

Fluorodinitroethyl Ortho-carbonate and -formate as Potential High Energy Dense Oxidizers

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Tetrakis(2-fluoro-2,2-dinitroethyl) ortho-carbonate (**1**) and tris(2-fluoro-2,2-dinitroethyl) ortho-formate (**2**) were synthesized by the reaction of carbon tetrachloride, respectively chloroform, with 2-fluoro-2,2-dinitroethanol and catalytic amounts of anhydrous iron(III) chloride. The compounds were characterized by single-crystal X-ray diffraction, vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis, and multi-temperature DSC measurements. The suitability of the compounds as potential oxidizers in energetic formulations has been investigated and discussed. The heats of formation of the products were determined experimentally using bomb calorimetric methods. With this value and the experimental (X-ray) density, several detonation parameters such as the detonation pressure, velocity, energy, and temperature were computed using the EXPLO5 code. The sensitivity towards impact, friction and electrostatic discharge was tested using the BAM drop hammer, a friction tester and a small-scale electrostatic discharge device.

Key words: Crystal Structure, Thermal Stability, 2-Fluoro-2,2-dinitroethyl, Ortho-carbonate, Ortho-formate

Introduction

In our current investigations we have focused our research towards highly nitrated CHNO compounds derived from 2,2,2-trinitroethanol as new potential chlorine free high energy dense oxidizers [1–7]. Especially the interesting compound tetrakis(2,2,2-trinitroethyl) ortho-carbonate seemed to be a promising candidate in replacing ammonium perchlorate (AP) as the widely used oxidizer in solid rocket propellants. AP comes along with known problems for the environment, like the large amount of hydrogen chloride produced during combustion. Additionally, scientific research indicates that perchlorate-contaminated water can disrupt the thyroid's ability to produce hormones needed for normal growth and development [8, 9]. Unfortunately, tetrakis(2,2,2-trinitroethyl) ortho-carbonate is very sensitive towards mechanical stimuli, which makes a future application rather unlikely.

A very important parameter for the development of new potential high energy dense oxidizers is the oxygen balance (Ω). It represents the relative amount of oxygen excess (or deficit) of a molecule, which can be used for further oxidation of an added fuel. For high energy dense oxidizers, this value should be positive and preferable greater than that of AP (34%). For calculating the oxygen balance of a CHFNO compound, it is assumed that the compounds are converted into H₂O, N₂, CO₂ and HF during the combustion. Alternatively, due to the high temperatures of combustion, CO can be assumed to be formed instead of CO₂. The oxygen balance can be calculated according to Eqs. 1 and 2 for a general formula C_aH_bF_cN_dO_e, where M is the molecular mass of the compound [9].

$$\Omega_{\text{CO}_2} = \frac{e - 2a - \frac{b-c}{2}}{M} \times 1600 \quad (1)$$

$$\Omega_{\text{CO}} = \frac{e - a - \frac{b-c}{2}}{M} \times 1600 \quad (2)$$

The specific impulse (I_s) is a key parameter for assessing the performance of a solid rocket propellant. It is proportional to the temperature inside the combustion chamber T_c and the reciprocal of the molecular weight of the decomposition products M (Eq. 3) [9].

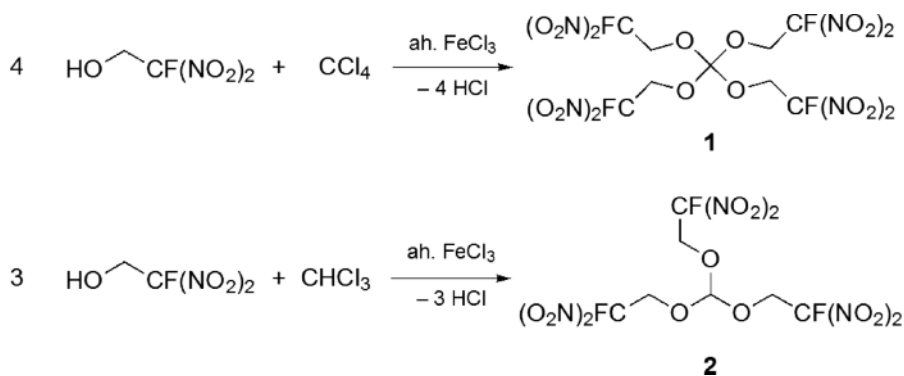
$$I_s \propto \sqrt{\frac{T_c}{M}} \quad (3)$$

An increase of the value for I_s by 20 s leads empirically to a doubling of the usual payload [9]. Obviously, it is of advantage, if the used oxidizer decomposes into small volatile molecules to increase the specific impulse of solid rocket boosters. Therefore, two interesting CHFNO derivatives, which were mentioned first in the 1960's with only very few analytical data [10–12], prior to our initial results [13], were investigated and are presented in this contribution.

