Selected Nitrocarbamates of Glycerine & Co. and the First Acetylene Derivative

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Dedicated to Professor Peter Klüfers on the Occasion of His 65th Birthday

Abstract. A simple two step synthesis route for the preparation of several energetic multivalent nitrocarbamates of easily available alcohols is presented. The carbamates were obtained by the reaction of the alcohols and the reactive reagent chlorosulfonyl isocyanate (CSI) with subsequent aqueous work-up. The nitration of the carbamates was performed with mixed acid (nitric and sulfuric acid). The thermal stabilities were explored by using differential scanning calorimetry and the energies of formation were calculated on the CBS-4M level of theory, as well as several detonation and propulsion parameters for the application as energetic materials. All compounds were fully characterized and discussed in addition with single X-ray diffraction.

Introduction

The first article, where nitrocarbamates were mentioned, was of *Thiele* and *Lachman* in 1895, who synthesized a nitrocarbamate from ethyl carbamate by nitration with ethyl nitrate.[1] After that, nitrocarbamates have received little to almost no attention. Recently, this class of compounds regained interest in respect of energetic materials. Several primary nitrocarbamates from various polynitroalcohols have been synthesized, as well as a tetravalent nitrocarbamate of pentaerythritol, which is also the starting material for the well-known explosive PETN (Pentaerythritol).[2] These new nitrocarbamates exhibit good physical and energetic properties with higher decomposition points and lower sensitivities against mechanical stimuli compared to the related nitrate esters.

The nitrate esters of glycerine and ethylene glycol, nitroglycerine (NG) and ethylene glycol dinitrate (EGDN) were both invented in the 19th century and are both extremely sensitive to impact.[3] Nevertheless, they are still in use in various applications, such as blasting gelatin, gun and double based propellants with a high oxygen content and good detonation parameters. Their corresponding primary nitrocarbamates of these easy available multivalent alcohols are unknown, and should show higher stability due to the possibility of hydrogen bonding of the nitrocarbamate moiety. Tris(hydroxymethyl)-

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nitromethane is a cheap commercially available industrial product and therefore became of interest to our research. In addition, a diol containing an acetylene moiety was selected, because nitrocarbamates with alkyne functionalities are unknown.

Results and Discussion

Synthesis

The most applied method to convert alcohols into the corresponding carbamates is performed by the reaction of urea or isocyanic acid.[4] In the case of polyols a two-step synthesis is necessary, due to a lowered reactivity, potential multi-addition and polymerization is possible. First, the alcohol is reacted with phosgene or phosgene substitutes such as phenyl chloroformate, followed by treatment with ammonia to generate the carbamate.[5] The carbamates of glycol **1a** and glycerine **1b** were previously prepared via this two-step phenyl chloroformate route.[5]

In our study now, we report the synthesis of the carbamates **2a–d** from four readily commercially available polyols ethylene glycol (**1a**), glycerine (**1b**), tris(hydroxymethyl)nitromethane (**1c**), and but-2-yne-1,4-diol (**1d**) in a one-step procedure with the reagent chlorosulfonyl isocyanate (CSI) (Scheme 1). CSI has also the advantage to form a chlorosulfonylamide intermediate preventing multi-addition, which is destroyed by the aqueous work-up.[6]

In contrast to the aforementioned two-step synthesis with phenyl chloroformate, the CSI route has the advantage of a simple and faster procedure and higher yields (86 % to 93 %). The nitration of the carbamates **2a–d** was performed in a mixture of anhydrous nitric acid and concentrated sulfuric acid.

Scheme 1. Synthesis of carbamates **2a–d** and nitrocarbamates **3a–d** from simple multivalent alcohols **1a–d**.

The conversion to the primary nitrocarbamates **3a–d** can also be achieved by the use of anhydrous nitric acid on its own as nitrating agent, but only with a large excess of anhydrous nitric acid for a complete nitration. The nitrocarbamates of ethylene glycol **3a** and but-2-yne-1,4-diol **3d** were separated by filtration after quenching the reaction mixture with ice-water. However, the carbamate **2a** was nitrated at room temperature, the temperature for **2d** has to be lower than 4 °C, since the alkyne moiety tends to be unstable in the nitration mixture, and gaseous decomposition products were formed accompanied with decreasing yields. The nitrocarbamates **3b** and **3c** are highly water-soluble, and therefore require extraction with ethyl acetate after quenching with ice-water. All four nitrocarbamates **3a–d** were obtained anhydrous, but **3b** and **3c** were shown to be rather hygroscopic, visible by melting and resolidification. On the other hand, **3a** and **3d** are recrystallized from water without inclusion of crystal water. In general, the nitrocarbamates are better soluble in water than their carbamate analogues.

NMR and Vibrational Spectroscopy

In the ^{1}H NMR spectrum of the carbamates the resonance of the methylene groups is found at δ = 4.61–4.01 ppm. This low field shift is typical for attached carbamate units compared to those of the corresponding alcohols (around 2 ppm). In the spectra of the nitrocarbamates this effect is further enhanced because of the electron withdrawing nature of the nitro group, resulting in an additional downfield shift of approximately 0.5 ppm for the methylene groups. A similar but weaker trend is observed for the CH$_2$ moiety in the ^{13}C NMR spectra. The resonance of the carbamate carbonyl carbon atom is found near 156 ppm, whereas for the nitrocarbamates a significant upfield shift to around 148 ppm occurs, due to the presence of the electron withdrawing nitro group.

