Supporting Information

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1. Experimental part and general methods

Caution! 3,3-Dinitratooxetane is a powerful energetic material with high sensitivities towards shock and friction. Therefore, proper security precautions (safety glass, face shield, earthened equipment and shoes, Kevlar gloves and ear plugs) have to be applied while synthesizing and handling the described compounds.

Chemicals and solvents were employed as received (Sigma-Aldrich, Acros, TCI, Spirochem AG). ^{1}H, ^{13}C and ^{14}N spectra were recorded using a Bruker AMX 400 instrument. The chemical shifts quoted in ppm refer to tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{14}N). Decompositions temperatures were determined on a Mettler Toledo DSC822e at a heating rate of 5 °C min^{-1} using 40 μL aluminum crucibles and nitrogen purge gas at a flow rate of 30 mL min^{-1}. Evaluations of thermal behavior were performed using the STAR^{e} Software Version 16.20. Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum One FT-IR instrument. Raman spectra were obtained using a Bruker MultiRam FT Raman spectrometer and a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (λ = 1064 nm, 1074 mW) . Elemental analyses were performed with an Elementar Vario el by pyrolysis of the sample and subsequent analysis of formed gases (standard deviation liquids: +/- 0.5%). The sensitivity data were collected using a BAM (Bundesanstalt für Materialforschung) drophammer[S1] according to STANAG 4489[S2] modified instruction[S3] and a BAM friction tester[S1] according to STANAG 4487[S4] modified instruction. [S5] The classification of the tested compounds results from the 'UN Recommendations on the Transport of Dangerous Goods'. [S6]

1.1 3,3-Dinitratooxetane

Oxetan-3-one (0.50 g, 6.94 mmol, 1.0 eq.) was dissolved in acetonitrile (5 mL) and added to a solution of dinitrogen pentoxide (2.25 g, 20.8 mmol, 3.0 eq.) in acetonitrile (10 mL) which was cooled to 0 °C. The mixture was stirred for 1 hour at 0 °C and then let come to ambient temperature over 30 minutes. The solution was poured into ice-water (70 mL) and was extracted with ethyl acetate (3x 25 mL). The organic layer was washed with saturated bicarbonate solution (2x 30 mL) prior to drying over sodium sulfate. The solvent was removed, and the product was dried under high vacuum to give 0.51 g of 3,3-dinitratooxetane (2.83 mmol, 41%) as colorless solid. The product has to be stored at -20°C under dry atmosphere to prevent decomposition. **DSC** (T_{onset}, 5 °C min^{-1}): 69.4 °C (mp.) , 93.3 °C (dec.); **FT-IR** (ATR): $\tilde{\nu}$ = 2962 (w), 1687 (m), 1655 (s), 1445 (w), 1305 (s), 1286 (m), 1180 (m), 1158 (s), 1113 (m), 982 (s), 961 (m), 935 (w), 884 (m), 842 (m), 791 (s), 739 (s), 669 (s), 591 (m), 438 (m) cm^{-1}; **^{1}H NMR** (400 MHz, Acetone-d$_6$, 25 °C): δ = 5.11 (s, 4H) ppm; **^{13}C NMR{^{1}H}** (101 MHz, Acetone-d$_6$, 25 °C): δ = 77.5, 103.8 ppm; **^{14}N NMR** (27 MHz, Acetone-d$_6$, 25 °C): δ = –56.3 ppm; **EA** ($C_3H_4N_2O_7$) calcd.: C 20.01, H 2.24, N 15.56; found: C 20.25, H 2.52, N 15.29; **BAM drophammer** < 1 J (> 500 µm); **Friction test** 1 N (> 500 µm).

1.2 3-Nitratooxetane

3-Nitratooxetane was prepared according to modified literature procedures. [S7]

Acetic anhydride (6.00 g, 58.8 mmol) was dissolved in dry dichloromethane (5.00 mL) and white fuming nitric acid (100%, 3.90 g, 61.9 mmol) was added at -10 °C using an ice bath with sodium chloride. The mixture was stirred for one hour prior to the addition of oxetan-3-ol (3.00 g, 40.5 mmol) in dry dichloromethane (5.00 mL). The solution was stirred for one hour and then poured onto ice (15.0 g). Dichloromethane (10.0 mL) was added and the layers were separated. The organic layer was washed with saturated sodium bicarbonate solution (3x 20 mL) and separated. The solvent was then removed by rotary evaporation to give a slightly yellowish liquid and sodium bicarbonate solution (10%, 20.0 mL) was added. The resulting emulsion was heavily stirred for 30 minutes (to remove any traces of acetyl nitrate) and the target compound subsequently extracted with dichloromethane (3x 30 mL). After drying over sodium sulfate, the solvent was removed to give 2.78 g (23.3 mmol, 58%) of 3-nitratooxetane as slightly yellowish liquid. The product may be further purified by distillation (27 mbar, 65 °C) to give colorless 3-nitratooxetane suitable for polymerization reactions.

DSC (T_{onset}, 5 °C min^{-1}): 152.8 °C (dec.); **FT-IR** (ATR): $\tilde{\nu}$ = 3112 (w), 2961 (m), 2887 (w), 2803 (w), 1629 (vs), 1373 (m), 1327 (m), 1275 (vs), 1175 (m), 1069 (m), 975 (s), 928 (w), 881 (s), 846 (s), 754 (m), 690 (m), 556 (w), 404 (w) cm^{-1}. **Raman** (1064 nm, 1074 mW): $\tilde{\nu}$ = 2975 (100), 2932 (78), 2892 (88), 1642 (14), 1480 (36), 1374 (32), 1328 (22), 1279 (63), 1177 (36), 1116 (20), 1071 (47), 1042 (27), 977 (15), 932 (32), 853 (75), 693 (25), 558 (41), 406 (19) $cm^{-}1$; **^{1}H NMR** (400 MHz, Acetone-d_6, 25 °C): δ = 4.68 (ddd, 2H, CH_2, *J* = 8.2, 4.9, 1.1 Hz), 4.93 (ddd, 2H, CH_2, *J* = 8.3, 6.2, 1.2 Hz), 5.68 (tt, 1H, CH, *J* = 6.2, 4.9 Hz) ppm; **^{13}C NMR{^{1}H}** (101 MHz, Acetone-d_6, 25 °C): δ =74.8, 75.3 ppm; **^{14}N NMR** (27 MHz, Acetone-d_6, 25 °C): δ = –45.6 ppm; **EA** ($C_3H_4N_2O_7$) calcd.: C 30.26, H 4.23, N 11.76; found: C 29.76, H 3.73, N 11.49; **BAM drophammer** > 40 J; **Friction test** > 160 N.