Results and Discussion

Synthesis

The reaction of 2,2,2-trinitroethanol with carbon tetrachloride, respectively chloroform, with catalytic amounts of a Lewis acid is the literature known synthesis for 2,2,2-trinitroethyl ortho-carbonate and the corresponding ortho-formate, which has also been investigated in our group [1, 14]. By using 2-fluoro-2,2-dinitroethanol instead of 2,2,2-trinitroethanol for this type of reaction, tetrakis(2-fluoro-2,2-dinitroethyl) ortho-carbonate (**1**) and tris(2-fluoro-2,2-dinitroethyl) ortho-formate (**2**) were synthesized with anhydrous iron(III) chloride as Lewis acid (Scheme 1).



Scheme 1. Synthesis of ortho-carbonate **1** and -formate **2**.

NMR spectroscopy

In the ^1H NMR spectra of **1** and **2** the resonances for the methylene hydrogen atoms were found as doublets at 5.24 and 5.15 ppm with $^3J_{\text{H-F}}$ coupling constants of 16.2 and 16.7 Hz, respectively; the ortho-formate hydrogen atom was found at 6.11 ppm. The ^{19}F NMR resonances were detected as broadened multiplets at -112.1 (**1**) and -112.2 (**2**) ppm, due to overlapping effects of the quadrupolar influence of the ^{14}N nucleus and coupling with nitrogen and hydrogen. The ^{13}C NMR resonances for the ortho-carbonate and -formate carbon atoms were detected at 119.1 (**1**) and 112.2 (**2**) ppm. The fluorodinitromethyl carbon atoms were found as doublets at 119.7 (**1**) and 120.4 (**2**) ppm, both with $^1J_{\text{C-F}}$ couplings of 293.3 Hz, and broadened by the quadrupolar influence of the ^{14}N nucleus. The methylene carbon atoms appeared as doublets both at 62.9 ppm ($^2J_{\text{C-F}} = 20.1$ (**1**), 18.8 (**2**) Hz). The ^{14}N NMR resonances of the nitro groups were found at -25 (**1**) and -24 (**2**) ppm.

Vibrational spectroscopy

In the vibrational spectra of **1** and **2** the characteristic asymmetric NO_2 stretching vibrations were assigned in the range of $1611 - 1592 \text{ cm}^{-1}$, and the symmetric stretching vibrations at $1324 - 1311 \text{ cm}^{-1}$ (Table 1). The C–H stretching vibrations for **1** and **2** were found in the range of $3016 - 2859 \text{ cm}^{-1}$. C–N, C–O, C–F and C–C vibrations of **1** and **2** were observed in the expected ranges [15, 16].

Table 1. IR and Raman bands of **1** and **2**, characteristic vibrations and their assignments ^a.

	1		2	
	Raman	IR	Raman	IR
ν CH	3010 (25) 2969 (71) 2888 (10)	3012 (w) 2969 (w) 2897 (w)	2960 (42) 2890 (8) 2859 (9)	3016 (w) 2957 (w) 2893 (w)
ν_{as} NO ₂	1593 (40)	1592 (vs)	1611 (14) 1590 (24)	1606 (vs)
ν_{s} NO ₂	1317 (30)	1311 (s)	1324 (14)	1311 (vs)
δ CNO ₂ / ν chain	852 (100)	851 (m)	854 (100)	850 (m)

^a In cm⁻¹; Raman intensities in parentheses; IR intensities: vs = very strong, s = strong, m = medium, w = weak.

