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Synthesis of Energetic Nitrocarbamates from Polynitro Alcohols and Their Potential as High Energetic Oxidizers

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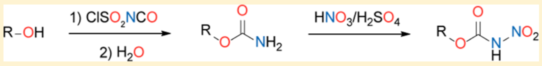
Ⓢ *Supporting Information*

ABSTRACT: A new synthesis strategy for the preparation of energetic carbamates and nitrocarbamates starting from readily available polynitro alcohols is introduced. The efficient synthesis of mainly new carbamates was performed with the reactive chlorosulfonyl isocyanate (CSI) reagent. The carbamates were nitrated using mixed acid to form the corresponding primary nitrocarbamates. The thermal stability of all synthesized compounds was studied using differential scanning calorimetry, and the energies of formation were calculated on the CBS-4 M level of theory. Detonation parameters and propulsion properties were determined with the software package EXPLO5 V6.02. Furthermore, for all new substances single-crystal X-ray diffraction studies were performed and are presented and discussed as Supporting Information.



INTRODUCTION

The chemistry of highly energetic materials is still a very active research topic, especially the issue of high energy dense oxidizers (HEDOs), which have been investigated intensively in recent years.[1] Oxidizers are compounds that release an excess of oxygen, which reacts with fuel and produce large amounts of hot gases for propulsion. An interesting but sparsely investigated energetic functionality which emerged is the primary nitrocarbamates.[1e,2] This energetic chemical moiety can be synthesized starting from polynitro alcohols. The previously described synthesis of carbamates starts with the reaction of the corresponding alcohol with phosgene to form the chloroformate, which is then further treated with ammonia; the carbamate is nitrated subsequently to the nitrocarbamate.[2a,3] In the case of 2,2,2-trinitroethanol, this synthesis route proceeds quite satisfactorily but has still some disadvantages.[1e] The hazardous handling with the highly toxic gas phosgene needs to be addressed, and the use of alkaline reagents is problematic because of the instability of polynitro alcohols in basic media.[3,4] It has been found that a much advanced versatile synthesis route of the carbamate moiety is a one-step synthesis with the reagent chlorosulfonyl isocyanate (CSI). CSI is a commercially available reagent and was discovered in Germany in 1956.[5] It consists of a sulfuryl center with two electron-withdrawing components, the chloro atom and the isocyanate group, which results in one of the most reactive isocyanates.[5a,6] The reaction with alcohols is very fast and proceeds via nucleophilic addition to the isocyanate carbon at low temperatures and without possible multiaddition prevented by the formation of a chlorosulfonylamide intermediate. This SO_2Cl group is removed by aqueous workup to form chlorosulfonate and produces the pure carbamate. In summary, the advantages of CSI are monosubstitution, fast reaction times, simple workup, and often nearly quantitative yields.

RESULTS AND DISCUSSION

Synthesis and Characterization. The carbamate of 2,2,2-trinitroethanol (**1a**) was first synthesized via the chloroformate–ammonia route.[1e] With the new methodology using the reagent chlorosulfonyl isocyanate (CSI), the 2,2,2-trinitroethyl carbamate (**2a**) is now conveniently synthesized in a one-step synthesis with a yield of 96% compared to previously 71%.[1e] Further advantages are the faster reaction time, the handling of the starting materials, and the simple workup, which leaves pure product without further purification. CSI also reacts effectively with less reactive alcohols such as 2-fluoro-2,2-dinitroethanol (**1b**). The corresponding carbamate **2b** was isolated in an almost quantitative yield of 98%; however, the synthesis of the corresponding chloroformate is quite complicated and time-consuming and can be synthesized with only 40% yield.[7] CSI also works very well with multivalent alcohols such as 2,2-dinitropropane-1,3-diol (**1c**). Scheme 1 displays the synthesis and the involved nitro alcohols. In all carbamate-forming

Scheme 1. Synthesis of Carbamates (2) and Nitrocarbamates (3) from Nitro Alcohols (1)

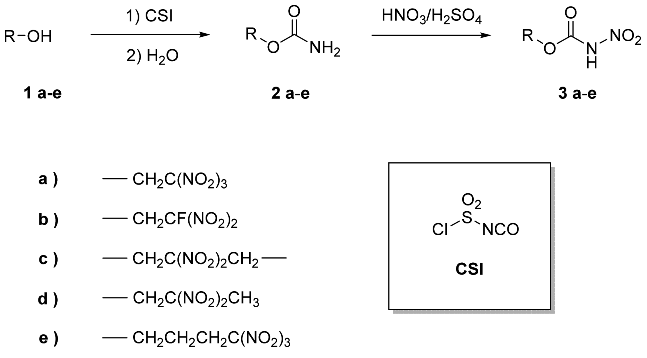


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Table 1. Physical Properties of Carbamates **2a**−**e** and Nitrocarbamates **3a**−**e**

	2a	**3a**	**2b**	**3b**	**2c**	**3c**	**2d**	**3d**	**2e**	**3e**
formula	$C_3H_4N_4O_8$	$C_3H_3N_5O_{10}$	$C_3H_4N_3O_6F$	$C_3H_3N_4O_8F$	$C_5H_8N_4O_8$	$C_5H_6N_6O_{12}$	$C_4H_7N_3O_6$	$C_4H_6N_4O_8$	$C_5H_8N_4O_8$	$C_5H_7N_5O_{10}$
FW (g mol^{-1})	224.09	269.08	197.08	242.08	252.14	342.13	193.11	238.11	252.14	297.14
T_m (onset)[a] (°C)	91	109	(liquid)	80	136	152	68	76	53	82
T_{dec} (onset)[b] (°C)	169	153	219	145	182	158	192	140	156	145
N[c] (%)	25.0	26.0	21.3	23.1	22.2	24.6	21.8	23.5	22.2	23.6
O[d] (%)	57.1	59.5	48.7	52.9	47.8	56.1	49.7	53.8	47.8	53.8
N + O[e] (%)	82.1	85.5	70.0	76.0	73.0	80.7	71.5	77.3	73.0	77.4
Ω_{CO}[f] (%)	+21.4	+32.7	+12.2	+26.4	−6.4	+18.7	+12.4	+20.2	−6.4	+8.1

[a] Onset melting (T_m) point from DSC measurements carried out at a heating rate of 5 °C min^{-1}. [b] Onset decomposition (T_{dec}) point from DSC measurements carried out at a heating rate of 5 °C min^{-1}. [c] Nitrogen content. [d] Oxygen content. [e] Combined nitrogen and oxygen content. [f] Oxygen balance assuming the formation of CO, H_2O, N_2, and HF. [g] Liquid at room temperature.