1.3 3-Nitrato-3-methyloxetane

3-Hydroxy-3-methyloxetane (0.50 g, 5.67 mmol) was added to a solution of dinitrogen pentoxide (674 mg, 6.24 mmol, 1.1 eq.) in dry dichloromethane (15 mL) at 0 °C using an ice-bath. The resulting solution was stirred for 1 h at the initial temperature and subsequently poured into ice-water (50 mL). Additional dichloromethane (20 mL) was added and the phases were separated. The organic phase was washed again with water (30 mL) and finally with saturated sodium bicarbonate solution (25 mL) prior to drying over sodium sulfate. The solvent was removed by rotary evaporation to give 0.74 g (3.92 mmol, 69%) as yellow liquid.

DSC (5 °C min^{-1}): 141.0 °C (dec.); **FT-IR** (ATR): $\tilde{\nu}$ = 3113 (m), 2962 (m), 2887 (m), 2803 (m), 1754 (w), 1628 (s), 1447 (m), 1385 (s), 1304 (vs), 1254 (m), 1178 (s), 1138 (m), 977 (s), 925 (m) ,850 (s), 755 (m), 691 (m) cm^{-1}. **Raman** (1064 nm, 1074 mW): $\tilde{\nu}$ = 2977 (69), 2942 (100), 2888 (70), 2751 (7), 1636 (11), 1480 (24), 1461 (19), 1349 (8), 1306 (47), 1254 (11), 1191 (12), 1139 (13), 992 (31), 982 (35), 855 (37), 736 (12), 693 (13), 506 (35), 433 (19) cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 1.81 (s, 3H, CH_3), 4.52 (d, 2H, CH_2, *J* = 8.6 Hz), 4.78 (d, 2H, CH_2, *J* = 8.6 Hz) ppm; **^{13}C-NMR{^{1}H}** (101 MHz, $CDCl_3$, 25 °C): δ = 20.6, 79.8, 83.4 ppm; **^{14}N NMR** (27 MHz $CDCl_3$, 25 °C): δ = –46.2 ppm; **EA** ($C_3H_4N_2O_7$) calcd.: C 36.10, H 5.30, N 10.52; found: C 36.37, H 5.17, N 10.26; **BAM drophammer** > 40 J; **Friction test** >160 N.