X-Ray diffraction

Because of an observed phase transition of **1** (α -**1** \rightleftharpoons β -**1**, for more details see below), only single crystals of β -**1** could be obtained by crystallization from chloroform. The modification β -**1** crystallizes in the tetragonal space group $P\bar{4}2_1c$ with two formula units per unit cell and a calculated maximum density of 1.84 g cm⁻³ at 258(2) K. The density is slightly higher compared to tetrakis(2,2,2-trinitroethyl) ortho-carbonate (1.81 g cm⁻³ at 258(2) K) [1], which

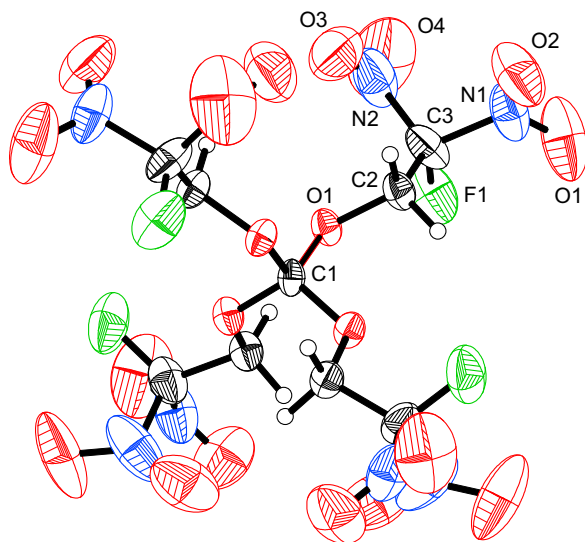


Fig. 1. Molecular structure of β -**1**. Displacement ellipsoids are shown at the 30% probability level. Selected distances (\AA) and angles (deg): C1–O1 1.386(3), O1–C2 1.422(7), C2–C3 1.48(1), C3–F1 1.38(1), C3–(NO₂)_{av.} 1.51; C1–O1–C2 115.7(3), O1–C2–C3 104.4(5), C2–C3–N1–O2 –22(2), C2–C3–N2–O4 51(1).

Table 2. Crystal data and numbers pertinent to data collection and structure refinement for β -**1**.

	β - 1
Empirical formula	C ₉ H ₈ F ₄ N ₈ O ₂₀
Formula weight, g mol ⁻¹	624.20
Temperature, K	258(2)
Crystal dimensions, mm ³	0.10 × 0.05 × 0.04
Crystal description	colorless block
Crystal system	tetragonal
Space group	$P\bar{4}2_1c$
a , \AA	11.027(3)
b , \AA	11.027(3)
c , \AA	9.254(6)
V , \AA^3	1125.3(9)
Z	2
$\rho_{\text{calcd.}}$, g cm ⁻³	1.84
$F(000)$, e	628
μ (MoK α), mm ⁻¹	0.2
Transmission max./min.	0.9921/0.9803
θ range, deg	4.13–25.21
Index ranges	–13 ≤ h ≤ 9; –13 ≤ k ≤ 13; –11 ≤ l ≤ 11
Refl. collected/unique/ R_{int}	5203/1005/0.054
Refl. obs. with $I > 2\sigma(I)$	645
Data/restraints/parameters	1005/0/93
$R1/wR2$ ($I > 2\sigma(I)$)	0.0897/0.2538
$R1/wR2$ (all data)	0.1257/0.2950
GOOF on F^2	1.037
x (Flack)	–4(6)
Residual electron density	–0.25/0.40
min/max, e \AA^{-3}	

also crystallizes in a tetragonal space group. All bond lengths and angles were found in the typical range for polynitro CH(F)NO compounds [17, 18]. The structure of β -**1** is shown in Fig. 1. The displacement vectors of β -**1** are shown only at the 30% probability level owing to the measurement temperature of 258 K. Below 247 K (–26 °C), α -**1** is the preferred conformation of **1**, which unfortunately could not be obtained as single crystals. The crystal structure and refinement data for β -**1** are given in Table 2.