Table 2. Calculated Detonation, Combustion Parameters (Using EXPLO5 V6.02 EOS BKWG-S), and Sensitivity Data of the Energetic Carbamates **2a**−**e** and Nitrocarbamates **3a**−**e**

	2a	**3a**	**2b**	**3b**	**2c**	**3c**	**2d**	**3d**	**2e**	**3e**	**AP**
density (RT)[a]	1.82	1.72	1.58	1.92	1.69	1.76	1.57	1.73	1.63	1.66	1.95
$\Delta_f H^{\circ}$[b] (kJ mol^{-1})	−459	−366	−659	−573	−902	−709	−553	−455	−523	−428	−296
$\Delta_f U^{\circ}$[c] kJ kg^{-1})	−1961	−1277	−3257	−2284	−3480	−1986	−2759	−1816	−1977	−1347	−2433
IS[d] (J)	40	10	40	10	30	4	40	20	40	20	15
FS[e] (N)	64	96	360	360	360	240	360	360	360	360	>360
ESD[f] (J)	0.15	0.10	(liquid)	0.15	>0.20	0.10	0.20	0.20	0.20	0.20	>1.5
Q_v[g] (kJ kg^{-1})	−5286	−4456	−3922	−4342	−3260	−5088	−3779	−4839	−4547	−5184	−1422
P_{CJ}[h] (V)	302	232	211	338	196	275	186	271	221	262	158
V_{Det}[i] (m s^{-1})	8530	7704	7273	8526	7256	8157	7130	7945	7524	7858	6368
I_s[j] (s)	246	232	227	237	182	245	196	242	220	251	157
I_s (15% Al)[k] (s)	254	251	248	252	228	254	238	259	253	265	235
I_s (15%Al + binder)[l] (s)	247	261	233	248	214	244	225	243	237	249	261

[a] RT densities are recalculated from X-ray densities. [b] Heat calculated with ab initio calculations on the CBS-4 M level. [c] Energy of formation calculated with ab initio calculations on the CBS-4 M level. [d] Sensitivity toward against impact. [e] Friction. [f] Electrostatic discharge. [g] Heat of detonation. [h] Detonation pressure. [i] Detonation velocity. [j] Specific impulse I_s. [k] Specific impulse I_s with aluminum. [l] Specific impulse I_s with binder (6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile, and 2% bisphenol A ether) at 70.0 kbar chamber pressure and isobaric combustion condition (1 bar).

reactions with CSI, the carbamates were isolated as colorless pure products in high yields, often practically quantitative (see the Experimental Section).

The carbamates **2a**−**e** were converted into the nitrocarbamates **3a**−**e** by a mixture of concentrated sulfuric (96%) and fuming nitric acid (100%) (1:1). After the reaction mixture is quenched with water, it is crucial that it is immediately extracted with ethyl acetate. Subsequent recrystallization is important to obtain pure products.

All carbamates and nitrocarbamates were characterized with multinuclear NMR, vibrational (IR, Raman) spectroscopy, and mass spectrometry. Furthermore, all compounds were evaluated for their thermal stabilities with differential scanning calorimetry (DSC), and the purity grade was checked with CHN elemental analysis.

In the NMR spectra clear trends are visible. In the ^1H NMR spectra of all carbamates, the NH_2 resonance is found in the region between 7 and 5 ppm as very broad signals because of the keto−enol delocalization of the nitrogen lone pair and the restricted rotation.[1e,8] In the case of the nitrocarbamates, this NH resonance is significantly downfield shifted below 13 ppm due to increased acidity. In the ^{13}C NMR spectra, the most obvious feature is the resonance of the carbamate carbonyl group, which changes to higher field from the carbamates **2** around 155 ppm to 149 ppm for the nitrocarbamates **3** due to increased shielding by the presence of adjacent nitro groups. The $^{14/15}N$ carbamate resonances are detected around −300 ppm (broadened in ^{14}N). Upon nitration to **3**, this resonance is significantly shifted downfield to around −200 ppm. Relatively sharp signals are present for the nitro groups, and those of the nitramine units are detected at −45 to −57 ppm.

In the vibrational spectra, the characteristic strong carbonyl stretching vibration of the carbamates are found in the range of 1744 to 1712 cm^{-1} and that of the nitrocarbamates shifted to slightly higher wave numbers at 1745 to 1772 cm^{-1}. The stretching vibrations of the NH_2 and NH groups are all above 3000 cm^{-1} showing multiple peaks, whereas only one peak remains for the nitrocarbamates.[9]

The physical properties of the carbamates **2** and nitrocarbamates **3** are summarized in Table 1. The melting points of the carbamates show a trend, namely that it decreases with the increasing of the carbon backbone. The exceptions are the bivalent carbamate **2c** with the higher possibility of hydrogen bonding of the two carbamate moieties and the fluoro compound **2b**, which is a liquid and has a relatively high decomposition point of 219 °C. This tendency toward high decomposition points of 2-fluoro-2,2-dinitroethanol (**1b**) derivatives compared to those of 2,2,2-trinitroethanol (**1a**) was confirmed elsewhere,[1b,10,11] except for the nitrocarbamate **3b**. The decomposition points of the nitrocarbamates are all in the same range. The doubly functionalized compound **3c** shows the highest melting (152 °C) and decomposition point of 158 °C. Some nitrocarbamates possess an high combined nitrogen/oxygen content, such as **3a** (85.5%) and the bivalent **3c** (80.7%).