The NH$_2$ resonance in the ^{1}H NMR spectrum of the carbamates is quite broad as a result of the restricted rotation around the C–N bond, and located around 6.5 ppm.[7] The linewidths of the NH resonances of the nitrocarbamates are smaller but shifted to lower field beyond 13 ppm, caused by the acidification due to the neighboring nitro group. For the carbamate **2a** and the corresponding nitrocarbamate **3a** exemplary the ^{15}N NMR spectrum was recorded, showing the *N*H$_2$ resonance at –310.0 ppm and the *N*HNO$_2$ shifted downfield to –196.2 ppm. The resonances of the nitro groups are found at –46.3 ppm, in a typical range for nitrocarbamates.[2b]

In the vibrational spectra, the characteristic bands of the carbonyl groups of the carbamates are located in the range of 1685–1613 cm^{-1}. For the nitrocarbamates these stretching frequencies are shifted to 1784–1743 cm^{-1}. Further, for all nitrocarbamates the typical asymmetric and symmetric stretching vibration of the NO$_2$ groups can be observed around 1600 and 1200 cm^{-1}. An additional intense peak in the Raman in the region of 1001–1031 cm^{-1} vibration can be assigned according to the literature to the N–N stretching vibration of the nitrocarbamate moiety.[8]

Single Crystal Structural Analysis

Single crystals suitable for X-ray diffraction studies were obtained by crystallization at room temperature from water (**2a**, **3a**, **3d**) and from acetonitrile (**3b**, **3c**). A full list of the crystallographic structure and refinement data are shown in Table 1 and further details are given in the Supporting Information.

For the purpose of a discussion and comparison of the energetic nitrocarbamates also a crystal structure of the carbamate **2a** was determined. The dicarbamate **2a** (Figure 1) crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit consists of a half molecule, due to an inversion center in the center of the glycol structure. The carbamate moiety and in addition the complete carbon backbone is nearly perfectly planar, which is displayed by the two torsion angles (O2–C2–O1–C1 = 2.3° and H4–N1–C2–O2 = –2.0°). However, this is not the case in the corresponding nitrocarbamate **3a**.

Compound **3a** crystallizes in the orthorhombic space group $Pdd2$ with one molecule as asymmetric unit (Figure 2). Compared to the carbamate, both nitrocarbamate ends are nonplanar and the nitro groups are turned out more than 10°, which was observed earlier in structures of nitrocarbamates.[8b] The short N–N bond lengths of the nitramines with 1.38 Å indicate significant double bond character and are achieved by delocalization of the nitrogen lone pair on N2 and N3. Furthermore, the distance of the C–O in the carbonyl groups and N–H bonds show compared to the carbamate structure of **2a** a slight shortening as a result of the electron withdrawing nitro group.

The nitrocarbamate **3b** with the glycerine backbone crystallizes in the triclinic space group $P\bar{1}$ with one water and two acetonitrile molecules (Figure 3). Similar geometric features are present, although here just two of the three nitrocarbamates moieties are turned significantly out of planarity.

The nitrocarbamate **3c** of the alcohol tris(hydroxymethyl) nitromethane crystallizes in the space group $P2_1/c$ with a large unit cell and with two unique molecules and two solvent (acetonitrile) molecules (Figure 4). The dihedral angles C–N–N–O of the nitrocarbamates moieties are all turned out of the plane more than 10° and show the same structure characteristics.

The nitrocarbamate **3d** with the alkyne group crystallizes in the monoclinic space group $P2_1/c$ with half of the molecule as asymmetric unit (Figure 5). In this case, the nitro group is rotated away to a large degree of 24.2° out of the plane and thus

Table 1. Crystal and structure refinement data for **2a** and **3a–d**.

	2a	3a	3b	3c	3d
Formula	$C_4H_8N_2O_4$	$C_4H_6N_4O_8$	$C_6H_8N_6O_{12}$ $(C_2H_3N)_2H_2O$	$C_7H_9N_7O_{14}$ $(C_2H_3N)_2$	$C_6H_6N_4O_8$
Formula weight /g·mol^{-1}	148.12	238.11	456.28	497.29	262.13
Temperature /K	173(2)	173(2)	173(2)	100(2)	294(2)
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group (no.)	$P2_1/c$ (14)	$Fdd2$ (43)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P2_1/n$ (14)
a /Å	8.8363(5)	16.3442(5)	8.2936(4)	9.8297(4)	4.3479(5)
b /Å	5.1148(4)	44.4286(14)	10.2439(4)	16.5363(7)	14.8725(13)
c /Å	7.0213(7)	4.7335(2)	13.9157(5)	26.6880(11)	7.9973(7)
α /°	90	90	97.09(1)	90	90
β /°	95.48(1)	90	106.83(1)	94.57(1)	93.70(1)
γ /°	90	90	113.80(1)	90	90
V /Å^3	315.9(1)	3437.2(2)	995.7(1)	4324.2(3)	516.1(1)
Z	2	16	2	8	2
$\rho_{calcd.}$ /g·cm^{-3}	1.557	1.841	1.522	1.528	1.687
μ /mm^{-1}	0.139	0.181	0.141	0.142	0.159
$F(000)$	156	1952	472	2048	268
Crystal habit	block	block	plate	plate	plate
Crystal color	colorless	colorless	colorless	colorless	colorless
Crystal size /mm	$0.18 \times 0.06 \times 0.06$	$0.12 \times 0.06 \times 0.06$	$0.23 \times 0.15 \times 0.04$	$0.22 \times 0.19 \times 0.03$	$0.28 \times 0.22 \times 0.05$
q range /°	4.61–29.36	4.44–28.98	4.33–25.34	4.24–25.50	4.84–26.37
Index ranges	$-11 \leq h \leq 11$ $-7 \leq k \leq 6$ $-9 \leq l \leq 3$	$-21 \leq h \leq 20$ $-60 \leq k \leq 59$ $-6 \leq l \leq 6$	$-9 \leq h \leq 9$ $-12 \leq k \leq 12$ $-16 \leq l \leq 16$	$-8 \leq h \leq 11$ $-20 \leq k \leq 18$ $-32 \leq l \leq 26$	$-5 \leq h \leq 5$ $-18 \leq k \leq 11$ $-9 \leq l \leq 7$
Reflections measured	1276	11070	16346	17232	2469
Reflections independent	758	2097	3613	7997	1054
Reflections unique	594	2016	2960	6280	810
R_{int}	0.025	0.022	0.028	0.023	0.020
R_1, wR_2 (2σ data)	0.0437, 0.1021	0.0214, 0.0535	0.0426, 0.1071	0.0437, 0.1051	0.0388, 0.0949
R_1, wR_2 (all data)	0.0583, 0.1157	0.0231, 0.0517	0.0527, 0.1172	0.0604, 0.1170	0.0537, 0.1054
Data / restraints / parameters	758 / 0 / 62	2097 / 1 / 163	3613 / 3 / 322	7997 / 0 / 671	1054 / 0 / 94
GOOF on F^2	1.069	1.069	1.046	1.027	1.051
Residual elec. den. /e·Å^{-3}	–0.23/0.28	–0.16/0.12	–0.38/0.49	–0.46/0.54	–0.21/0.23
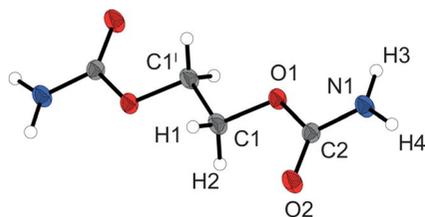
Figure 1. Molecular structure of ethane-1,2-diyl dicarbamate (**2a**). Selected bond lengths /Å and angles /°: C1–O1 1.439(2), C2–N1 1.321(2), C2–O1 1.357(2), C2–O2 1.224(2), N1–H3 0.91(2), N1–H4 0.93(3), C2–O1–C1 114.8(1), O2–C2–O1–C1 2.3(2), H4–N1–C2–O2 –2(2).
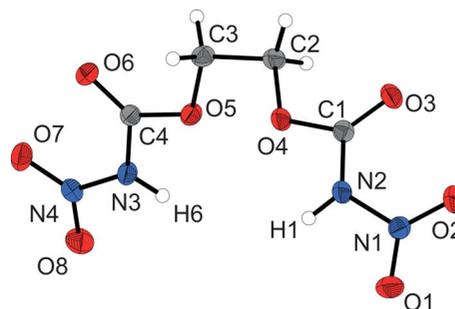
Figure 2. Molecular structure of ethane-1,2-diyl bis(nitrocarbamate) (**3a**). Selected bond lengths /Å and angles /°: C1–N2 1.390(1), C1–O3 1.195(1), C1–O4 1.332(1), C2–O4 1.461(2), N2–H1 0.84(2), N1–N2 1.377(1), N1–N2–H1 111(1), H1–N2–C1 121(1), N1–N2–C1 122.44(9), N1–N2–C1–O3 –15.0(2), O1–N1–N2–C1 160.75(2).