The average N–O bond length of the fluorodinitromethyl moiety is 1.20(3) \AA . C1 is surrounded by four symmetry-equivalent oxygens (O1) in a tetrahedral coordination. In contrast to tetrakis(2,2,2-trinitroethyl) ortho-carbonate [1], the structure of β -**1** does not show attractive intramolecular interactions between the nitro groups. This structure motif is also found in the starting material 2-fluoro-2,2-dinitroethanol and further derivatives [6]. The C–F dis-

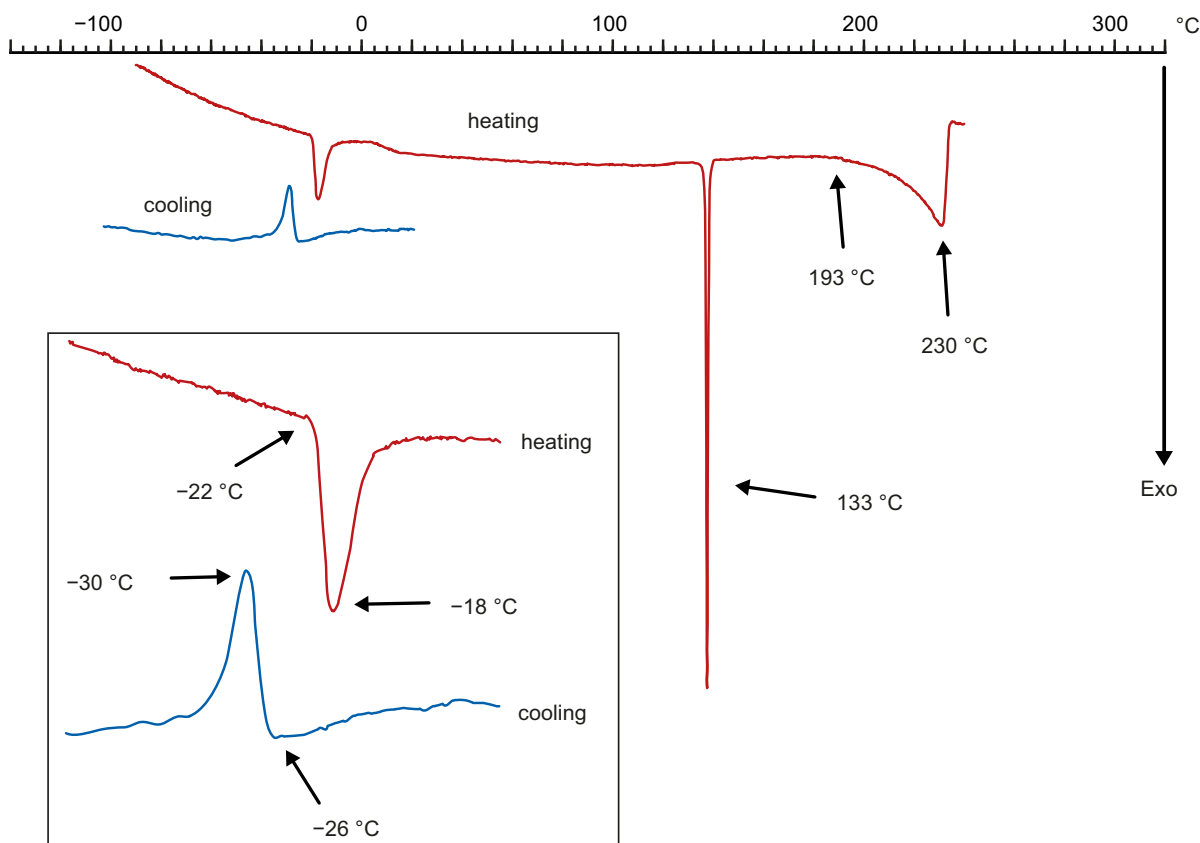


Fig. 2. DSC measurement of **1** from -100 to 240 °C with a cooling/heating rate of ± 5 °C min^{-1} .

tance with $1.38(3)$ Å is comparable with a C–F single bond and in the usual range for a fluorodinitromethyl moiety [6, 7, 13].

Thermal and energetic properties

The investigated physical and chemical properties of compound **1** and **2** are shown in Table 3. Even though compound **1** has to be prepared under inert gas conditions, the pure compound is stable towards moisture and air. DSC measurements of compound **1** have shown that the product melts at 133 °C. The compound starts to boil at 193 °C (onset), an exothermic decomposition was not detected at higher temperatures. Additional measurements at low temperatures revealed a phase transition (exothermic peak) between the α - and β -configuration of **1** starting at -26 °C (onset) during cooling the compound to -80 °C. Upon reheating the sample an endothermic signal appeared at

-22 °C (onset), which indicates the phase transition reversibility. The rate of heating was ± 5 °C. Therefore, the α -configuration of **1** is metastable above -22 °C. Between -26 and -22 °C both phases of **1** are coexistent (Fig. 2). 2,2-Dinitroethene-1,1-diamine (FOX-7) and tetrakis(2,2,2-trinitroethyl) ortho-carbonate show a comparable behavior between two different phases at a temperature of 116 °C for the former and with hysteresis between -16 and 33 °C for the latter one [1, 19].