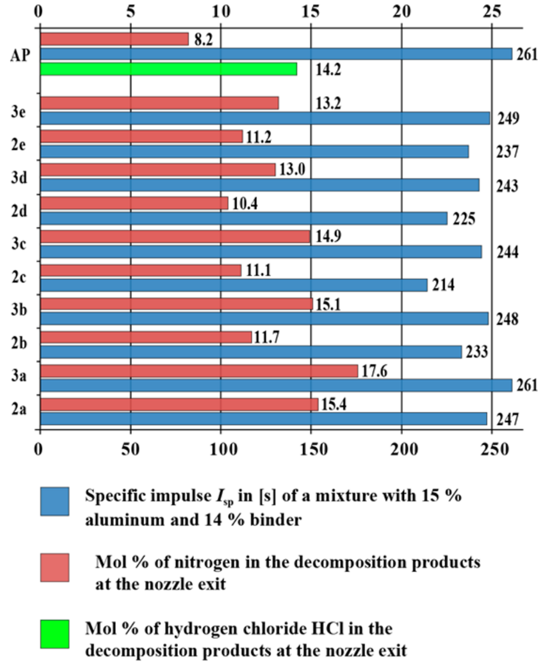
Energetic Properties. For the manipulation of energetic materials the sensitivity is very important. The sensitiveness to impact (IS) of a solid or liquid material is tested by the action of a falling mass on the sample for its decompose or explosion. The friction sensitivity (FS) is determined by rubbing a small amount between porcelain with different contact pressures.[12] All compounds show no sensitivity against friction, except the compounds with the 2,2,2-trinitroethyl unit (**2a** and **3a**), which are classified as friction sensitive. The nitrocarbamate of the diol **3c** shows the highest sensitivity of 3 J (very sensitive) against impact and is therefore just as sensitive as the common explosive pentaerythritol tetranitrate (PETN).[12] All other nitrocarbamates can be ranked as sensitive and all carbamates as less sensitive to impact.

The most important performance parameter for rocket propellants is the specific impulse I_s, which is defined as the impulse change per mass unit (kg) of the propellant mixture.[1a] The I_s depends mainly on the burning temperature in the combustion chamber and reciprocal to the average molar mass of the gaseous decomposition products (for more information, see the Supporting Information). To achieve a high combustion temperature a fuel is added to the oxidizer. Aluminum is mainly used as fuel, as it has a very high heat of combustion Δ_cH, is cheap, and it and the combustion (Al_2O_3) products are not harmful to the environment.[13] The best specific impulse with an admixture of 15% aluminum was achieved with **3e** (265 s) and is therefore much higher than the standard oxidizer ammonium perchlorate (**AP**) (235 s) (see Table 2). The standard mixture consists of **AP** (76%), aluminum (15%), and a polymeric binder (14%) results in a value for I_s of 261 s. The compound that best compares is the nitrocarbamate **3a** with an identical value of 261 s. However, not only is the absolute performance of the propellant mixture important but other properties, such as the ecological and toxicological point of view of the used compounds and the decomposition products, are important.[14] **AP** produces the toxic gas hydrogen chloride when burned, which is generated in a significant amount of 14.2% (see Scheme 2).[14] If nitrocarbamate **3a** is compared with **AP**, the nitrogen content is more than doubled, and in addition, no halogenated products were produced, which makes RADAR detection of the rocket emission more difficult.[1a]

■ CONCLUSION

A facile, two-step synthesis route for nitrocarbamates is presented by the reaction of polynitro alcohols with chlorosulfonyl isocyanate (CSI) and subsequent nitration. The carbamate-forming reaction with CSI has several advantages such as fast reaction times, simple manageable starting materials, and very high yields. The nitration to the nitrocarbamate proceeds in all cases with a mixture of nitric and sulfuric acid. All new compounds were fully characterized, including the X-ray molecular structure. The specific impulse I_s of compositions are comparable with compositions using ammonium perchlorate (AP) as oxidizer. Favorably, the burning and combustion of these compounds produces no toxic substances such as hydrogen chloride.

Scheme 2. Specific Impulse I_s and the Nitrogen/Hydrogen Chloride Content (mol %) of the Decomposition Products Calculated with EXPLO5 V.6.02