represents a maximum value so far observed. A reason for this observation could be the result of competing conjugation requirements of the alkyne, the carbamate, and the nitro functional group. In the literature is also discussed, that with increasing alkyl chain length of the alkoxy group a decrease in planarity of the nitrocarbamate moiety seems to occur.[8b]

Thermal Stabilities and Energetic Properties

The nitrate esters of the four alcohols glycol, glycerine, tris(hydroxymethyl)nitromethane, and but-2-yne-1,4-diol are reported and the first two are well established. The nitrate ester of tris(hydroxymethyl)nitromethane is reported to be fairly unstable and impossible to stabilize;[3] whereas that of but-2-yne-1,4-diol has been mentioned previously, but remains questionable as no details of the compound are available.[9] The four herein presented nitrocarbamates are all solids compared to their nitrate ester analogues, which are oily liquids partially with high vapor pressures. Another advantage of the nitrocarbamates is the higher nitrogen content of approximately 5 %,
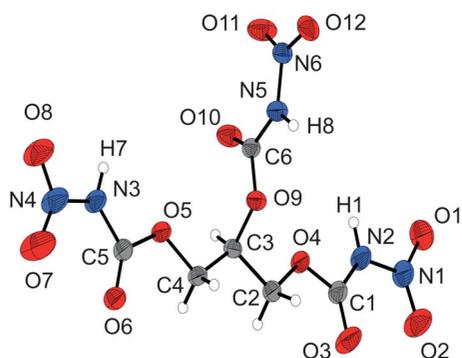
Figure 3. Molecular structure of propane-1,2,3-triyl tris(nitrocarbamate) (**3b**). Selected bond lengths /Å and angles /°: C1–N2 1.379(3), C1–O3 1.189(2), C1–O4 1.328(2), N1–N2 1.376(2), N2–H1 0.85(2), C6–N5–N6–O12 –177.5(2), O1–N1–N2–C1 –170.5(2).
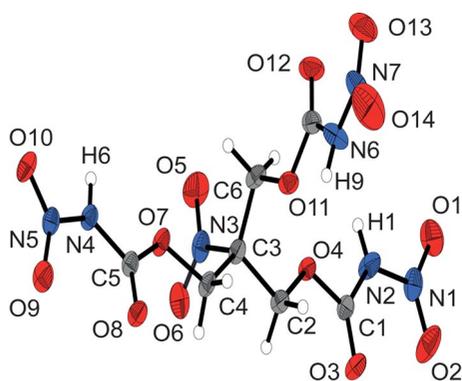
Figure 4. Molecular structure of one unique molecule of nitroisobutyl-glycerol trinitrocarbamate (**3c**). Selected bond lengths /Å and angles /°: N2–C1 1.376(3), N2–H1 0.86(3), N3–C3–C6 106.6(2), N3–C3–C4 107.6(2), N3–C3–C2 107.6(2), N1–N2–C1–O4 175.2(2), O1–N1–N2–C1 –172.3(2).
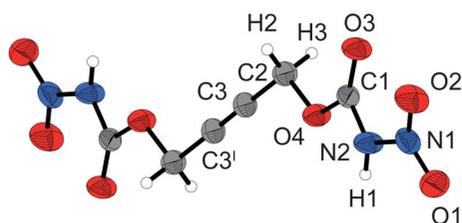
Figure 5. Molecular structure of but-2-yne-1,4-diyl bis(nitrocarba-mate) (**3d**). Selected bond lengths /Å and angles /°: C1–N2 1.381(2), C1–O3 1.187(2), C1–O4 1.322(2), C2–C3 1.458(2), C3–C3' 1.183(2), C2–O4 1.452(2), O4–C2–C3 105.8(1), O3–C1–O4–C2 7.5(2), N1–N2–C1–O3 7.4(3), O1–N1–N2–C1 155.8(2).