The ortho-formate **2** was prepared under similar conditions as **1**. It is stable towards air and moisture and decomposes notably at 211 °C after melting at 110 °C. However, here no phase transition was observed.

The results of the performed sensitivity tests against friction, impact and electrostatic discharge (ESD) are given in Table 4. Compound **1** showed moderate sensitivities with 9 J (impact), 192 N (friction) and 0.25 J

Table 3. Physical and chemical properties of **1** and **2**.

	1	2
Formula	C ₉ H ₈ F ₄ N ₈ O ₂₀	C ₇ H ₇ F ₃ N ₆ O ₁₅
Mol. mass, g mol ⁻¹	624.20	472.16
T _m , °C ^a	133	110
T _d , °C ^b	193 (boiling)	211
N, % ^c	17.95	17.80
N + O, % ^d	69.21	68.63
Ω _{CO} , % ^e	23.1	20.3
Ω _{CO₂} , % ^f	0	-3.4
ρ, g cm ⁻³ ^g	1.84	1.80
-ΔU _f ^o , kJ kg ⁻¹ ^h	2548.7	2512.3
-ΔH _f ^o , kJ kg ⁻¹ ⁱ	1640.5	1224.6

^{a,b} Melting (T_m) and decomposition (T_d) point from DSC measurement carried out at a heating rate of 5 °C min⁻¹; ^c nitrogen content; ^d combined nitrogen and oxygen content; ^e oxygen balance assuming the formation of CO; ^f oxygen balance assuming the formation of CO₂; ^g experimentally determined density at ambient temperature from X-ray diffraction experiments (**1**) or pycnometer measurements (**2**); ^h energy of formation at 298 K; ⁱ heat of formation at 298 K.

(ESD). With 25 J towards impact and 0.45 J (ESD), compound **2** is even much less sensitive. Additionally, **2** is insensitive towards friction.

Predictions of the detonation parameters using the EXPLO5 code have been performed based on heats of formation calculated *ab initio* using the GAUSSIAN 09 program package [20, 21] (Table 4). The densities at ambient temperature needed for the estimation of the detonation parameters with the EXPLO5 code [22] were derived from the single-crystal X-ray structure for **1** and experimentally by gas pycnometer measurements for **2**. The resulting heats of detonation (Q_v), detonation temperatures (T), pressures (p) and velocities (D) for **1** and **2** are shown in Table 4, as well as the oxygen balances (Ω). The detonation velocity of **1** (8440 m s⁻¹) is comparable with that of pentaerythritol tetranitrate (PETN, 8400 m s⁻¹) and tetrakis(2,2,2-trinitroethyl) ortho-carbonate (8419 m s⁻¹) [1, 23]. The predicted velocity of **2** (8404 m s⁻¹) is only slightly below that of compound **1**.

The specific impulses of compounds **1** and **2** were calculated for compositions of 70% oxidizer (compound **1** or **2**), 16% aluminum, 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile and 2% bisphenol A ether modeled on rocket motor compositions for solid rocket boosters used by the NASA Space Shuttle program [25, 26]. These impulses were compared with the calculated impulse of ammonium perchlorate (AP) in an analogous composition. The chosen mixture with AP as oxidizer provides a spe-

Table 4. Predicted detonation and combustion parameters and sensitivity data for **1** and **2**.

