

Supplementary Information

Tetranitratoethane

Dennis Fischer, Thomas M. Klapötke*, Jörg Stierstorfer

*Energetic Materials Research, Department of Chemistry,
University of Munich (LMU), Butenandtstr. 5-13, D-81377, Germany
Fax: +49 89 2180 77492
E-mail: tmk@cup.uni-muenchen.de*

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1. Experimental Part and General Methods

*Caution! Tetranitratoethane 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, Fluka, Acros). ^1H and ^{13}C spectra were recorded using a JEOL EX 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standard tetramethylsilane (^1H , ^{13}C) in CDCl_3 as the solvent. A DSC measurement to determine the decomposition point was performed at a heating rate of 5°C min^{-1} with an Linseis PT10 instrument. Infrared spectra were measured with a Perkin–Elmer FT-IR Spectrum BXII instrument equipped with a Smith Dura SamplIR II ATR unit. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment D418 equipped with an Nd-YAG-Laser (1064 nm) and an LN-Ge diode as detector.

The impact sensitivity tests were carried out according to STANAG 4489¹ modified instruction² using a Bundesanstalt für Materialforschung (BAM) drophammer.³ The friction sensitivity tests were carried out according to STANAG 4487⁴ modified instruction⁵ using the

BAM friction tester. The classification of the tested compounds results from the 'UN Recommendations on the Transport of Dangerous Goods'.^{6,7}

10 g of dehydrated and powdered glyoxal were mixed with 30 g of P_4O_{10} and slowly heated with a heat gun in a 50 mL flask until the material turned black. The green vapors were introduced into an ice cooled solution of 8 g N_2O_5 in 40 mL CH_3CN . Then the reaction was poured on 100 mL ice water and immediately extracted with four times 50 mL CH_2Cl_2 . The organic phase was washed with 1 % $NaHCO_3$ until neutral and dried over $MgSO_4$. After carefully (RT) removing the solvent under vacuum the crude material was sublimed at 70 °C under high vacuum against dry ice yielding 1 – 2 g of a colorless solid. **DSC** (5 °C min⁻¹, °C): 90°C (dec.); **IR** (ATR, cm⁻¹): $\tilde{\nu}$ = 3000 (w), 2948 (w), 1678 (s), 1664 (s), 1537 (w), 1465 (w), 1342 (w), 1271 (s), 1140 (w), 1048 (m), 989 (s), 821 (m), 771 (vs), 732 (s), 720 (s), 684 (s), 596 (s), 563 (m); **Raman** (1064 nm, 200 mW, 25 °C, cm⁻¹): $\tilde{\nu}$ = 2997 (54), 2859 (6), 1729 (6), 1693 (50), 1671 (10), 1465 (6), 1356 (45), 1306 (90), 1278 (13), 1148 (47), 1074 (10), 1014 (15), 855 (100), 790 (6), 778 (14), 757 (11), 734 (8), 675 (64), 626 (22), 579 (53); **¹H NMR** (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.21; **¹³C NMR{¹H}** (400 MHz, $CDCl_3$, 25 °C, ppm) δ = 91.3; **BAM drophammer**: 2 J (>500 μ m); **friction tester**: < 5 N (>500 μ m).

2. X-ray Diffraction

To determine the molecular structures of **1** in the crystalline state an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector was used. The data collection was performed using the CRYSLISPro software,⁸ The solution and refinement of the structure was performed using the program SIR-92,⁹ and SHELXL-97¹⁰ implemented in the WINGX software package¹¹ and finally checked with the PLATON software.¹² The absorptions were corrected with the SCAL3 ABSPACK multi-scan method.¹³

The crystals used for XRD unfortunately had twinning problems. Therefore we have done twin integration using the following two twin matrices: Species 1 1.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 0.0000 1.0000; Species 2 1.0000 -0.0007 0.2499 0.0000 -1.0001 0.0003 0.0001 0.0003 -1.0001.