whereas the oxygen balance Ω is lower. The sensitivity against mechanical stimuli is very important for a safe handling and use of energetic materials. The sensitivity against friction (FS) is determined by rubbing a small amount between a porcelain plate and a pin with different contact pressures. No significant differences in the comparison of the nitrate esters EGDN and NG and the nitrocarbamates **3a** and **3b** were observed (Table 2 and Supporting Information); both groups of materials show only slight sensitivity to friction ($\geq$ 360 N insensitive, 360–

80 N sensitive, 80–10 N very sensitive, $\leq$ 10 N extremely sensitive). The more important value is the sensitiveness towards impact (IS) of a compound which is tested by the action of a dropping weight on a sample.[10] The nitrates EGDN and NG exhibit an extraordinarily high sensitivity of 0.2 J and must be classified in the most dangerous class ($\geq$ 40 J insensitive, 40–35 J less sensitive, 35–4 J sensitive, $\leq$ 3 J very sensitive).[3,10] However, the nitrocarbamates **3a** and **3b** are much less sensitive; they have to be classified as sensitive (from 8 to 15 J) but can be handled without the risk of spontaneous detonation, which is not the case for EGDN and NG. The sensitivity values for the nitrocarbamates **3a/b/c** are fairly similar, except an impact sensitivity of 8 J for the alkyne derivative **3d** at the border to very sensitive.

Table 2. Physical and chemical properties of **3a**–**3d**.

	3a	3b	3c	3d
T_m /°C[a]	151	–	–	–
T_{dec} /°C[b]	157	152	148	149
ρ (RT) /g·cm^{-3}[c]	1.82	1.78	1.72	1.68
IS /J[d]	15	10	15	8
FS /N[e]	360	240	360	240
ESD /J[f]	0.20	0.15	0.15	0.15
N /%[g]	23.5	23.6	23.6	21.4
O /%[h]	53.8	53.9	54.0	48.8
N+O /%[i]	77.3	77.5	77.6	70.2
Ω_{CO_2} /%[j]	–20.2	–18.0	–17.3	–42.7
Ω_{CO} /%[k]	+8.9	+9.0	+9.6	–6.1

a) Onset melting point T_m from DSC measurement carried out at a heating rate of 5 K·min^{-1}. b) Onset decomposition point T_{dec} from DSC measurement carried out at a heating rate of 5 K·min^{-1}. c) Density at room temperature from pycnometer measurement. d) Impact sensitivity. e) Friction sensitivity. f) Sensitivity towards electrostatic discharge. g) Nitrogen content. h) Oxygen content. i) Sum of nitrogen and oxygen content. j) Oxygen balance Ω assuming the formation of CO_2 at the combustion. k) Oxygen balance Ω assuming the formation of CO at the combustion.

The performance of energetic materials can be calculated by the computer code EXPLO5 (V.6.02).[11] The major parameters are the detonation velocity V_{Det}, heat of explosion Q_v, and the detonation pressure P_{CJ}. These values depend in turn on the density and the energy of formation of the material at room temperature. The detonation and combustion parameters are summarized in Table 3 (for further values especially for the nitrate esters see Supporting Information).

The nitrocarbamate of glycol **3a** shows the highest detonation velocity of 8014 m·s^{-1} in the discussed selection. The corresponding nitrate ester, nitroglycol EGDN, has a significantly lower detonation velocity of 7502 m·s^{-1}, due to the much lower density (1.59 g·cm^{-1}) and in spite of the good oxygen balance Ω. Furthermore, all nitrocarbamates show an advantageously lower detonation temperature with still good detonation pressures. Moreover, the alkyne nitrocarbamate **3d** shows good properties, especially in propellant mixtures with aluminum as fuel, which achieves a specific impulse I_s of 252 s with an admixture of 15 % aluminum as the best ratio.

Table 3. Calculated heats of formation, predicted detonation and combustion parameters (using the EXPLO5 V6.02 code) for **3a**–**3d**.

	3a	3b	3c	3d
ΔH°_{f} /kJ·mol^{-1} a)	–685	–985	–1023	–339
ΔU°_{f} /kJ kg^{-1} b)	–2784	–2676	–2373	–1208
Q_v /kJ kg^{-1} c)	–4013	–4064	–4294	–4816
T_{ex} /K d)	2944	3038	3216	3406
V_0 /L·kg^{-1} e)	731	727	734	745
P_{CJ} /kbar f)	278	261	248	236
V_{Det} /m·s^{-1} g)	8014	7842	7703	7594
I_s /s h)	218	221	228	221
I_s /s (5 % Al) i)	230	231	238	235
I_s /s (10 % Al) i)	241	240	246	247
I_s /s (15 % Al) i)	246	246	250	252
I_s /s (20 % Al) i)	249	249	253	246
I_s /s (15 % Al, binder) j)	236	236	237	238

a) Enthalpy calculated by the CBS-4 M method using Gaussian 09[17,18]. b) Energy of formation calculated by the CBS-4 M method using Gaussian 09[17,18]. c) Heat of explosion. d) Detonation temperature. e) Volume of gaseous products. f) Detonation pressure. g) Detonation velocity calculated by using the EXPLO5 (Version 6.02) program package.[11] h) Specific impulse of the neat compound using the EXPLO5 (Version 6.02) program package at 70.0 bar chamber pressure and with equilibrium expansion.[11] i) Specific impulse for compositions with different percentage of aluminum. j) Specific impulse for composition with aluminum and binder (6 % polybutadiene acrylic acid, 6 % polybutadiene acrylonitrile, and 2 % bisphenol A ether).

Conclusions

The synthesis route of choice for the preparation of multivalent nitrocarbamates is the two step synthesis starting with the carbamate preparation from alcohols with chlorosulfonyl isocyanate (CSI) and subsequent nitration. Full characterization of the materials including discussion of the energetic properties in addition with molecular structures of all nitrocarbamates was performed. The nitrocarbamates are solids with low sensitivity to mechanic stimuli and good thermal stabilities. The nitrocarbamate of glycol, ethane-1,2-diyl bis(nitrocarbamate) (**3a**), exhibits good detonation performances, which are much higher than values of the corresponding nitrate ester EGDN. The simple synthetic route, the good physical properties especially those of **3a** and the acetylene nitrocarbamate, but-2-yne-1,4-diyl bis(nitrocarbamate) (**3d**), suggest potential application as energetic materials.