	1	2
-Q _v , kJ kg ⁻¹	4539	4826
T _{ex} , K ^a	3800	3906
V ₀ , L kg ⁻¹ ^b	700	702
p, kbar ^c	372	362
D, m s ⁻¹ ^d	8440	8405
Impact, J ^e	9	25
Friction, N ^e	192	360
ESD, J ^f	0.25	0.45
Grain size, μm ^g	100–250	100–250
Thermal shock ^h	burns	burns
I _s , sec ⁱ	249	252
I _{s(comp)} , sec ^j	246	246
Ω _{comp} , % ^k	-53.96	-56.33

^a Temperature of the explosion gases; ^b volume of the explosion gases (assuming only gaseous products); ^c detonation pressure; ^d detonation velocity; ^e impact and friction sensitivities according to standard BAM methods [24]; ^f sensitivity towards electrostatic discharge; ^g grain size of the samples used for sensitivity tests; ^h response to fast heating in the “flame test”; ⁱ specific impulse of the neat compound predicted by the EXPLO5 code [22]; ^j specific impulse for compositions. The specific impulse for a similar composition with ammonium perchlorate (I_s(AP) = 258 s, Ω_{comp}(AP) = -30.13%) has been calculated; ^k oxygen balance for the composition used for combustion calculations.

cific impulse of 258 s. The impulses for **1** and **2** in the modeled compositions were calculated with a value of 246 s for both, which is below the predicted value for an AP composition. A reason might be the decreased oxygen balance within the mixture of -53.96% for **1** and -56.33% for **2**, respectively (Ω_{comp}(AP) = -30.13%). Interestingly, the impulses for the neat compounds **1** (249 s) and even 252 s for **2** are greater compared with the chosen mixtures and are therefore in the range of a typical composition using AP as oxidizer.

Conclusion

Tetrakis(2-fluoro-2,2-dinitroethyl) ortho-carbonate (**1**) and tris(2-fluoro-2,2-dinitroethyl) ortho-formate (**2**) were synthesized and fully characterized using multinuclear NMR, IR and Raman spectroscopy, as well as mass spectrometry and elemental analysis. These compounds were also examined in terms of sensitivity, compared with tetrakis(2,2,2-trinitroethyl) ortho-carbonate, and found to be less sensitive. Both materials might be of potential interest for application in metal-free propulsion systems.

Experimental Section

General procedures

The synthesis and manipulation of air- and moisture-sensitive materials were performed under an inert atmosphere of dry nitrogen in flame-dried glass vessels by Schlenk techniques [27]. The solvents carbon tetrachloride and chloroform (both Sigma Aldrich) were dried by standard methods and freshly distilled prior to use. Anhydrous iron(III) chloride and 2-fluoro-2,2-dinitroethanol were prepared according to literature known procedures [6, 28, 29]. Raman spectra were recorded with a Bruker MultiRAM FT-Raman instrument equipped with a Klatsch DENICAFC LC-3/40 Nd:YAG laser source ($\lambda = 1064$ nm, 300 mW) and a liquid nitrogen-cooled germanium detector. Infrared (IR) spectra were measured with a Perkin-Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSampIR II ATR device. All spectra were recorded at ambient temperature, the samples were neat solids. Densities were determined at ambient temperature using a Quantachrome Ultrapyc1200e gas pycnometer equipped with helium gas (Air Liquide, purity 5.6). NMR spectra were recorded at 25 °C with a Jeol Eclipse 400 instrument, and chemical shifts were determined with respect to external Me_4Si (^1H , 399.8 MHz; ^{13}C , 100.5 MHz), MeNO_2 (^{14}N , 28.9 MHz) and CCl_3F (^{19}F , 376.5 MHz). Mass spectrometric data were obtained with a Jeol MStation JMS 700 spectrometer (DEI+). Elemental analyses (C/H/N) were performed with an Elementar vario EL analyzer. Melting points were measured with a Perkin-Elmer Pyris6 DSC instrument, with a heating rate of 5 °C min^{-1} and checked by a Büchi Melting Point B-540 apparatus. Sensitivity data (impact, friction and electrostatic discharge) were performed with a drophammer, friction tester and electrostatic discharge device conform to the directive of the Federal Institute for Materials Research and Testing (BAM) [24].

Computational details

All quantum-chemical calculations were carried out using the program package GAUSSIAN 09 (revision C.01) [21], visualized with GAUSSVIEW 5 (version 5.0.8) [20]. The initial geometries of the structures were taken from the experimentally determined crystal structure (**1**) or from the previously calculated *ab initio*-optimized structure (**2**). The enthalpies (H) and free energies (G) were calculated by the complete basis set (CBS) method in order to obtain very accurate values [30–32]. The CBS model uses 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) structure 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 re-parametrized CBS-4M method additionally implements a MP4(SDQ)/6-31+(d,p) calculation to approximate higher-order contributions and also includes some additional empirical corrections [37, 38].