■ EXPERIMENTAL SECTION

General Information. All chemicals were used as supplied. The nitro alcohols 2,2,2-trinitroethanol,[4a] 2-fluoro-2,2-dinitroethanol,[1b] 2,2-dinitropropan-1,3-diol,[15] 2,2-dinitropropanol,[16] and 4,4,4-trinitrobutanol[17] were synthesized according to the literature. Raman spectra were recorded in a glass tube with Nd:YAG laser excitation up to 1000 mW (at 1064 nm) in the range between 400 and 4000 cm^{-1}. Infrared spectra were measured with an ATR device. All spectra were recorded at ambient temperature. NMR spectra were recorded with a 400 Hz instrument, and chemical shifts were determined with respect to external standard (Me_4Si ^1H and ^{13}C, $MeNO_2$ ^{14}N, and ^{15}N). The low-temperature (173 K) single-crystal X-ray diffraction were performed with Mo Kα radiation (λ =0.71073 Å). Data collection was performed using CRYSALIS CCD software.[18] The data reduction was carried out using CRYSALIS RED software.[19] The solution of the structure was performed by direct methods (SIR97),[20] refined by the full-matrix least-squares on F2 (SHELXL)[21] implemented in the WINGX software package,[22] and finally checked with the PLATON software.[23] All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were located in a difference Fourier map. ORTEP plots are shown with thermal ellipsoids at the 50% probability level. Melting and decomposition points were measured with a DSC with a heating rate of 5 °C min^{-1} in a temperature range of 15−300 °C. The melting points were checked by a melting point apparatus (not corrected). The sensitivity data were performed using a BAM drophammer and a BAM friction tester.[24] All ab initio calculations were carried out using the program package Gaussian 09 (Rev. A.03)[25] and visualized by GaussView 5.08.[26] Structure optimizations and frequency analyses were performed with Becke's B3 three-parameter hybrid functional using the LYP correlation functional (B3LYP). For C, H, N, and O, a correlation consistent polarized double-ζ basis set was used (cc-pVDZ). The structures were optimized with symmetry constraints, and the energy is corrected with the zero-point vibrational energy.[27] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method in order to obtain accurate values. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 starts with a HF/3-21G(d) geometry optimization, which is the initial guess for the following SCF calculation as a base energy and a final MP2/6-31+G calculation with a CBS extrapolation to correct the energy in second order. The used CBS-4 M method additionally implements a MP4(SDQ)/6-31+(d,p) calculation to approximate higher order contributions and also includes some additional empirical corrections.[28] The enthalpies of the gas-phase species were estimated according to the atomization energy method.[29] All calculations affecting the detonation parameters were carried out using the program package EXPLO5 V6.02 (EOS BKWG-S).[30] The detonation parameters were calculated at the CJ point with the aid of the steady-state detonation model using a modified Becker–Kistiakowski–Wilson equation of state for modeling the system. The CJ point is found from the Hugoniot curve of the system by its first derivative. The specific impulses were also calculated with the program package EXPLO5 V6.02 program, assuming an isobaric combustion of a composition of an oxidizer, aluminum as fuel, 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile as binder, and 2% bisphenol A as epoxy curing agent.[30b] A chamber pressure of 70.0 bar, an initial temperature of 3300 K, and an ambient pressure of 1.0 bar with frozen expansion conditions were estimated for the calculations.

CAUTION! All compounds are energetic materials with sensitivity toward heat, impact, and friction. No hazards occurred during preparation and manipulation; additional proper protective precautions (face shield, leather coat, earthened equipment and shoes, Kevlar gloves, and ear plugs) should be used when undertaking work with these compounds.

*2,2,2-Trinitroethyl Carbamate (**2a**).* 2,2,2-Trinitroethanol (**1a**) (0.76 g, 4.2 mmol) was dissolved in dry acetonitrile (10 mL) and placed in an ice bath. Chlorosulfonyl isocyanate (CSI) (0.64 g, 4.5 mmol) was added very slowly at 0 °C. The ice bath was removed, and stirring at room temperature was continued for 1.5 h. The reaction mixture was again cooled with an ice bath, water (50 mL) was added with caution, and the mixture was stirred for 10 min at room temperature. The precipitate was filtered to obtain 0.90 g (96%) colorless 2,2,2-trinitroethyl carbamate (**2a**). DSC (5 °C min^{-1}): 91–92 °C (mp range), 169 °C (onset dec). IR: (ATR, cm^{-1}): ν = 3447 (w), 3354 (w), 3302 (w), 2963 (m), 1729 (m), 1590 (s), 1441 (w), 1399 (m), 1367 (w), 1325 (m), 1300 (m), 1248 (w), 1166 (w), 1138 (w), 1105 (m), 1027 (w), 910 (w), 873 (w), 858 (w), 804 (m), 784 (m), 771 (m), 746 (w), 673 (w), 646 (w), 606 (w), 544 (m). Raman: (400 mW, cm^{-1}): ν = 3301 (4), 3003 (23), 2962 (51), 2828 (4), 1719 (17), 1629 (31), 1609 (28), 1587 (18), 1445 (17), 1404 (8), 1369 (54), 1304 (31), 1250 (15), 1171 (10), 1145 (10), 1112 (9), 1091 (9), 1027 (17), 911 (21), 878 (13), 860 (100), 802 (14), 786 (12), 745 (10), 681 (10), 646 (12), 550 (18), 426 (55), 397 (46), 378 (72), 307 (48), 266 (21), 212 (33). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ = 6.76 (s, 1H, NH_2), 6.47 (s, 1H, NH_2), 5.68 (s, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR (acetone-d_6, 100.5 MHz) δ = 154.5 (CO_2N), 125.7 ($C(NO_2)_3$), 61.8 (CH_2) ppm. ^{14}N NMR (acetone-d_6, 28.9 MHz) δ = −33 ($C(NO_2)_3$), −310 (br, NH_2) ppm. MS (DEI+) *m/e*: 225 (15) [(M + H)$^+$]. Anal. Calcd for $C_3H_4N_4O_8$: C, 16.08; H, 1.80; N, 25.00. Found: C, 15.89; H, 1.78; N, 25.12. BAM drophammer: >40 J. Friction tester: 64 N. ESD: 0.15 J (grain size <500 μm).

*2,2,2-Trinitroethyl Nitrocarbamate (**3a**).* Prepared according ref 1e.