2. NMR Spectra of prepared compounds

2.1 3,3-Dinitratooxetane

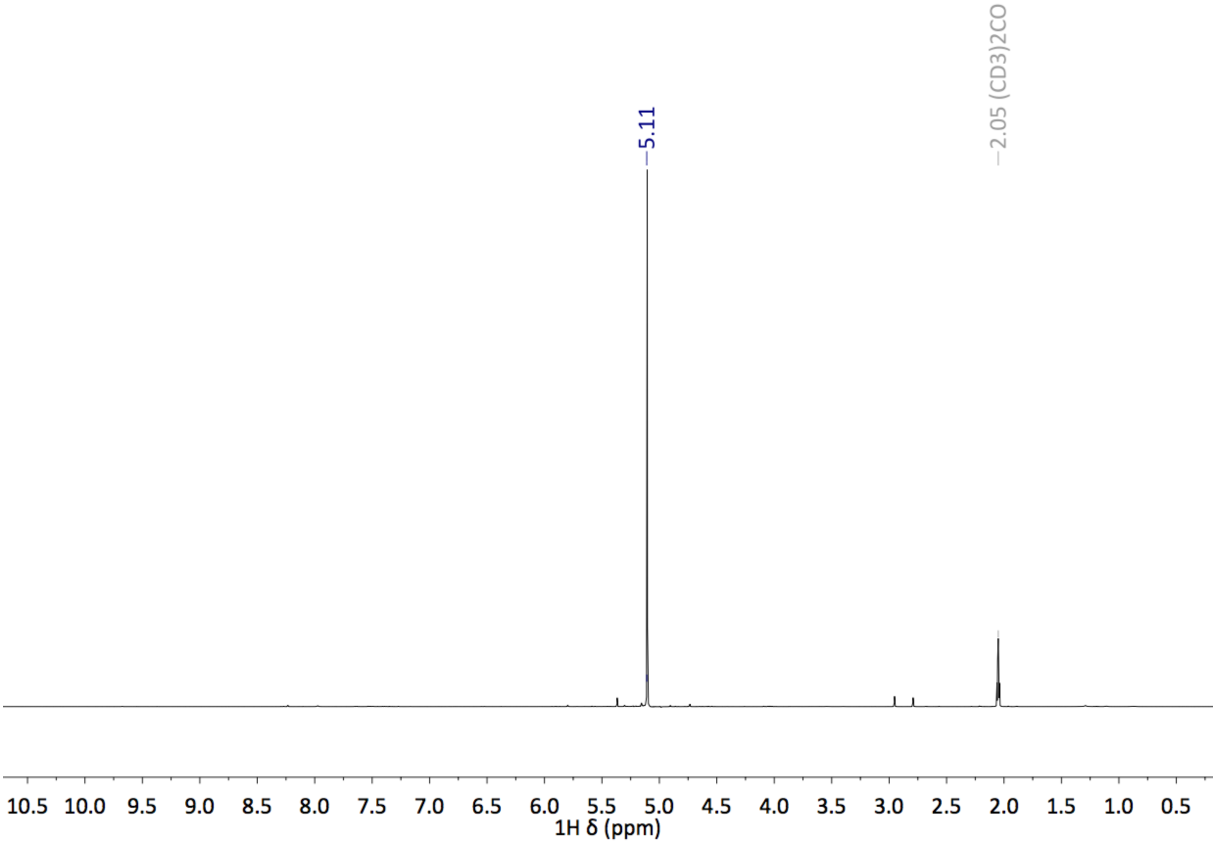

Figure S1: *Proton spectrum (^{1}H) of 3,3-dinitratooxetane.*

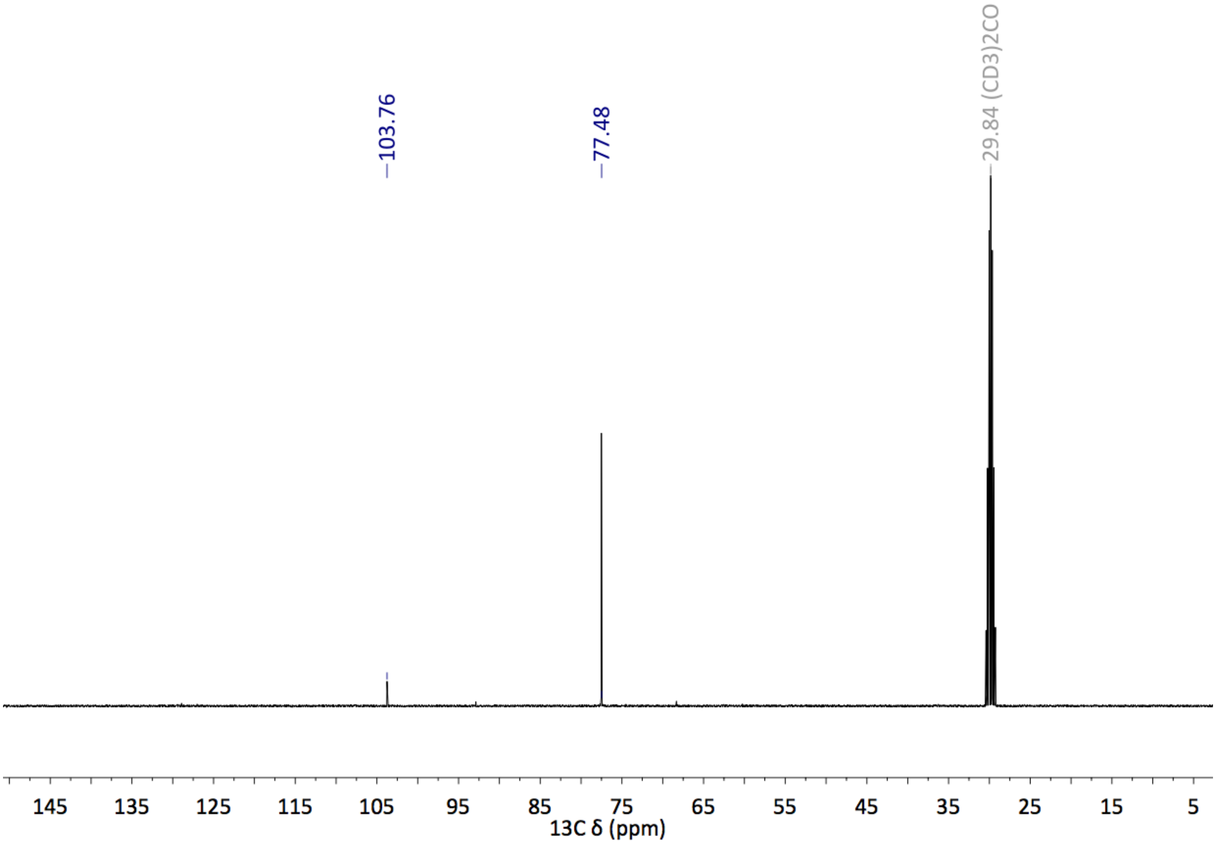

***Figure S2**: Carbon spectrum (^{13}C) of 3,3-dinitratooxetane.*

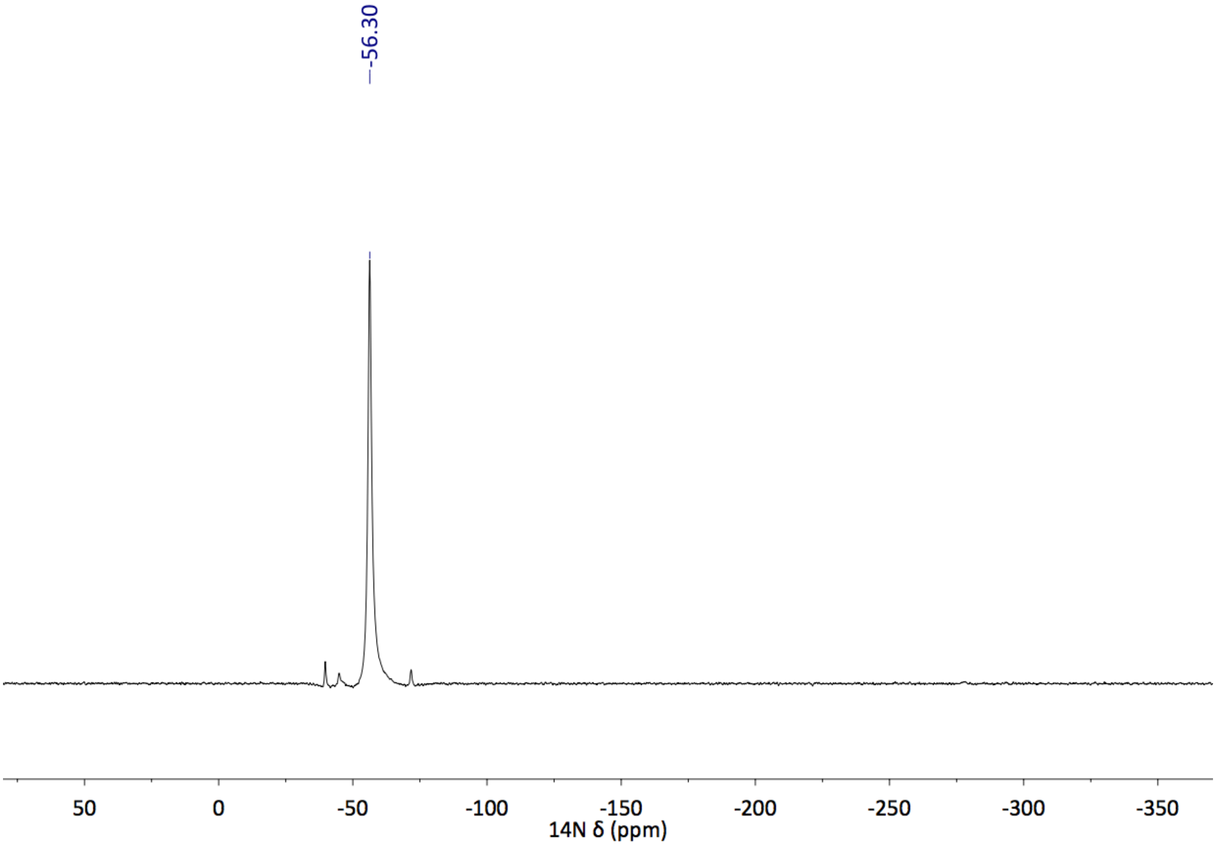

Figure S3: *Nitrogen spectrum (^{14}N) of 3,3-dinitratooxetane.*

2.2 3-Nitratooxetane

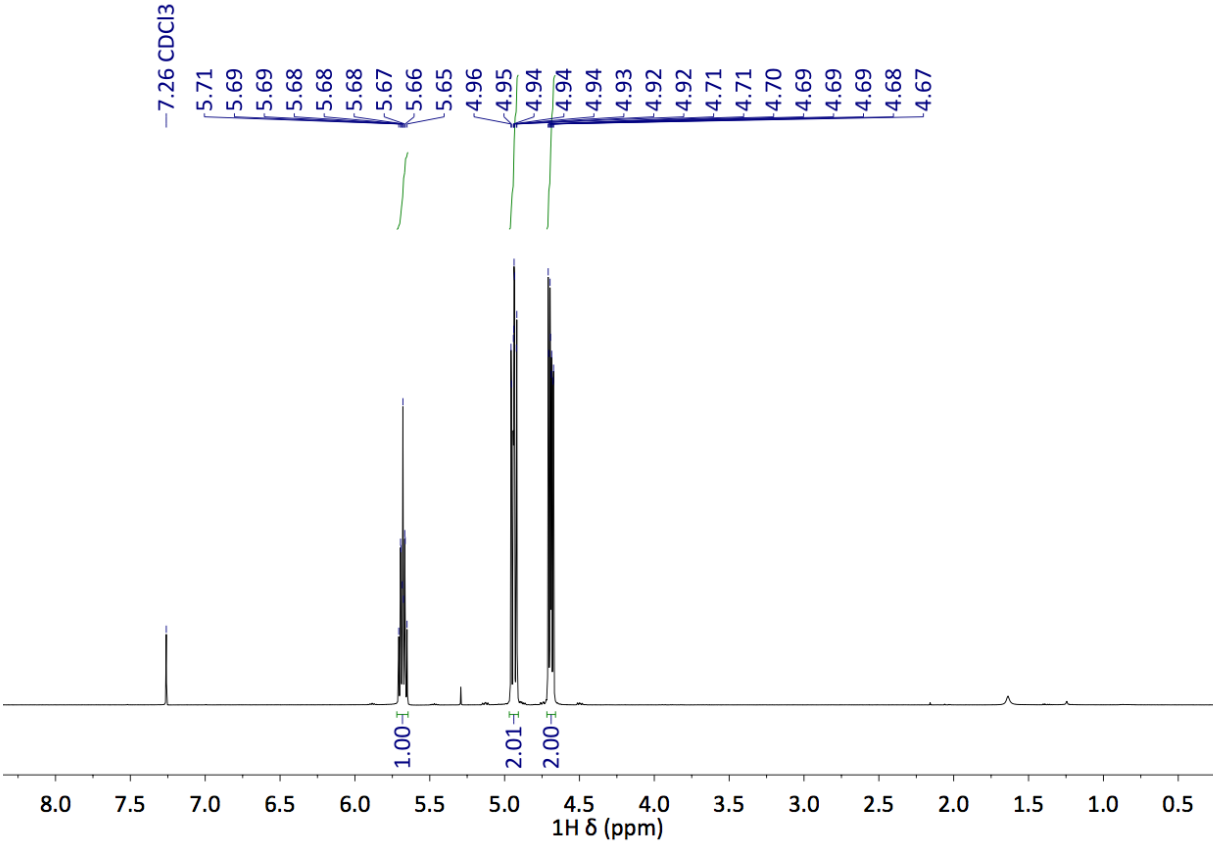

Figure S4: *Proton spectrum (^{1}H) of 3-nitratooxetan.*