The solid-state enthalpies and energies of formation were calculated from the corresponding enthalpy derived from these quantum chemical CBS-4M calculations ($H_{\text{CBS-4M}}$). Therefore, the enthalpies of formation of the gas-phase species were computed according to the atomization energy method [30, 33–35]. All calculations affecting the detonation parameters were carried out using the program package EXPLO5 V6.01 [22, 36]. 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 [36, 37]. The specific impulses were also calculated with the EXPLO5 V6.01 program, assuming an isobaric combustion of a composition of 70% oxidizer, 16% aluminum (as fuel), 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile (both as binder) and 2% bisphenol A ether (as epoxy curing agent) [25, 26]. A chamber pressure of 70.0 bar and an ambient pressure of 1.0 bar with equilibrium expansion conditions were estimated for the calculations.

CAUTION! All nitrogen- and oxygen-rich compounds are potentially explosive energetic materials, although no hazards were observed during preparation and handling of these compounds. Nevertheless, this necessitates additional meticulous safety precautions (earthed equipment, Kevlar® gloves, Kevlar® sleeves, face shield, leather coat, and ear plugs). In addition, especially 2-fluoro-2,2-dinitroethanol shows significant degrees of toxicity [38, 39]. Data include our own recent results [40]. Particular care should be exercised in handling of these materials and derivatives.

Tetrakis(2-fluoro-2,2-dinitroethyl) ortho-carbonate (**1**)

2-Fluoro-2,2-dinitroethanol (1.54 g, 10.0 mmol) and anhydrous iron(III) chloride (0.15 g, 0.92 mmol) were diluted in carbon tetrachloride (4.2 mL) under careful exclusion of moisture. The mixture was heated up in an oil bath (85 °C) and refluxed for 24 h. The solvent was removed *in vacuo*. To remove the remaining iron(III) chloride, the residue was washed with iced dilute hydrochloric acid (25 mL, 1 M), and the product was filtered off. After crystallization of the crude product from chloroform, 0.89 g of **1** (57%) was obtained. – DSC: $T_m = 133$ °C, $T_{\text{dec}} = 193$ °C. – Raman: $\nu = 3010$ (25), 2969 (71), 2888 (10), 2794 (5), 1593 (40), 1455 (37), 1395 (18), 1359 (79), 1317 (30), 1255 (16), 1171 (6), 1116 (15), 1068 (21), 1025 (16), 930 (21), 859 (89), 852 (100), 815 (5), 806 (6), 775 (5), 747 (6), 579

(8), 518 (13), 468 (9), 421 (49), 377 (54), 351 (29), 306 (14), 266 (6), 213 (23) cm^{-1} . – IR: $\nu = 3012$ (w), 2969 (w), 2897 (w), 1740 (w), 1592 (vs), 1449 (w), 1402 (w), 1358 (w), 1311 (s), 1252 (w), 1159 (s), 1133 (s), 1109 (vs), 1067 (s), 1009 (m), 919 (w), 851 (m), 803 (s), 776 (w), 764 (w), 745 (w), 678 (w) cm^{-1} . – ^1H NMR ([D₆]acetone): $\delta = 5.24$ (d, CH_2 , $^3J_{\text{H-F}} = 16.2$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]acetone): $\delta = 119.7$ (d, $\text{CF}(\text{NO}_2)_2$, $^1J_{\text{C-F}} = 293.3$ Hz), 119.1 ($\text{C}(\text{OCH}_2)_4$), 62.9 (d, OCH_2 , $^2J_{\text{C-F}} = 20.1$ Hz). – ^{19}F NMR ([D₆]acetone): $\delta = -112.1$ (m, br, $\text{CF}(\text{NO}_2)_2$). – ^{14}N NMR ([D₆]acetone): $\delta = -25$ (NO_2). – MS (DEI+): m/z (%) = 471 (5) $[\text{M-OCH}_2\text{CF}(\text{NO}_2)_2]^+$, 395 (2) $[\text{M-CH}_2\text{CF}(\text{NO}_2)_2-2 \text{NO}_2]^+$, 319 (4) $[\text{M-2 OCH}_2\text{CF}(\text{NO}_2)_2+\text{H}]^+$, 137 (18) $[\text{CH}_2\text{CF}(\text{NO}_2)_2]^+$, 46 (35) $[\text{NO}_2]^+$, 30 (100) $[\text{NO}]^+$. – EA for $\text{C}_9\text{H}_8\text{F}_4\text{N}_8\text{O}_{20}$ (624.20): calcd. C 17.32, H 1.29, N 17.95; found C 17.39, H 1.24, N 17.72%. – Sensitivities (grain size: 100–500 μm): impact: 9 J; friction: 192 N; electrostatic: 0.25 J.