Experimental Section

General Methods: All chemicals were used as supplied. Raman spectra were recorded in a glass tube with Nd:YAG laser excitation up to 1000 mW (at 1064 nm). Infrared spectra were measured with an ATR device. All spectra were recorded at ambient temperature. NMR spectra were recorded with a JEOL/Bruker instrument, and chemical shifts were determined with respect to external Me$_4$Si (^{1}H, 399.8 MHz; ^{13}C, 100.5 MHz) and MeNO$_2$ (^{15}N, 40.6 MHz; ^{14}N, 28.9 MHz). Melting and decomposition points were measured with a DSC with a heating rate of 5 °C·min^{-1} in a temperature range of 15–400 °C. The melting points were checked by a melting point apparatus (not corrected). The sensitivity data were performed with a BAM drophammer and a BAM friction tester.[10,12]

X-ray Crystallography: Crystals suitable for X-ray crystallography were selected by means of a polarization microscope and mounted of a glass fiber. The measurements were investigated with an Oxford XCalibur3 KappaCCD diffractometer. The diffractometer was equipped with a generator (voltage 50 kV, current 40 mA) and a KappaCCD detector operating with Mo-K_α radiation ($\lambda = 0.7107$ Å). The solution of the structure was performed by direct methods (SIR97)[13] and refined by full-matrix least-squares on F^2 (SHELXL)[14] implemented in the WINGX software package[15] and finally checked with the PLATON software[16]. 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.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1429437 (**2a**), CCDC-1429438 (**3a**), CCDC-1429439 (**3b**), CCDC-1429440 (**3d**), and CCDC-1429441 (**3c**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Quantum Chemical Calculations: All ab initio calculations were carried out using the program package Gaussian 09 (Rev. A.02)[17] and visualized by GaussView 5.08.[18] 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-ξ basis set cc-pVDZ was used. The structures were optimized with symmetry constraints and the energy was corrected with the zero point vibrational energy.[19] 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 used 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 M started with a HF/3-21G(d) structure optimization, which was 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.[20] The enthalpies of the gas-phase species were estimated according to the atomization energy method.[21]

Calculation of Energetic Performance: All calculations affecting the detonation parameters were carried out using the program package EXPLO5 V6.02.[11,22] The detonation parameters were calculated at the Chapman-Jouguet (CJ) condition 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 EXPLO5 V6.02 program, assuming an isobaric combustion of a composition of oxidizer with different amounts of aluminum as fuel. A chamber pressure of 70.0 bar and an ambient pressure of 1.0 bar with equilibrium expansion conditions were estimated for the calculations.

General Syntheses Procedure

CAUTION! Nitrocarbamates are potential energetic materials and are sensitive 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 handling these compounds.

Carbamates 2a–d: The respective alcohol (**1a–d**) (10 mmol) was diluted in fresh distilled acetonitrile (20 mL) and placed in an ice bath and chlorosulfonyl isocyanate (CSI) (1.05 per equivalent hydroxyl group) was added slowly. 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, and quenched carefully with water (20 mL). The stirring was continued at room temperature for 0.5 h and the organic solvent was removed. The formed precipitate was filtered, washed thoroughly with water and dried under high vacuum to obtain colorless pure carbamate (**2a**, 72 %; **2b**, 82 %; **3c**, 62 %; **2d**, 92 %).

Nitrocarbamate 3a: Fuming nitric acid (>99.5 %, 4 mL) was dropped into cooled concentrated sulfuric acid (98.5 %, 4 mL) below 5 °C. To this chilled mixed acid the carbamate **2a** (296 mg, 2 mmol) was added in small portions. The mixture was stirred for 10 min at this temperature and 1.5 h at ambient temperature. The reaction mixture was poured onto ice-water (50 mL) and stirred for further. The formed precipitate was filtered off and washed with water. After recrystallization from water, 357 mg (75 %) of colorless pure product **3a** was obtained.

Nitrocarbamates 3b and 3c: Fuming nitric acid (>99.5 %, 3 mL) was dropped into concentrated sulfuric acid (98.5 %, 3 mL) at 0 °C. To this chilled nitration mixture the carbamate **2b** or **2c** (221 mg, 1 mmol or 280 mg, 1 mmol) in small portions was added. The suspension was stirred for 15 min at this temperature and 1.5 h at ambient temperature. The mixture was poured onto ice-water (100 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water and brine and dried sufficient with magnesium sulfate. The solvent was removed under reduced pressure to obtain an oily product, which turns into a colorless precipitate by treating the slurry with chloroform. After recrystallization from acetonitrile and drying under high vacuum pure colorless nitrocarbamate was obtained (**2b**, 281 mg, 79 %; **2c**, 195 mg, 47 %).

Nitrocarbamate 3d: Fuming nitric acid (>99.5 %, 4 mL per equivalent) was dropped into concentrated sulfuric acid (98.5 %, 4 mL) below 5 °C in an ice bath. Into this chilled mixed acid the carbamate **2d** (344 mg, 2 mmol) was added in small portions. The mixture was stirred for 50 min below 4 °C and poured onto ice-water (50 mL) and further stirred. The formed precipitate was filtered off and washed with water. After recrystallization from water, 278 mg (56 %) of colorless pure product **3d** was obtained.

Ethane-1,2-diyl dicarbamate (2a): ^{1}**H NMR** ([D$_6$]DMSO): δ = 6.51 (s, 4 H, NH_2), 4.01 (s, 4 H, CH_2) ppm. ^{13}**C{^{1}H} NMR** ([D$_6$]DMSO): δ = 157.1 (*C*O), 62.7 (*C*H$_2$) ppm. ^{15}**N{^{1}H} NMR** ([D$_6$]DMSO): δ = –310.0 (*N*H$_2$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3422 (m), 3339 (w), 3266 (m), 3209 (m), 2990 (w), 2915 (w), 1643 (s), 1614 (s), 1483 (w), 1395 (s), 1308 (s), 1227 (w), 1090 (s), 894 (m), 776 (m), 696 (m) cm^{-1}. **Raman** (1064 nm, 500 mW): $\tilde{\nu}$ = 3410 (6), 3267 (8), 3208 (14), 2975 (65), 2922 (40), 1694 (25), 1673 (15), 1646 (8), 1631 (16), 1483 (28), 1442 (9), 1374 (7), 1276 (26), 1123 (100), 1080 (19), 968 (56), 663 (50), 573 (13), 307 (32), 236 (18) cm^{-1}. **MS** (DEI+) *m/e*: 149.1 [[M + H]$^+$]. C$_4$H$_8$N$_2$O$_4$ (148.12): calcd. C 32.44, H 5.44, N 18.91 %; found: C 32.42, H 5.62, N 18.78 %. DSC (5 °C min^{-1}, onset): 166 °C (melt.), 225 °C (dec.). BAM drophammer: >40 J. Friction tester: >360 N (grain size 100–500 μm).