*2-Fluoro-2,2-dinitroethyl Carbamate (**2b**).* 2-Fluoro-2,2-dinitroethanol (**2a**) (1.70 g, 11.0 mmol) was dissolved in dry acetonitrile (25 mL) and placed in an ice bath. Chlorosulfonyl isocyanate CSI (1.84 g, 13.0 mmol) was added very slowly at 0 °C. The ice bath was removed, and stirring at room temperature was continued for 1 h. The reaction mixture was again cooled with an ice bath, water (10 mL) was added with caution, and the mixture was stirred for 10 min at room temperature. The organic solvent was removed on the rotary evaporator. The aqueous solution was extracted with dichloromethane (5 × 50 mL). The combined organic phases were washed with brine (2 × 80 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure to obtain a slightly yellow oil 2.12 g (98%) of 2-fluoro-2,2-dinitroethanol carbamate (**2b**). DSC (5 °C min^{-1}): 212 °C (boil), 219 °C (onset dec). IR: (ATR, cm^{-1}): ν = 3357 (w), 2924 (w), 2260 (w), 1744 (m), 1587 (vs), 1445 (w), 1402 (w), 1352 (w), 1314 (m), 1230 (w), 1082 (m), 1003 (w), 918 (w), 878 (w), 850 (m), 798 (s), 759 (w). Raman (1064 nm, 500 mW, cm^{-1}): ν = 3353 (5), 3313 (4), 3190 (4), 3026 (13), 2971 (40), 2258 (4), 1733 (9), 1595 (24), 1435 (11), 1370 (56), 1324 (22), 1247 (8), 1127 (20), 1027 (14), 923 (10), 852 (100), 796 (8), 760 (5), 676 (7), 569 (12), 504 (14), 423 (27), 378 (26), 352 (34), 237 (20). ^{1}H NMR ($CDCl_3$, 399.8 MHz) δ: 5.42 (br, 1H, NH_2), 5.27 (br, 1H, NH_2), 5.15 (d, ^3J (H,F) = 15.9 Hz, 2H; CH_2) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100.5 MHz) δ: 154.2 (CO), 119.2 (d, ^1J (C,F) = 294.3 Hz; $C(NO_2)_2F$), 60.9 (d, ^2J (C,F) = 19.2 Hz; CH_2) ppm. ^{14}N NMR ($CDCl_3$, 28.9 MHz) δ: −25 (NO_2), −311 (NH_2) ppm. ^{19}F NMR ($CDCl_3$, 376.3 MHz) δ: −111.8 (t, br) ppm. Anal. Calcd for $C_3H_4N_3O_6F$: C, 18.28; H, 2.05; N, 21.32. Found: C, 18.52; H, 2.17; N, 20.98. MS *m/e* (EI): 198.1 [(M + H)$^+$]. BAM drophammer: 40 J. Friction tester: 360 N (liquid).

*2-Fluoro-2,2-dinitroethyl Nitrocarbamate (**3b**).* Into concentrated sulfuric acid (2 mL) was dropped fuming nitric acid (>99.5%, 2 mL) at 0 °C. To this chilled nitration mixture 2-fluoro-2,2-dinitroethyl carbamate (**2b**) (0.39 mg, 2.0 mmol) in small portions was added. The solution was stirred for 10 min at this temperature and 1 h at ambient temperature. The mixture was poured onto ice–water (200 mL) and extracted with ethyl acetate (3 × 75 mL). The combined organic phases were washed with water (2 × 100 mL) and brine (1 × 80 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure to get a crude oily solid, which solidified after drying. After recrystallization from carbon tetrachloride, 0.33 mg (98%) of colorless pure 2-fluoro-2,2-dinitroethyl nitrocarbamate (**3b**) was obtained. DSC (5 °C min^{-1}): 80–81 °C (mp range), 145 °C (onset dec). IR (ATR, cm^{-1}): ν = 3244 (w), 3021 (w), 2976 (w), 1768 (s), 1611 (s), 1595 (s), 1453 (m), 1444 (s), 1351 (m), 1305 (s), 1244 (m), 1179 (s), 1128 (s), 1114 (m), 1041 (w), 1007 (w), 973 (s), 930 (m), 849 (w), 826 (m), 773 (s), 748 (m), 734 (m), 660 (w). Raman (1064 nm, 700 mW, cm^{-1}): ν = 3223 (25), 3126 (24), 3022 (48), 2979 (88), 2869 (9), 2816 (25), 1830 (24), 1769 (73), 1698 (25), 1642 (29), 1612 (55), 1603 (52), 1588 (49), 1534 (26), 1470 (34), 1447 (56), 1390 (46), 1362 (75), 1318 (97), 1276 (27), 1246 (35), 1206 (32), 1127 (41), 1112 (31), 1043 (96), 1007 (100), 973 (34), 932 (30), 853 (81), 778 (32), 733 (27), 576 (35), 492 (56), 459 (76), 416 (75), 369 (89), 333 (74), 282 (51), 223 (84). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ: 13.58 (br, 1H, NH), 5.67 (d, ^3J (H,F) = 15.9 Hz, 2H; CH_2) ppm. ^{13}C {^{1}H} NMR (acetone-d_6, 100.5 MHz) δ: 146.7 (CO), 119.5 (d, ^1J (C,F) = 294.4 Hz; $C(NO_2)_2F$), 61.9 (d, ^2J (C,F) = 20.0 Hz; CH_2) ppm. ^{15}N NMR (acetone-d_6, 40.6 MHz) δ = −24.8 (CNO_2), −47.8 (NHNO_2), −190.5 (NHNO$_2$) ppm. ^{19}F NMR (acetone-d_6, 376.3 MHz) δ = −111.7 (br) ppm. Anal. Calcd for $C_3H_3N_4O_8F$: C, 14.88; H, 1.25; N, 23.14. Found: C, 15.08; H, 1.28; N, 22.81. MS (DEI+) *m/e*: 243.1 [(M + H)$^+$]. BAM drophammer: 10 J. Friction tester 360 N, ESD: 0.15 J (grain size 100–500 μm).