Tris(2-fluoro-2,2-dinitroethyl) ortho-formate (2)

2-Fluoro-2,2-dinitroethanol (2.5 g, 16.2 mmol) and anhydrous iron(III) chloride (0.2 g, 1.23 mmol) were dissolved in dry chloroform (5 mL) under careful exclusion of moisture. The mixture was heated up in an oil bath (85 °C) and refluxed for 120 h. Upon cooling, the reaction mixture was poured into diethyl ether (60 mL). The ether phase was washed with water (3 \times 60 mL) and dried over sodium sulfate. Removing the solvent left a cream-colored crude product, which was re-crystallized from dichloromethane/pentane (50 : 50). 1.9 g (74%) of **2** was obtained as colorless crystals. – DSC: $T_m = 110$ °C, $T_{\text{dec}} = 211$ °C. – Raman: $\nu = 2960$ (42), 2890 (8), 2859 (9), 2427 (3), 1611 (14), 1590 (24), 1456 (18), 1397 (11), 1375 (20), 1358 (35), 1324 (14), 1246 (9), 1118 (10), 1079 (8), 1025 (11), 969 (5), 924 (8), 854 (100), 760 (4), 725 (3), 625 (4), 542 (10), 421 (28), 380 (37), 361 (23), 300 (5), 221 (5) cm^{-1} . – IR: $\nu = 3016$ (w), 2957 (w), 2893 (w), 1606 (vs), 1452 (w), 1399 (w), 1311 (vs), 1250 (w), 1172 (w), 1134 (s), 1114 (s), 1074 (s), 1026 (m), 1010 (m), 928 (w), 850 (m), 817 (w), 801 (vs), 761 (w) cm^{-1} . – ^1H NMR ([D₆]acetone): $\delta = 6.11$ (CH), 5.15 (d, CH_2 , $^3J_{\text{H-F}} = 16.7$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]acetone): $\delta = 120.4$ (d, $\text{CF}(\text{NO}_2)_2$, $^1J_{\text{C-F}} = 293.3$ Hz), 112.2 ($\text{CH}(\text{OCH}_2)_3$), 62.9 (d, OCH_2 , $^2J_{\text{C-F}} = 18.8$ Hz). – ^{19}F NMR ([D₆]acetone): $\delta = -112.2$ (m, br, $\text{CF}(\text{NO}_2)_2$). – ^{14}N NMR ([D₆]acetone): $\delta = -24$ (NO_2). – MS (DEI+): m/z (%) = 471 (1) $[\text{M-H}]^+$, 319

(10) $[\text{M-OCH}_2\text{CF}(\text{NO}_2)_2]^+$, 137 (16) $[\text{CH}_2\text{CF}(\text{NO}_2)_2]^+$, 91 (4) $[\text{CH}_2\text{CFNO}_2]^+$, 46 (23) $[\text{NO}_2]^+$, 30 (100) $[\text{NO}]^+$. – EA for $\text{C}_7\text{H}_7\text{F}_3\text{N}_6\text{O}_{15}$ (472.16): calcd. C 17.81, H 1.49, N 17.80; found C 17.88, H 1.47, N 17.60%. – Sensitivities (grain size: 100–250 μm): impact: 25 J; friction: 360 N; electrostatic: 0.45 J.

X-Ray structure determination

For compound **1**, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using MoK_α radiation ($\lambda = 0.71073$ Å). The structures were solved by Direct Methods (SIR97 [41]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [42–44]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference Fourier maps and placed with a C–H distance of 0.99 Å for CH_2 groups. Table 2 summarizes the most important crystal structure data.

CCDC 951973 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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