitroformate (2): IR (KBr): $\tilde{\nu}$ = 3418, 3131, 1628, 1532, 1486, 1272, 1155, 617 cm^{-1}. ^1H NMR: δ = 8.68 (s, 4 H), 7.42 (br., 4 H) ppm. ^{13}C NMR: δ = 145.3, 151.2 ppm. $C_5H_9N_{11}O_6$ (319.07): calcd. C 18.81, H 2.84, N 48.27; found C 18.88, H 2.71, N 48.32.

1,2,4-Triazolium Nitroformate (3): IR (KBr): $\tilde{\nu}$ = 3424, 3130, 2793, 1572, 1536, 1404, 1335, 1159, 825 cm^{-1}. ^1H NMR: δ = 8.92 (br., 2 H) ppm. ^{13}C NMR: δ = 143.3, 39.8 ppm. $C_3H_4N_6O_6$ (220.11): calcd. C 16.37, H 1.83, N 38.18; found C 16.55, H 2.21, N 38.53.

Guanidinium Nitroformate (4): IR (KBr): $\tilde{\nu}$ = 3398, 1642, 1533, 1495, 1409, 1283, 868, 787 cm^{-1}. ^1H NMR: δ = 6.0 (br., 6 H) ppm. $C_2H_6N_6O_6$ (210.11): calcd. C 11.43, H 2.88, N 40.00; found C 11.49, H 2.72, N 39.27.

3-Amino-1,2,4-triazolium Nitroformate (5): IR (KBr): $\tilde{\nu}$ = 3360, 3152, 2765, 1686, 1561, 1482, 1284, 1153, 951, 785 cm^{-1}. ^1H NMR: δ = 10.12 (br., 4 H), 8.66 (s, 1 H) ppm. ^{13}C NMR: δ = 143.3 ppm. $C_3H_5N_7O_6$ (235.12): calcd. C 15.33, H 2.14, N 41.70; found C 15.44, H 1.94, N 41.72.

Aminoguanidinium Nitroformate (6): IR (KBr): $\tilde{\nu}$ = 3406, 3277, 3168, 1678, 1554, 1484, 1315, 1157, 787 cm^{-1}. ^1H NMR: δ = 7.41 (br., 1 H), 6.51 (br., 2 H), 5.92 (br., 2 H), 4.14 (br., 2 H) ppm. $C_2H_7N_7O_6$ (225.12): calcd. C 10.67, H 3.13, N 43.55; found C 10.80, H 2.87, N 43.01.

Imidizolium Nitroformate (7): IR (KBr): $\tilde{\nu}$ = 3398, 3150, 2983, 1587, 1537, 1484, 1370, 1285, 1157, 829 cm^{-1}. ^1H NMR: δ = 10.75 (br., 2 H), 8.57 (s, 1 H), 7.45 (s, 2 H) ppm. ^{13}C NMR: δ = 135.0, 120.2 ppm. $C_4H_5N_5O_6$ (219.11): calcd. C 21.93, H 2.30, N 31.96; found C 22.27, H 2.39, N 31.32.

Pyrazolium Nitroformate (8): IR (KBr): $\tilde{\nu}$ = 3131, 3061, 2839, 1763, 1561, 1391, 1245, 1040, 825 cm^{-1}. ^1H NMR: δ = 8.00 (s, 2 H), 6.65 (s, 1 H) ppm. ^{13}C NMR: δ = 135.0, 107.7 ppm. $C_4H_5N_5O_6$ (219.11): calcd. C 21.93, H 2.30, N 31.96; found C 21.88, H 2.11, N 31.83.

2-Methylimidazolium Nitroformate (9): IR (KBr): $\tilde{\nu}$ = 3403, 3121, 2993, 2721, 1625, 1537, 1483, 1269, 1157, 756 cm^{-1}. ^1H NMR: δ = 7.28 (s, 2 H), 2.61 (s, 3 H) ppm. ^{13}C NMR: δ = 119.4, 11.7 ppm. $C_5H_7N_5O_6$ (233.14): calcd. C 25.76, H 3.03, N 30.04; found C 25.54, H 2.70, N 29.86.

3,6-Diguanidino-1,2,4,5-tetrazinium Nitroformate (10): IR (KBr): $\tilde{\nu}$ = 3400, 3345, 3281, 2945, 2872, 1703, 1592, 1417, 947 cm^{-1}. ^1H NMR: δ = 7.79 (br., 10 H) ppm. ^{13}C NMR: δ = 159.6, 155.9 ppm. $C_6H_{10}N_{16}O_{12}$ (498.24): calcd. C 14.46, H 2.02, N 44.98; found C 14.26, H 2.18, N 45.64.

***N*-Guanylurea Nitroformate (11):** IR (KBr): $\tilde{\nu}$ = 3400, 3345, 3281, 2945, 2872, 1703, 1592, 1417, 947 cm^{-1}. ^1H NMR: δ = 7.29 (br., 5 H), 5.90 (br., 2 H) ppm. ^{13}C NMR: δ = 156.7, 154.7 ppm. $C_3H_7N_7O_7$ (253.13): calcd. C 14.23, H 2.79, N 38.73; found C 14.22, H 2.59, N 37.94.

Supporting Information (see also the footnote on the first page of this article): Synthesis of nitroform.

Acknowledgments

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