1	
Formula	C ₂ H ₂ N ₄ O ₁₀
FW [g mol ⁻¹]	274.08
Crystal system	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
Color / Habit	Colorless rod
Size [mm]	0.05 x 0.30 x 0.42
<i>a</i> [Å]	7.5489(4)
<i>b</i> [Å]	7.2995(3)
<i>c</i> [Å]	8.3759(8)
α [°]	90
β [°]	97.935(6)
γ [°]	90
<i>V</i> [Å ³]	457.12(5)
<i>Z</i>	2
ρ _{calc.} [g cm ⁻³]	1.991
μ [mm ⁻¹]	0.216
<i>F</i> (000)	276
λ _{MoKα} [Å]	0.71073
<i>T</i> [K]	173
θ min-max [°]	4.4, 27.0
Dataset <i>h</i> ; <i>k</i> ; <i>l</i>	-9:9; -9:9; -10: 10
Reflect. coll.	1801
Independ. refl.	1801
<i>R</i> _{int}	---
Reflection obs.	1366
No. parameters	87
<i>R</i> ₁ (obs)	0.0274
<i>wR</i> ₂ (all data)	0.0675
<i>S</i>	0.94
Resd. Dens.[e Å ⁻³]	-0.19, 0.17
Device type	Oxford XCalibur3 CCD
Solution	SIR-92
Refinement	SHELXL-97
Absorpt. corr.	multi-scan
CCDC	1420413

3. Heat of Formation Calculation

The heat of formation was calculated using the atomization method (equation S1) using the atom enthalpies summarized in Table S1

$$\Delta_f H^\circ_{(g, M, 298)} = H_{(Molecule, 298)} - \sum H^\circ_{(Atoms, 298)} + \sum \Delta_f H^\circ_{(Atoms, 298)} \quad (S1)$$

Table S1 CBS-4M electronic enthalpies for atoms C, H, N and O and their literature values for atomic $\Delta_f H^\circ_{298} / \text{kJ mol}^{-1}$

	$-H^{298} / \text{a.u.}$	NIST ¹⁴
H	0.500991	218.2
C	37.786156	717.2
N	54.522462	473.1
O	74.991202	249.5

Quantum chemical calculations were carried out using the Gaussian G09 program package.¹⁵ The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. 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 CBS limit. CBS-4 begins with an HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and an MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31+ (d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS.

The gas phase enthalpy of formation of **1** was converted to the solid state one by subtraction of a calculated sublimation enthalpy using the Trouton's rule ($\Delta H_{\text{sub}} = 188 \cdot T_m = 72.0 \text{ kJ mol}^{-1}$). The molar standard enthalpy of formation (ΔH_m) was used to calculate the molar solid state energy of formation (ΔU_m) according to equation S2.

$$\Delta U_m = \Delta H_m - \Delta n RT \quad (S2)$$

(Δn being the change of moles of gaseous components)

Table S2. Heat of formation calculation results.

M	$-H^{298} \text{ [a]} / \text{a.u.}$	$\Delta_f H^\circ(g, M) \text{ [b]}$ / kJ mol^{-1}	$\Delta_{\text{sub}} H^\circ(M) \text{ [c]}$ / kJ mol^{-1}	$\Delta_f H^\circ(s) \text{ [d]}$ / kJ mol^{-1}	Δn	$\Delta_f U(s) \text{ [e]}$ / kJ kg^{-1}
1	1197.253051	-321.6	63.0	-384.6	9	-1321.9

[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.

4. References

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 - 2 WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, November 8, **2002**.
 - 3 <http://www.bam.de>.
 - 4 NATO Standardization Agreement (STANAG) on Explosives, *Friction Sensitivity Tests*, no. 4487, 1st Edn., August 22, **2002**.
 - 5 WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, November 8, **2002**.
 - 6 Impact: Insensitive >40 J, less sensitive ≤ 35 J, sensitive ≤ 4 J, very sensitive ≤ 3 J; friction: Insensitive >360 N, less sensitive = 360 N, sensitive <360 N a. >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.
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 - 8 *CrysAlisPro*, Agilent Technologies, **2014**.
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