Ethane-1,2-diyl bis(nitrocarbamate) (3a): ^{1}**H NMR** ([D$_6$]acetone): δ = 13.4 (br., 2 H, NH), 4.51 (s, 4 H, CH_2) ppm. ^{13}**C{^{1}H} NMR** ([D$_6$]acetone): δ = 148.4 (*C*O), 64.1 (*C*H$_2$) ppm. ^{15}**N{^{1}H} NMR**

([D$_6$]acetone): δ = –46.3 (NH*N*O$_2$), –196.2 (*N*HNO$_2$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3285 (w), 3147 (w), 3040 (w), 2968 (w), 1754 (m), 1741 (m), 1619 (m), 1600 (m), 1592 (m), 1551 (w), 1492 (w), 1465 (w), 1437 (m), 1366 (m), 1321 (m), 1278 (w), 1246 (w), 1195 (s), 1168 (s), 1048 (w), 1033 (m), 996 (m), 983 (m), 880 (s), 796 (m), 756 (m), 737 (m), 725 (w), 665 (w) cm^{-1}. **Raman** (1064 nm, 800 mW): $\tilde{\nu}$ = 3020 (24), 3000 (35), 2977 (53), 2970 (72), 1745 (55), 1627 (29), 1595 (28), 1529 (24), 1464 (40), 1446 (38), 1406 (35), 1341 (59), 1325 (87), 1279 (57), 1249 (32), 1197 (31), 1181 (29), 1124 (29), 1099 (37), 1037 (55), 1001 (100), 891 (32), 806 (37), 764 (32), 726 (35), 463 (65), 454 (62), 401 (69), 299 (48), 279 (51) cm^{-1}. **MS** (DEI+) *m/e*: 239.1 [[M + H]$^+$]. C$_4$H$_6$N$_4$O$_8$ (238.11): calcd. C 20.18, H 2.54, N 23.53 %; found: C 20.17, H 2.61, N 23.40 %. DSC (5 °C·min^{-1}, onset): 151 °C (melt.), 157 °C (dec.). BAM drophammer: 40 J. Friction tester: 360 N (grain size 100–500 μm).

Propane-1,2,3-triyl tricarbamate (2b): ^{1}**H NMR** ([D$_6$]DMSO): δ = 6.57 (s, 6 H, NH_2), 4.87 (m, 1 H, CH), 4.04 (m, 4 H, CH_2) ppm. ^{13}**C{^{1}H} NMR** ([D$_6$]DMSO): δ = 156.9 (*C*ONH$_2$), 156.5 (*C*ONH$_2$), 70.2 (*C*H), 62.9 (*C*H$_2$) ppm. ^{14}**N NMR** ([D$_6$]DMSO): δ = –308 (*N*H$_2$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3431 (m), 3342 (m), 3279 (m), 3218 (m), 2966 (w), 2930 (w), 1710 (m), 1685 (s), 1616 (m), 1610 (m), 1470 (m), 1449 (m), 1409 (s), 1355 (m), 1344 (m), 1317 (s), 1247 (w), 1140 (s), 1070 (s), 1055 (s), 1041 (s), 978 (m), 939 (w), 928 (m), 868 (w), 829 (w), 780 (s), 751 (w), 762 (m) cm^{-1}. **Raman** (1064 nm, 500 mW): $\tilde{\nu}$ = 3413 (10), 3276 (13), 3249 (15), 3205 (27), 3020 (48), 2987 (57), 2968 (100), 2932 (57), 1696 (35), 1639 (25), 1630 (28), 1475 (21), 1456 (15), 1423 (22), 1299 (48), 1251 (25), 1128 (40), 1054 (18), 979 (29), 930 (68), 830 (67), 668 (36), 523 (22), 504 (60) cm^{-1}. **MS** (DEI+) *m/e*: 222.1 [[M + H]$^+$]. C$_6$H$_{11}$N$_3$O$_6$ (221.17): calcd. C 32.58, H 5.01, N 19.00 %; found: C 32.19, H 5.27, N 18.69 %. DSC (5 °C min^{-1}, onset): 167 °C (melt.). BAM drophammer: >40 J. Friction tester: >360 N (grain size <100 μm).

Propane-1,2,3-triyl tris(nitrocarbamate) (3b): ^{1}**H NMR** ([D$_6$]DMSO): δ = 13.6 (br., 3 H, NH), 5.47 (m, CH$_2$CHCH$_2$), 4.67 (m, 2 H, CHHCHCHH), 4.50 (m, 2 H, CHHCHCHH) ppm. ^{13}**C{^{1}H} NMR** ([D$_6$]DMSO): δ = 148.1 (*C*(OCH$_2$), 147.9 (*C*(OCH), 71.4 (O*C*H(CH$_2$)$_2$), 63.7 (O*C*H$_2$(CH)) ppm. ^{14}**N NMR** ([D$_6$]DMSO): δ = –46 (NH*N*O$_2$), –196 (br., *N*HNO$_2$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3513 (w), 3377 (w), 3145 (w), 3029 (w), 2869 (w), 2293 (w), 2261 (w), 1753 (s), 1608 (s), 1430 (m), 1404 (m), 1328 (m), 1283 (w), 1155 (vs), 1076 (m), 994 (m), 976 (m), 944 (m), 923 (m), 875 (m), 802 (m), 749 (m), 733 (m), 725 (m) cm^{-1}. **Raman** (1064 nm, 500 mW): $\tilde{\nu}$ = 3130 (10), 2980 (71), 2945 (81), 2903 (14), 2294 (8), 2261 (38), 1791 (22), 1760 (34), 1611 (17), 1461 (31), 1360 (29), 1326 (61), 1286 (26), 1241 (14), 1208 (13), 1142 (20), 1108 (25), 1078 (21), 1014 (100), 923 (17), 881 (11), 803 (16), 743 (12), 643 (8), 460 (46), 389 (31), 287 (17) cm^{-1}. **MS** (DEI+) *m/e*: 357.2 [[M + H]$^+$]. C$_6$H$_8$N$_6$O$_{12}$ (356.16): calcd. C 20.23, H 2.26, N 23.60 %; found: C 22.22, H 2.33, N 23.09 %. DSC (5 °C min^{-1}, onset): 152 °C (dec.). BAM drophammer: 8 J. Friction tester: 120 N (grain size <100 μm).