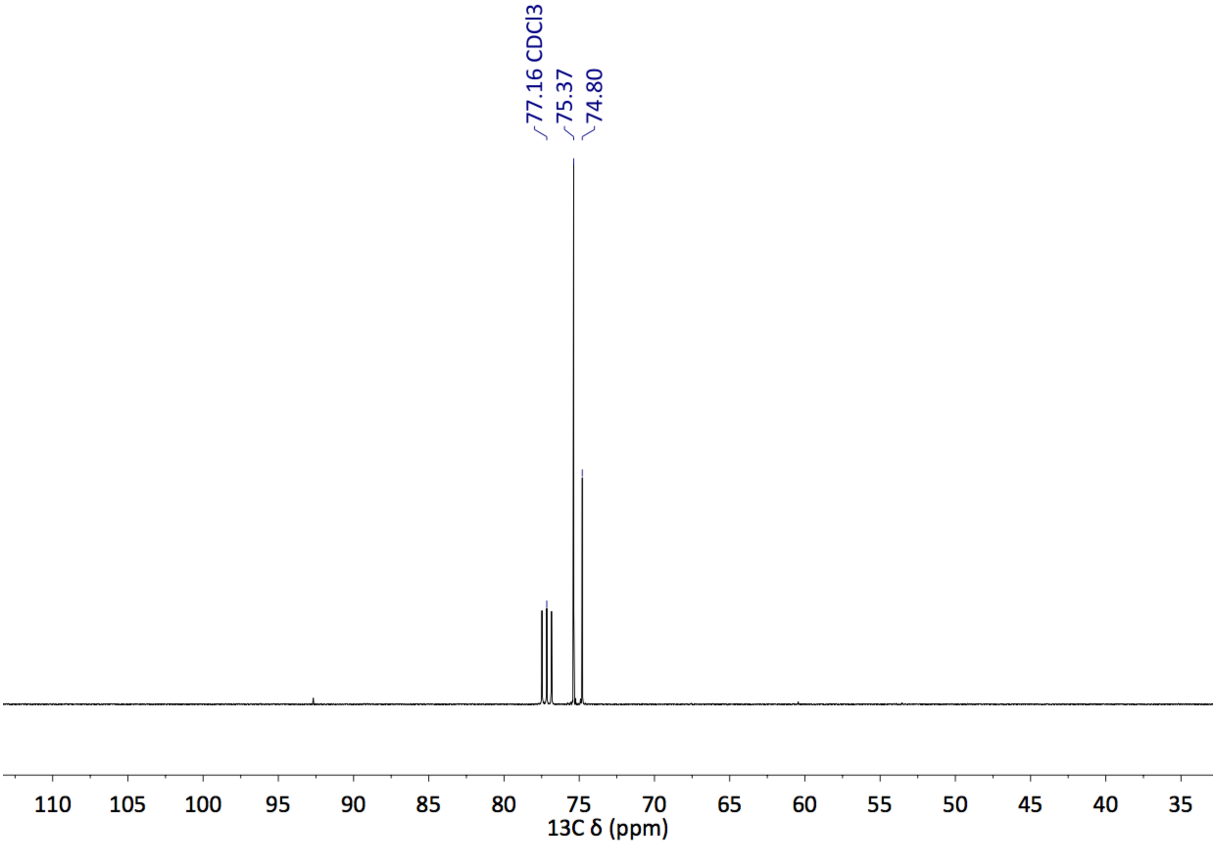

Figure S5: *Carbon spectrum (^{13}C) of 3-nitratooxetane.*

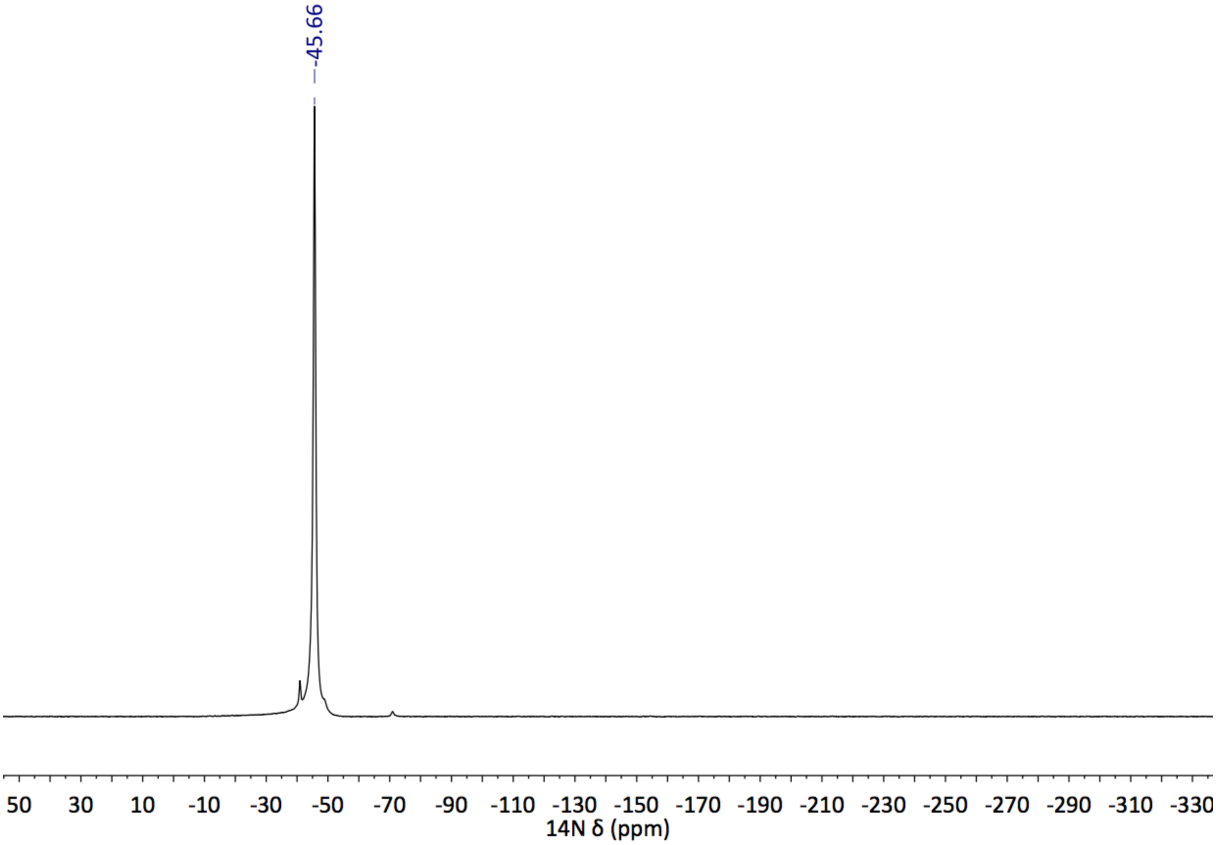

Figure S6: *Nitrogen spectrum (^{14}N) of 3-nitratooxetane.*

2.3 3-Nitrato-3-methyloxetane

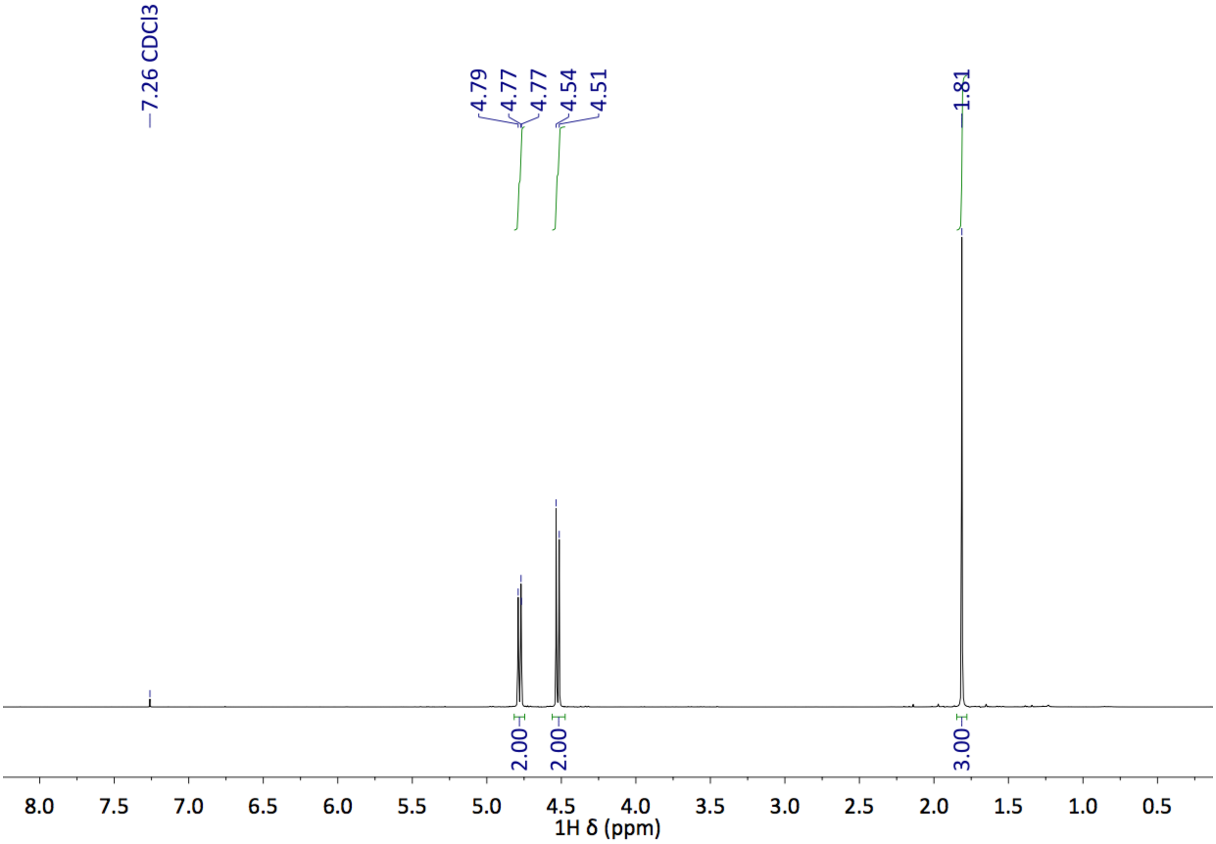

Figure S7: *Proton spectrum (^1H) of 3-nitrato-3-methyloxetane.*

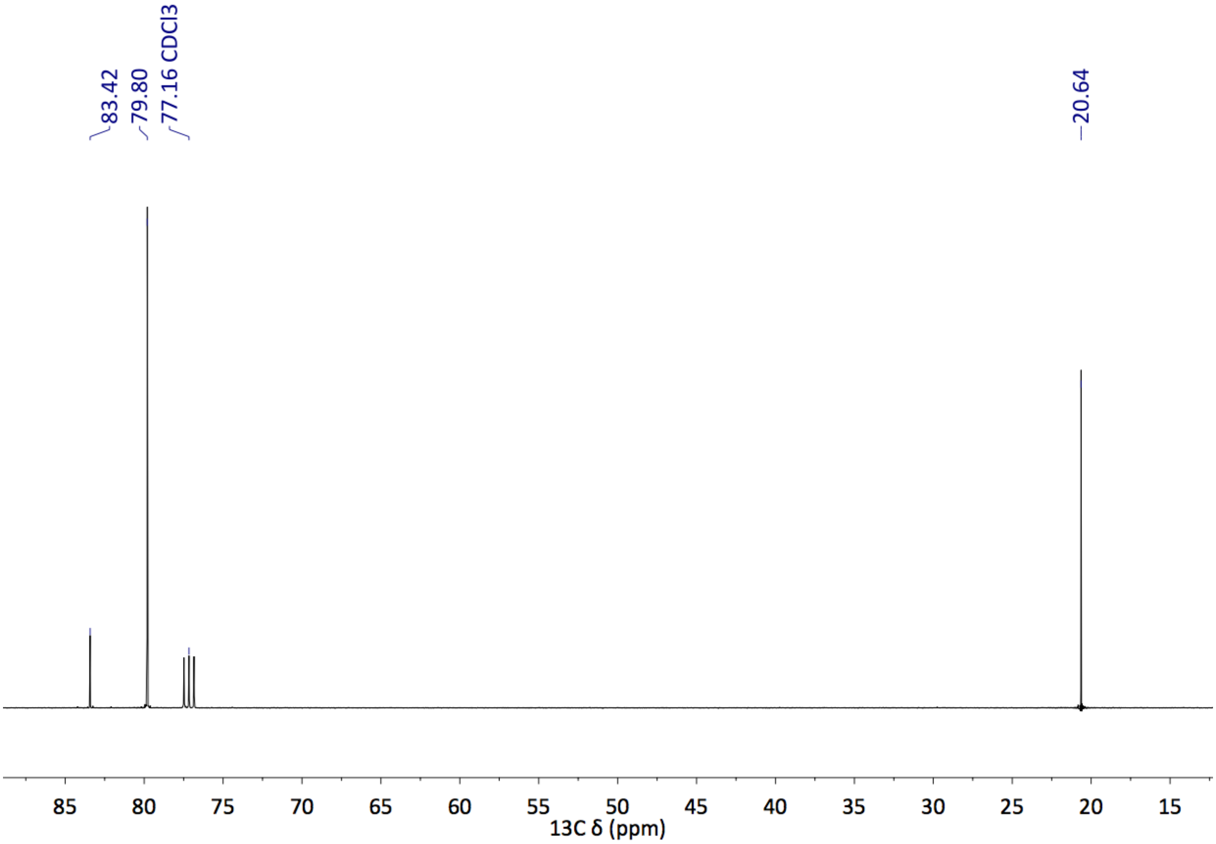

Figure S8: *Carbon spectrum (^{13}C) of 3-nitrato-3-methyloxetane.*

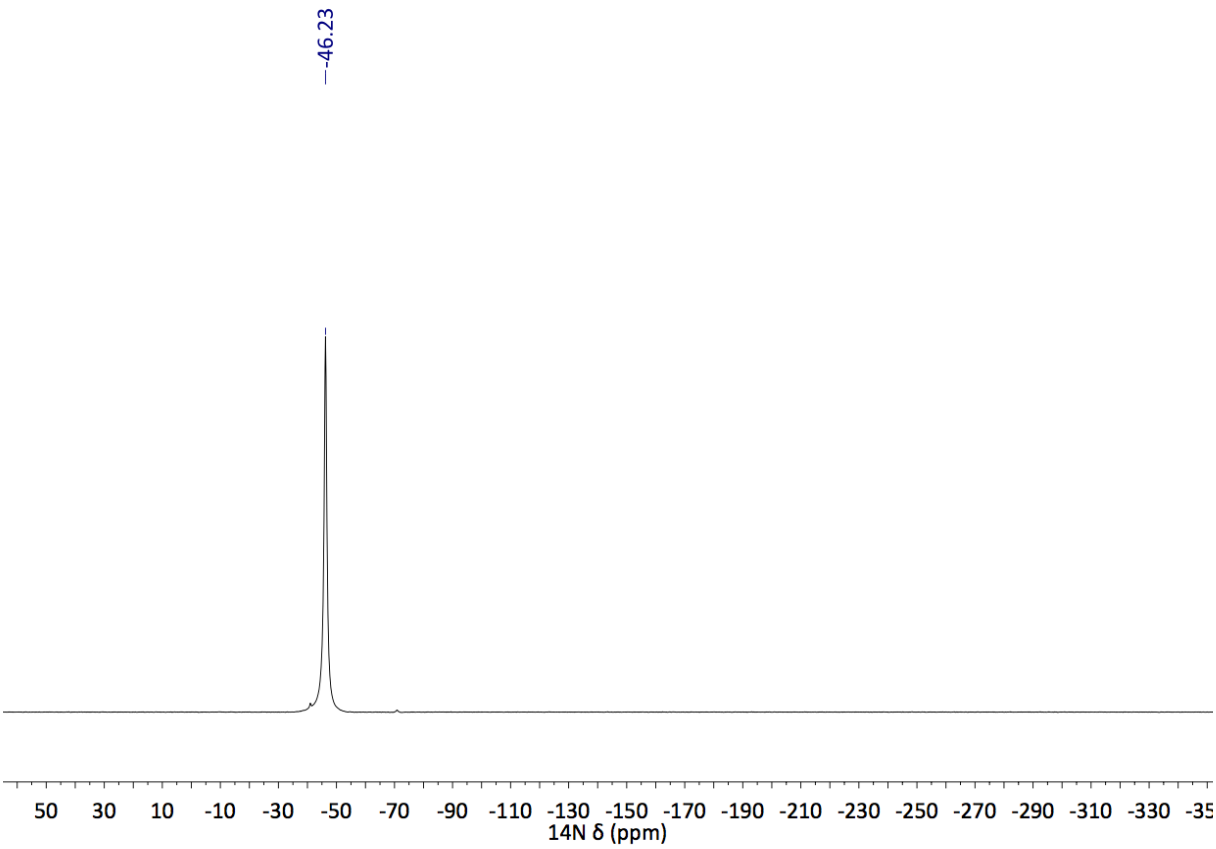

Figure S9*: Nitrogen spectrum (^{14}N) of 3-nitrato-3-methyloxetane.*

3. X-Ray Diffraction & Hirshfeld Analysis

The crystals unfortunately had a twinning problem. Data collection was performed with an Oxford Xcalibur3 diffractometer with a CCD area detector, equipped with a multilayer monochromator; a Photon 2 detector and a rotating-anode generator were employed for data collection using Mo Kα radiation (λ = 0.7107 Å). Data collection and reduction were carried out using the CRYSALISPRO software. [S8] The structures were solved by direct methods (SIR-2014) [S9] and refined (SHELXLE) [S10] by full-matrix least-squares on F2 (SHELXL) [S11, S12] and finally checked using the PLATON software[S13] integrated in the WINGX software suite. [S14] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located and freely refined. All Diamond 3 plots are shown with thermal ellipsoids at the 50% probability level, and hydrogen atoms are shown as small spheres of arbitrary radius. The twin reflexes were cut out.