*2,2-Dinitropropane-1,3-diyl Dicarbamate (**2c**).* 2,2-Dinitropropane-1,3-diol (1.66 g, 10.0 mmol) was dissolved in dry acetonitrile (20 mL) and placed in an ice bath, and chlorosulfonyl isocyanate CSI (3.26 g, 23 mmol) was added very slowly at 0 °C. The ice bath was removed, and stirring at room temperature was continued for 2 h. The reaction mixture was again cooled with an ice bath, water (5 mL) was added with caution, and the mixture was stirred for 10 min at room temperature. Upon cooling, a white precipitate formed that was filtered and washed with cold water. The solid was dried under high vacuum to obtain 2.43 g (96%) of colorless pure 2,2-dinitropropane-1,3-diyl dicarbamate (**2c**). DSC (5 °C min^{-1}): 136–137 °C (mp range), 182 °C (onset dec). IR (ATR, cm^{-1}): ν = 3414 (m), 3337 (m) 3286 (m), 2959 (w), 1766 (w), 1713 (s), 1613 (m), 1584 (vs), 1568 (s), 1452 (m), 1442 (m), 1393 (s), 1334 (vs), 1299 (s), 1256 (m), 1151 (m), 1126 (m), 1066 (vs), 932 (m), 886 (m), 853 (s), 785 (m), 775 (s), 760 (m), 741 (m), 680 (m). Raman (1064 nm, 1000 mW, cm^{-1}): ν = 3008 (39), 2972 (73), 1712 (40), 1611 (7), 1583 (34), 1456 (31), 1444 (7), 1376 (41), 1330 (25), 1303 (19), 1259 (25), 1143 (31), 1104 (10), 984 (9), 933 (58), 888 (30), 858 (95), 762 (12), 683 (33), 582 (14), 557 (10), 522 (27), 506 (11), 409 (81), 360 (42), 292 (28), 225 (19). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ: 6.53 (br, 2H, NH_2), 6.28 (br, 2H, NH_2), 5.00 (s, 4H, CH_2) ppm. ^{13}C{1H} NMR (acetone-d_6, 100.5 MHz) δ: 154.4 ($CO(NH_2)OR$), 115.2

($C(NO_2)_2$), 60.9 (CH_2) ppm. ^{14}N NMR (acetone-d_6, 28.9 MHz) δ: −16 (NO_2), −309 (NH_2) ppm. Anal. Calcd for $C_5H_8N_4O_8$: C, 23.82; H, 3.20; N, 22.22. Found: C, 23.90; H, 3.18; N, 22.22. MS (DEI+) *m*/*e*: 254.1 [$(M + 2H)^+$], 253 [$(M + H)^+$]. BAM drophammer: 30 J. Friction tester: 360 N. ESD: >0.2 J (grain size 100–250 μm).

*2,2-Dinitropropane-1,3-diyl Bis(nitrocarbamate) (**3c**).* Fuming nitric acid (>99.5%, 4 mL) was dropped into concentrated sulfuric acid (4 mL) at 0 °C. To this nitration mixture chilled in an ice bath was added 2,2-dinitropropane-1,3-diyl dicarbamate **3b** (504 mg, 2.0 mmol) in small portions, and the mixture was stirred 10 min at 0 °C and 1 h at ambient temperature. The nitration mixture was poured onto ice–water (200 mL) and extracted immediately with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (3 × 100 mL) and brine (1 × 100 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure to get crude slight yellow oily product. A colorless precipitate could be obtained by treating the slurry with chloroform and was recrystallized from 1,1-dichloroethane to obtain 540 mg (79%) of colorless pure 2,2-dinitropropane-1,3-diyl bis(nitrocarbamate) (**3c**). DSC (5 °C min^{-1}): 152–153 °C (mp range), 158 °C (onset dec). IR (ATR, cm^{-1}): ν = 3240 (w), 3198 (w), 3055 (w), 2897 (w), 1773 (m), 1617 (m), 1597 (m), 1564 (m), 1446 (m), 1363 (w), 1322 (m), 1291 (w), 1185 (s), 1169 (s), 1104 (w), 1010 (w), 974 (m), 880 (w), 866 (w), 822 (m), 746 (m), 724 (w), 675 (w). Raman (1064 nm, 800 mW, cm^{-1}): ν = 3211 (7), 3038 (16), 3021 (17), 2993 (33), 2976 (32), 2888 (7), 1769 (39), 1604 (18), 1593 (24), 1566 (10), 1454 (35), 1400 (14), 1365 (20), 1323 (61), 1273 (20), 1196 (16), 1177 (10), 1133 (12), 1081 (22), 1025 (100), 980 (16), 949 (12), 869 (47), 828 (11), 763 (12), 725 (9), 590 (11), 459 (37), 419 (42), 332 (34), 287 (20), 256 (33), 225 (20). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ: 13.75 (br, 2H; NH), 5.35 (s, 4H; CH_2) ppm. ^{13}C {^{1}H} NMR (acetone-d_6, 100.5 MHz) δ: 147.5 (CO), 114.6 ($C(NO_2)_2$), 62.9 (CH_2) ppm. ^{14}N NMR (acetone-d_6, 28.9 MHz) δ: −20 (NO_2), −48 (NO_2NH), −206 ($NHNO_2$) ppm. Anal. Calcd for $C_5H_6N_6O_{12}$: C, 17.55; H, 1.77; N, 24.56. Found: C, 17.85; H, 1.76; N, 24.39. MS (DEI+) *m*/*e*: 343.1 [$(M + H)^+$]. BAM drophammer: 4 J. Friction tester: 240 N, ESD: 0.10 J (grain size 100–500 μm).