Nitroisobutylglycerol tricarbamate (2c): ^{1}**H NMR** ([D$_6$]acetone): δ = 6.16 (s, 6 H, NH_2), 4.49 (s, 6 H, CH_2) ppm. ^{13}**C{^{1}H} NMR** ([D$_6$]acetone): δ = 155.5 (*C*O), 89.6 (*C*NO$_2$), 61.2 (*C*H$_2$) ppm. ^{14}**N NMR** ([D$_6$]acetone): δ = –5 (*N*O$_2$), –299 (*N*H$_2$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3447 (w), 3349 (w), 3290 (w), 3223 (w), 1719 (s), 1703 (m), 1613 (m), 1560 (m), 1546 (m), 1467 (m), 1459 (m), 1449 (m), 1430 (w), 1396 (m), 1358 (m), 1333 (s), 1312 (m), 1299 (m), 1163 (m), 1106 (m), 1079 (s), 964 (w), 922 (w), 904 (w), 859 (w), 836 (w), 776 (w), 769 (m), 689 (w), 678 (w) cm^{-1}. **Raman** (1064 nm, 700 mW): $\tilde{\nu}$ = 3257 (13), 3202 (14), 3038 (38), 3002 (54), 2971 (100), 2900 (13), 1711 (37), 1648 (23), 1588 (12), 1549 (30), 1467 (40), 1439 (21), 1393 (17),

1362 (29), 1337 (22), 1317 (34), 1241 (28), 1202 (17), 1143 (37), 1110 (41), 1004 (19), 966 (17), 923 (94), 895 (35), 838 (65), 751 (17), 685 (29), 669 (24), 598 (27), 585 (32), 560 (31), 520 (27), 493 (28), 354 (46), 333 (29), 259 (51), 222 (26) cm^{-1}. **MS** (DEI+) m/e: 281.2 [[M + H]$^+$]. $C_7H_{12}N_4O_8$ (280.19): calcd. C 30.01, H 4.32, N 20.00 %; found: C 30.00, H 4.25, N 19.92 %. DSC (5 °C min^{-1}, onset): 188 °C (mp.), 202 °C (dec.). BAM drophammer: >40 J. Friction tester: >360 N (grain size 100–500 µm).

Nitroisobutylglycerol tris(nitrocarbamate) (3c): **^{1}H NMR** ([D$_6$]acetone): δ = 13.7 (br., 3 H, NH), 4.88 (s, 6 H, CH_2) ppm. **^{13}C{^{1}H} NMR** ([D$_6$]acetone): δ = 147.2 (CO), 88.2 (CNO$_2$), 62.6 (CH$_2$) ppm. **^{14}N NMR** ([D$_6$]acetone): δ = –8 (CNO$_2$), –46 (NHNO$_2$) ppm. **IR** (ATR): $\tilde{v}$ = 3247 (w), 3197 (w), 3053 (w), 2360 (w), 1772 (s), 1614 (s), 1571 (w), 1553 (m), 1445 (m), 1387 (w), 1355 (w), 1329 (m), 1198 (s), 1174 (s), 1012 (w), 979 (m), 955 (m), 861 (w), 819 (w), 801 (w), 747 (w), 718 (w) cm^{-1}. **Raman** (1064 nm, 500 mW): $\tilde{v}$ = 3198 (9), 3022 (18), 2983 (32), 2918 (10), 2708 (7), 1774 (43), 1619 (16), 1573 (10), 1555 (12), 1468 (33), 1357 (28), 1323 (42), 1268 (14), 1207 (14), 1180 (11), 1101 (12), 1031 (100), 981 (20), 862 (35), 816 (11), 732 (12), 647 (16), 464 (35), 350 (29), 234 (27) cm^{-1}. **MS** (DCI+) m/e: 416.2 [[M + H]$^+$]. $C_7H_9N_7O_{14}$ (415.18): calcd. C 20.25, H 2.18, N 23.62 %; found: C 20.34, H 2.33, N 23.92 %. DSC (5 °C min^{-1}, onset): 149 °C (dec.). BAM drophammer: 15 J. Friction tester: 360 N (grain size <100 µm).

But-2-yne-1,4-diyl dicarbamate (2d): **^{1}H NMR** ([D$_6$]DMSO): δ = 6.7 (br., 4 H, NH_2), 4.61 (s, 4 H, CH_2) ppm. **^{13}C{^{1}H} NMR** ([D$_6$]DMSO): δ = 156.3 (CO), 82.0 (C_{sp}), 51.8 (CH$_2$) ppm. **^{14}N NMR** ([D$_6$]DMSO): δ = –302 (NH$_2$) ppm. **IR** (ATR): $\tilde{v}$ = 3445 (m), 3333 (w), 3251 (m), 3188 (w), 2954 (w), 1722 (s), 1601 (m), 1445 (m), 1406 (m), 1319 (s), 1225 (m), 1154 (m), 1121 (m), 1039 (s), 1003 (m), 927 (m), 773 (s), 723 (m), 686 (w) cm^{-1}. **Raman** (1064 nm, 500 mW): $\tilde{v}$ = 3446 (3), 3247 (6), 3184 (6), 2980 (31), 2955 (100), 2903 (7), 2879 (9), 2327 (36), 2254 (79), 1714 (18), 1608 (13), 1454 (45), 1402 (22), 1335 (19), 1234 (24), 1136 (20), 1053 (20), 990 (13), 933 (37), 832 (15), 643 (33), 561 (38), 432 (26), 355 (73), 249 (18) cm^{-1}. **MS** (DEI+) m/e: 173.1 [[M + H]$^+$]. $C_6H_8N_2O_4$ (172.14): calcd C 41.86, H 4.68, N 16.27 %; found: C 41.69, H 4.67, N 16.49 %. DSC (5 °C·min^{-1}, onset): 187 °C (melt.), 264 °C (dec.). BAM drophammer: >40 J. Friction tester: >360 N (grain size <100 µm).