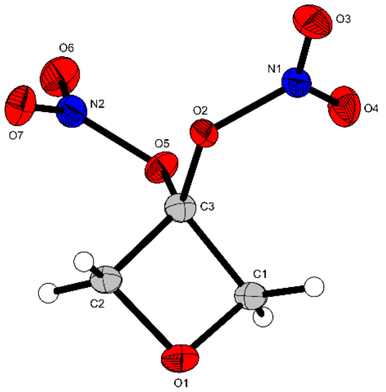

Figure S10*: Molecular structure of 3,3-dinitratooxetane. Thermal ellipsoids are drawn at 50% probability level.*

Table 1*: Detailed crystallographic information of 3,3-dinitratooxetane (****1****).*

	1
Formula	$C_3H_4N_2O_7$
FW [g mol^{-1}]	180.08
Crystal System	monoclinic
Space Group	$P2_1/c$
Color / Habit	colorless block
Size [mm]	0.20 x 0.12 x 0.05
a [Å]	9.259(2)
b [Å]	12.501(3)
c [Å]	5.7467(11)
α [°]	90
β [°]	92.46(2)
γ [°]	90
V [Å ^{3}]	664.6(3)
Z	4
$\rho_{calc.}$ [g cm^{-3}]	1.800
μ [mm^{-1}]	0.183
F (000)	368
$\lambda_{MoK\alpha}$ [Å]	0.71073
T [K]	107
ϑ min-max [°]	2.739, 26.370
Dataset h; k; l	-11:11; -8:15; -7:7
Reflect. coll.	1313
Independ. Refl.	1313
$R_{int.}$	0.057
Reflection obs.	822
No. parameters	109
R1 (obs.)	0.0749
wR2 (all data)	0.1672
S	1.049
Resd. Dens. [e Å^{-3}]	-0.395, 0.365
Device Type	Oxford XCalibur3 CCD
Solution	Sir2014
Refinement	SHELXLE
Absorpt. corr.	Multi-scan
CCDC	2013564

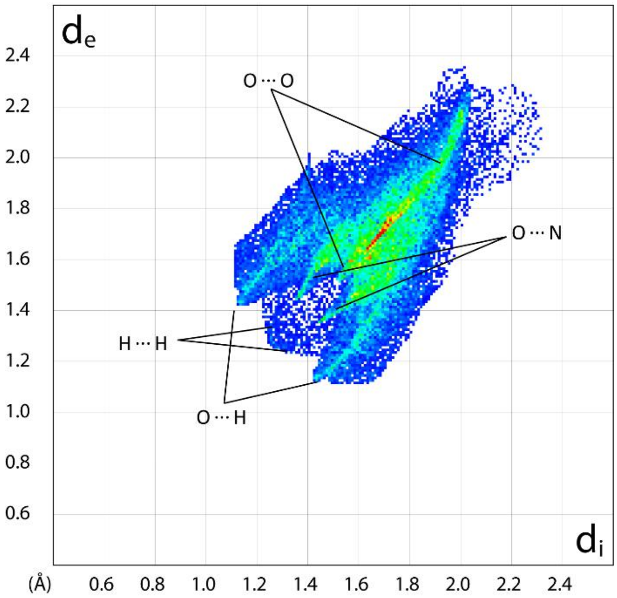

Figure S11: Two-dimensional fingerprint plot in crystal stacking of 3,3-dinitratooxetane.

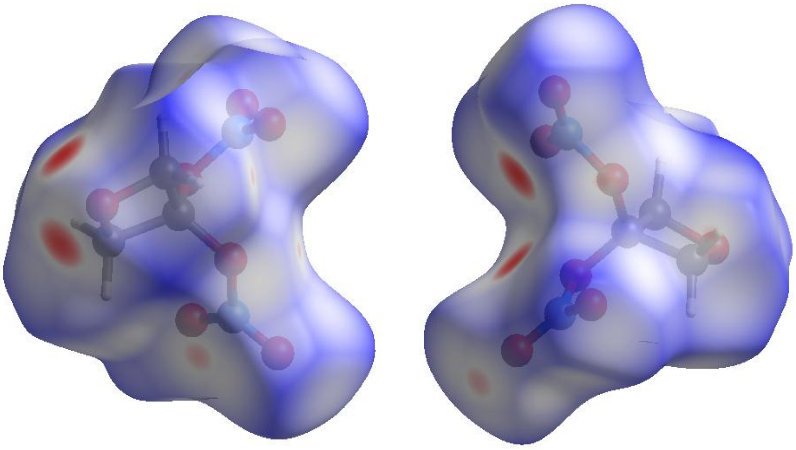

***Figure S12**: Calculated Hirshfeld surface of compound 1.*

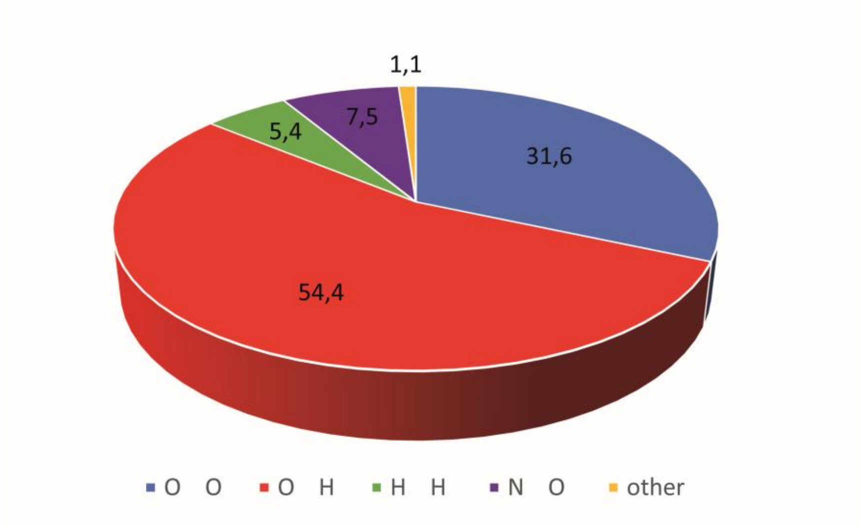

***Figure S13:** Population of close contacts in compound **1**.*

4. Heat of formation calculation and thermal analysis

The atomization was used to determine the heat of formation of **1**–**3** using the atom energies in Table S2.