*2,2-Dinitropropyl Carbamate (**2d**).* 2,2-Dinitropropanol (1.50 g, 10.0 mmol) was dissolved in dry acetonitrile (15 mL) and placed in an ice bath, and chlorosulfonyl isocyanate CSI (1.70 g, 12 mmol) was added very slowly at 0 °C. The ice bath was removed, and stirring at room temperature was continued for 1 h. The reaction mixture was again cooled with an ice bath, water (10 mL) was added with caution, and the mixture was stirred for 10 min at room temperature. The organic solvent was removed on the rotary evaporator. The residue crystallized on cooling, was filtered, and was washed with cold water. The precipitate was recrystallized from a hot mixture of water (25 mL) and ethanol (5 mL) and afterward dried under high vacuum to obtain 1.71 g (90%) of colorless pure 2,2-dinitropropyl carbamate (**2d**). DSC (5 °C min^{-1}): 68–70 °C (mp range), 192 °C (onset dec). IR (ATR, cm^{-1}): ν = 3437 (w), 3343 (w), 3291 (w), 2897 (w), 1712 (s), 1615 (w), 1583 (s), 1561 (s), 1459 (w), 1447 (w), 1400 (s), 1383 (m), 1325 (s), 1274 (w), 1224 (w), 1157 (w), 1122 (w), 1086 (s), 977 (w), 946 (w), 901 (w), 870 (m), 847 (m), 777 (m), 769 (m), 726 (w), 692 (w), 660 (w). Raman (1064 nm, 500 mW, cm^{-1}): ν = 3031 (48), 3021 (32), 2986 (41), 2956 (58), 2929 (6), 1710 (18), 1596 (9), 1575 (29), 1447 (25), 1391 (29), 1366 (26), 1331 (22), 1277 (10), 1229 (7), 1127 (17), 1103 (11), 979 (14), 948 (18), 904 (16), 873 (10), 849 (100), 770 (11), 728 (8), 693 (14), 661 (6), 567 (19), 504 (21), 469 (10), 414 (43), 365 (15), 338 (42), 248 (17), 211 (26). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ: 6.41 (br, 1H; NH_2), 6.25 (br, 1H; NH_2), 4.96 (s, 2H; CH_2O), 2.28 (s, 3H; CH_3) ppm. ^{13}C {^{1}H} NMR (acetone-d_6, 100.5 MHz) δ: 155.6 (CO), 117.7 ($C(NO_2)_2$), 64.5 (CH_2), 20.7 (CH_3) ppm. ^{14}N NMR (acetone-d_6, 28.9 MHz) δ: = −10 (NO_2), −310 (NH_2) ppm. Anal. Calcd for $C_4H_7N_3O_6$: C, 24.88; H, 3.65; N, 21.76. Found: C, 24.95; H, 3.79; N, 21.61. MS (DEI+) *m*/*e*: 194.1 [$(M + H)^+$]. BAM drophammer: 40 J. Friction tester: 360 N. ESD: 0.20 J (grain size <100 μm).

*2,2-Dinitropropyl Nitrocarbamate (**3d**).* Fuming nitric acid (>99.5%, 2 mL) was dropped into concentrated sulfuric acid (2 mL) at 0 °C. To this nitration mixture chilled in an ice bath was added the 2,2-dinitropropyl carbamate **2d** (0.38 g, 2.0 mmol) in small portions. The mixture was stirred for a further 60 min at this temperature and poured onto ice–water (200 mL). The aqueous solution was extracted with ethyl acetate (3 × 75 mL). The combined organic phases were washed with water (2 × 100 mL) and brine (1 × 80 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure to give a pale yellow oil, which solidified after drying after 2 days. After recrystallization from carbon tetrachloride, 0.41 g (85%) of colorless pure 2,2-dinitropropyl nitrocarbamate (**2d**) was obtained. DSC (5 °C min^{-1}): 76–77 °C (mp range), 140 °C (onset dec). IR (ATR, cm^{-1}): ν = 3264 (w), 2982 (w), 1762 (s), 1611 (s), 1589 (s), 1565 (s), 1447 (s), 1397 (m), 1348 (m), 1326 (m), 1274 (w), 1181 (s), 1152 (s), 1124 (m), 1017 (w), 976 (s), 876 (w), 849 (m), 822 (m), 760 (w), 750 (m), 739 (m), 729 (w), 669 (w). Raman (1064 nm, 700 mW, cm^{-1}): ν = 3040 (58), 2985 (68), 2958 (88), 2925 (14), 1763 (45), 1639 (13), 1609 (23), 1580 (38), 1566 (19), 1450 (52), 1400 (37), 1360 (39), 1332 (41), 1319 (53), 1275 (18), 1237 (13), 1203 (18), 1128 (28), 1108 (18), 1017 (100), 978 (26), 947 (20), 878 (22), 851 (87), 826 (15), 760 (14), 731 (23), 671 (18), 572 (34), 503 (39), 458 (57), 412 (63), 357 (41), 319 (44), 234 (55). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ: 13.56 (br, 1H; NH), 5.21 (s, 2H; CH_2O), 2.34 (s, 3H; CH_3) ppm. ^{13}C {^{1}H} NMR (acetone-d_6, 100.5 MHz) δ: 147.1 (CO), 116.1 ($C(NO_2)_2$), 64.8 (CH_2), 19.7 (CH_3) ppm. ^{14}N NMR (acetone-d_6, 28.9 MHz) δ: −11 (CNO_2), −47 ($NHNO_2$), −201 ($NHNO_2$) ppm. Anal. Calcd for $C_4H_6N_4O_8$: C, 20.18; H, 2.54; N, 23.53. Found: C, 20.43; H, 2.65; N, 23.12. MS (DEI+) *m*/*e*: [$(M + H)^+$]. BAM drophammer: 20 J. Friction tester: 360 N, ESD: 0.20 J (grain size <100 μm).