But-2-yne-1,4-diyl bis(nitrocarbamate) (3d): **^{1}H NMR** ([D$_6$]acetone): δ = 13.5 (br., 2 H, NH), 4.95 (s, 4 H, CH_2) ppm. **^{13}C{^{1}H} NMR** ([D$_6$]acetone): δ = 147.9 (CO), 81.0 (C_{sp}), 53.9 (CH$_2$) ppm. **^{14}N NMR** ([D$_6$]acetone): δ = –46 (NO$_2$), –199 (NH) ppm. **IR** (ATR): $\tilde{v}$ = 3168 (w), 3048 (w), 1737 (m), 1606 (m), 1442 (m), 1374 (m), 1319 (m), 1235 (m), 1189 (s), 1159 (s), 1011 (m), 995 (w), 936 (s), 816 (m), 754 (w), 731 (w), 662 (w) cm^{-1}. **Raman** (1064 nm, 500 mW): $\tilde{v}$ = 3173 (5), 2998 (20), 2967 (71), 2885 (7), 2336 (21), 2271 (25), 2258 (30), 1738 (20), 1628 (15), 1458 (14), 1442 (10), 1375 (38), 1329 (42), 1239 (8), 1196 (21), 1013 (100), 992 (14), 949 (10), 935 (12), 783 (10), 532 (12), 467 (26), 346 (41), 287 (5) cm^{-1}. **MS** (DEI+) m/e: 263.1 [[M + H]$^+$]. $C_6H_6N_4O_8$ (262.13): calcd. C 27.49, H 2.31, N 21.37 %; found: C 27.42, H 2.42, N 21.19 %. DSC (5 °C·min^{-1}, onset): 148 °C (dec.). BAM drophammer: 8 J. Friction tester: 240 N (grain size 100–500 µm).

Supporting Information (see footnote on the first page of this article): Selected bond lengths, angles, torsion angles, information on hydrogen bonds for the compounds 2a, 3a–d are available.

Acknowledgements

References

[1] J. Thiele, A. Lachman, *Justus Liebigs Ann. Chem.* **1895**, *288*, 267–311.

[2] a) Q. J. Axthammer, B. Krumm, T. M. Klapötke, *J. Org. Chem.* **2015**, *80*, 6329–6335; b) Q. J. Axthammer, B. Krumm, T. M. Klapötke, *Eur. J. Org. Chem.* **2015**, *2015*, 723–729; c) Q. J. Axthammer, T. M. Klapötke, B. Krumm, *Chem. Asian J.* DOI: 10.1002/asia.201501241.

[3] J. Köhler, R. Meyer, A. Homburg, *Explosivstoffe*, Wiley-VCH, Weinheim, Germany, **2008**.

[4] A. R. Modarresi-Alam, F. Khamooshi, M. Nasrollahzadeh, H. A. Amirazizi, *Tetrahedron* **2007**, *63*, 8723–8726.

[5] M. G. Kim, *J. Appl. Polym. Sci.* **2011**, *122*, 2209–2220.

[6] a) R. Graf, *Chem. Ber.* **1956**, *89*, 1071–1079; b) D. N. Dhar, K. S. K. Murthy, *Synthesis* **1986**, *1986*, 437–449.

[7] Q. J. Axthammer, T. M. Klapötke, B. Krumm, R. Moll, S. F. Rest, *Z. Anorg. Allg. Chem.* **2014**, *640*, 76–83.

[8] a) G. Gattow, W. K. Knoth, *Z. Anorg. Allg. Chem.* **1983**, *499*, 194–204; b) D. S. Bohle, Z. Chua, *Inorg. Chem.* **2014**, *53*, 11160–11172.

[9] a) T. Urbanski, W. Tarantowicz, *Bull. Acad. Pol. Sci. Ser. Sci. Chim. Geol. Geogr.* **1958**, *6*, 289–292; b) A. D. Nikolaeva, A. P. Kirsanov *SU504749A1* **1976**; c) S. Narasimhan, S. K. Srinivasan, N. Venkatasubramanian, *Magn. Reson. Chem.* **1987**, *25*, 91–92.

[10] T. M. Klapötke, *Chemistry of High-Energy Materials*, 2nd ed., de Gruyter, Berlin, **2012**.

[11] M. Sućeska, *EXPLO5 V.6.02*, Zagreb (Croatia), **2013**.

[12] M. Göbel, T. M. Klapötke, *Adv. Funct. Mater.* **2009**, *19*, 347–365.

[13] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[14] a) G. M. Sheldrick, SHELX-97, Programs for Crystal Structure Determination, **1997**; b) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[15] L. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

[16] A. Spek, *Acta Crystallogr., Sect. D* **2009**, *65*, 148–155.

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. B. G. Scalmani, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.

Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Rev. A.02 ed., Gaussian, Inc., Wallingford CT (USA), **2009**.

[18] R. D. Dennington II, T. A. Keith, J. M. Millam, *GaussView*, Ver. 5.08 ed., Semichem, Inc., Wallingford CT (USA), **2009**.

[19] J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532–6542.

[20] J. W. Ochterski, G. A. Petersson, J. A. Montgomery, *J. Chem. Phys.* **1996**, *104*, 2598–2619.

[21] E. F. C. Byrd, B. M. Rice, *J. Phys. Chem. B* **2005**, *109*, 1005–1013.

[22] M. Sućeska, *Propellants Explos. Pyrotech.* **1991**, *16*, 197–202.