$$\Delta_f H°_{(g, M, 298)} = H_{(molecule, 298)} - \sum H°_{(atoms, 298)} + \sum \Delta_f H°_{(atoms, 298)}$$

***Table S2**: CBS-4M electronic enthalpies for atoms C, H, N and O and their literature values.*

	$-H^{298}$ / a.u.	$\Delta_f H°_{gas}$[S15]
H	0.500991	217.998
C	37.786156	716.68
N	54.522462	472.68
O	74.991202	249.18

The Gaussian16 program package was used to calculate room temperature enthalpies on the CBS-4M level of theory. [S16] In order to obtain the energy of formation for the solid phase of **1**, the Trouton's Rule has to be applied ($\Delta H_{sub} = 188 \cdot T_m$). As compounds **2** and **3** are liquid, a different factor is applied ($\Delta H_{sub} = 90 \cdot T_m$).

***Table S3**: Heat of formation calculation results for compounds **1–3**.*

M	$-H^{298}$ [a] [a.u.]	$\Delta_f H°(g, M)$ [b] [kJ mol^{-1}]	$\Delta_{sub} H°$ (M) [c] [kJ mol^{-1}]	$\Delta_f H°(s)$ [d] [kJ mol^{-1}]	Δn	$\Delta_f U(s)$ [e] [kJ kg^{-1}]
1	751.610116	−233.4	69.2122	−302.6	−6.5	−1590.9
2	472.193794	−129.6	38.3355	−168.0	−5.0	−1306.5
3	511.451024	−208.6	37.2735	−245.8	−6.0	−1735.1

[a] CBS-4M electronic enthalpy; [b] gas phase enthalpy of formation; [c] sublimation enthalpy; [d] standard solid state enthalpy of formation; [e] solid state energy of formation.

The thermal behavior of compounds **1**–**3** was analyzed by DSC at a heating rate of 5°C min^{-1}. The obtained thermogram and its evaluation is depicted in Figure S14.

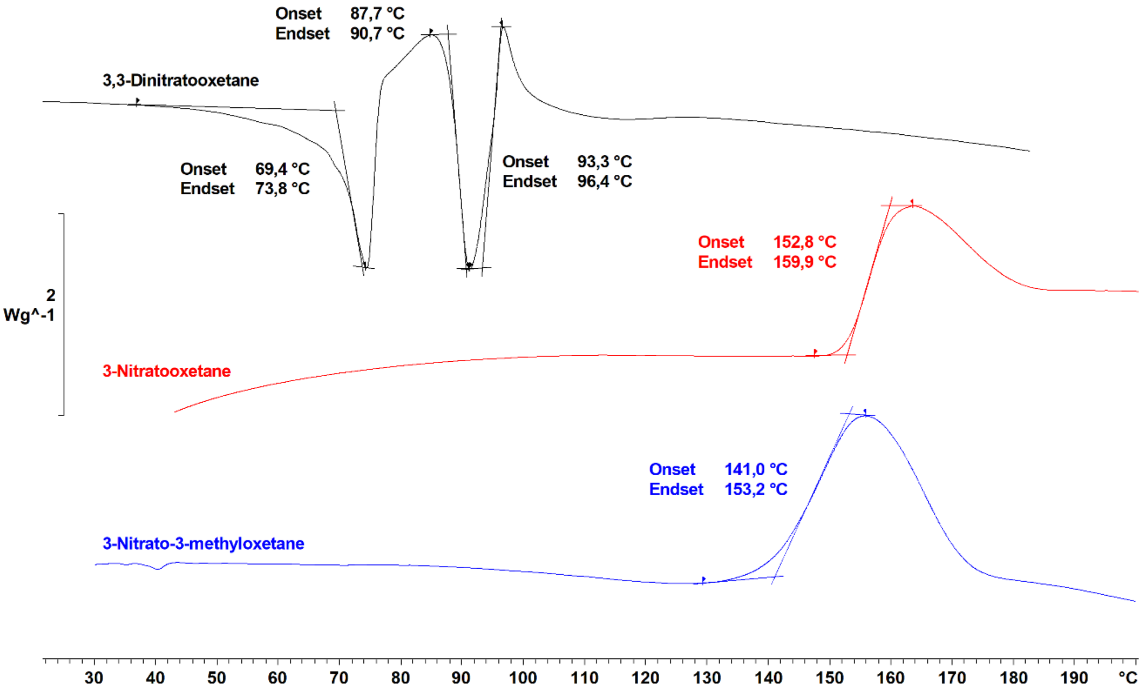

***Figure S14**: DSC evaluation result for compounds **1–3** (exo-up).*

References

S1 http://www.bam.de

S2 NATO Standardization Agreement (STANAG) on Explosives, *Impact Sensitivity Tests*, no. 4489, 1st ed., September 17, **1999**.

S3 WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, November 8, **2002**.

S4 NATO Standardization Agreement (STANAG) on Explosives, *Friction Sensitivity Tests*, no. 4487, 1st ed., August 22, **2002**.

S5 WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, November 8, **2002**.

S6 Impact: Insensitive >40 J, less sensitive ≤35 J, sensitive ≤4 J, very sensitive ≤3 J; friction: Insensitive >360 N, less sensitive=360 N, sensitive 80 N, very sensitive ≤80 N, extreme sensitive ≤10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

S7 R. L. Willer, K. Baum, W.-H. Lin, *US 8030440 B1*, 2011.

S8 CrysAlisPRO (Version 171.33.41); Oxford Diffraction Ltd., **2009**.

S9 Burla, M. C.; Caliandro, R.; Carrozzini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G. Crystal structure determination and refinement via SIR2014. *J. Appl. Crystallogr*. **2015**, *48*, 306.

S10 Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr*. **2011**, *44*, 1281.

S11 Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen: Germany, **1997**.

S12 Sheldrick, M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.

S13 Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University: The Netherlands, **1991**.

S14 Farrugia, L. J., WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **2012**, *45*, 849.

S15 M. W. Chase Jr., NIST-JANAF Thermochemical Tables, Fourth Edition, *J. Phys. Chem. Red. Data, Monograph 9*, **1998**, 1 – 1951.

S16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian16 ,Gaussian, Inc., Wallingford, CT, USA, **2016**.