*4,4,4-Trinitrobutyl Carbamate (**2e**).* 4,4,4-Trinitrobutanol (1.04 g, 5.0 mmol) was dissolved in dry acetonitrile (20 mL) and placed in an ice bath, and chlorosulfonyl isocyanate CSI (0.72 g, 5.1 mmol) was added very slowly at 0 °C. The ice bath was removed, and stirring at room temperature was continued for 1 h. The reaction mixture was again cooled with an ice bath, water (10 mL) was added with caution, and the mixture was stirred for 10 min at room temperature. The organic solvent was removed on the rotary evaporator. The yellow oily residue was recrystallized from a hot mixture of water (90 mL) and ethanol (10 mL), filtered, and washed with cold water. The solid was dried under high vacuum to obtain 1.22 g (96%) of colorless pure 4,4,4-trinitrobutanol carbamate (**2e**). DSC (5 °C min^{-1}): 53–54 °C (mp range), 156 °C (onset dec). IR (ATR, cm^{-1}): ν = 3485 (w), 3322 (w), 3252 (w), 2983 (w), 2358 (w), 1731 (w), 1698 (m), 1574 (s), 1474 (w), 1441 (w), 1410 (m), 1383 (w), 1333 (m), 1301 (s), 1252 (w), 1225 (w), 1141 (w), 1114 (w), 1089 (m), 1074 (s), 1024 (w), 940 (w), 870 (w), 854 (m), 805 (m), 791 (s), 784 (s), 743 (w), 708 (w), 680 (w). Raman (1064 nm, 500 mW, cm^{-1}): ν = 2983 (39), 2971 (39), 2946 (57), 2915 (21), 1687 (12), 1603 (29), 1476 (18), 1445 (9), 1428 (20), 1364 (35), 1307 (39), 1256 (10), 1228 (10), 1118 (20), 1090 (18), 1024 (9), 970 (14), 941 (13), 872 (26), 857 (100), 797 (11), 723 (9), 675 (14), 562 (16), 505 (19), 415 (35), 375 (70), 334 (21), 279 (25). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ: 5.92 (br, 2H; NH_2), 4.15–4.12 (m, 2H; CH_2O), 3.46–3.42 (m, 2H; CH_2), 2.09–2.01 (m, 2H; CH$_2$CH_2CH$_2$O) ppm. ^{13}C {^{1}H} NMR (acetone-d_6, 100.5 MHz) δ: 156.5 (CO), 131.1 ($C(NO_2)_3$), 62.0 (CH_2O), 31.0 ($CH_2C(NO_2)_3$), 24.0 (CH_2CH_2O) ppm. ^{14}N NMR (acetone-d_6, 28.9 MHz) δ: −28 (CNO_2), −314 (NH_2) ppm. Anal. Calcd for $C_5H_8N_4O_8$: C, 23.82; H, 3.20; N, 22.22. Found: C, 23.87; H, 3.31; N, 22.05. MS (FAB+) *m*/*e*: 253.1 [$(M + H)^+$]. BAM drophammer: 40 J. Friction tester: 360 N. ESD: 0.20 J (grain size 100–500 μm).

*4,4,4-Trinitrobutyl Nitrocarbamate (**3e**).* Fuming nitric acid (>99.5%, 2 mL) was dropped into concentrated sulfuric acid (2 mL) at 0 °C. To this nitration mixture chilled in an ice bath was added the 4,4,4-trinitrobutyl carbamate **2e** (504 mg, 2.0 mmol) in small portions. The mixture was stirred for a further 60 min at this temperature and poured onto ice–water (200 mL). The aqueous solution was extracted with ethyl acetate (3 × 75 mL). The combined organic phases were washed with water (2 × 100 mL) and brine (1 × 80 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure to obtain a pale yellow oil, which solidified

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after several hours under high vacuum. After recrystallization from a mixture of water/ethanol (10:1), 172 mg (29%) of colorless pure 4,4,4-trinitrobutyl nitrocarbamate was obtained (**3e**). DSC (5 °C min^{-1}): 82−84 °C (mp range), 145 °C (onset dec). IR (ATR, cm^{-1}): ν = 3167 (w), 3047 (w), 1745 (s), 1616 (m), 1594 (m), 1578 (s), 1469 (w), 1443 (m), 1389 (w), 1371 (w), 1307 (m), 1253 (w), 1228 (w), 1186 (s), 1144 (m), 1118 (w), 1083 (w), 1030 (w), 996 (w), 966 (w), 942 (m), 903 (w), 882 (m), 856 (w), 822 (w), 799 (m), 758 (w), 732 (w). Raman (1064 nm, 500 mW, cm^{-1}): ν = 3159 (6), 2981 (49), 2947 (64), 2876 (9), 2831 (6), 2739 (6), 1756 (26), 1612 (45), 1473 (19), 1447 (24), 1423 (24), 1362 (44), 1331 (42), 1309 (39), 1256 (16), 1228 (12), 1195 (10), 1119 (14), 1084 (20), 1007 (51), 962 (10), 885 (12), 856 (100), 793 (10), 729 (10), 565 (15), 471 (19), 450 (28), 374 (55), 332 (18), 296 (25). ^{1}H NMR (acetone-d_6, 399.8 MHz) δ: 13.33 (br, 1H; N*H*), 4.46−4.43 (m, 2H; CH_2O), 3.56−3.52 (m, CH_2), 2.22−2.12 (m, 2H; $CH_2CH_2CH_2O$) ppm. ^{13}C {^{1}H} NMR (acetone-d_6, 100.5 MHz) δ: 148.3 (CO), 130.9 ($C(NO_2)_3$), 64.6 (CH_2O), 30.8 ($CH_2C(NO_2)_3$), 23.3 (CH_2CH_2O) ppm. ^{14}N NMR (acetone-d_6, 28.9 MHz) δ: −28 (CNO_2), −45 ($NHNO_2$), −204 ($NHNO_2$) ppm. Anal. Calcd for $C_5H_7N_5O_{10}$: C, 20.21; H, 2.37; N, 23.57. Found: C, 20.33; H, 2.39; N, 23.36. MS (DEI+) *m*/*e*: 298.1 [$(M + H)^+$]. BAM drophammer: 20 J. Friction tester: 360 N. ESD: 0.20 J (grain size <100 μm).

■ ASSOCIATED CONTENT

Supporting Information

Computational details as well as ^{1}H and ^{13}C spectra. Further data regarding the X-ray molecular structures and more detailed calculations of combustion parameters of different compositions. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00655.

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Notes

The authors declare no competing financial interest.

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