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Polynitramino compounds outperform PETN†

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New polynitramino compounds were synthesized and fully characterized using IR and multinuclear (^{1}H, ^{13}C, ^{15}N) NMR spectroscopy, and elemental analysis as well as single-crystal X-ray diffraction.

Various energetic compounds have been investigated as precursors of high density energetic nitrimino,[1] nitramino,[2] nitro,[3] or nitrato[1a,3c,d] compounds. In particular, high-energy polyazapolycyclic caged polynitramines have emerged as a promising family of high-energy density materials.[2d] The current well known polynitramino compounds are RDX, HMX and CL-20.

Primary nitramine molecules [dinitrourea (DNU),[4] methylene dinitramine (MDNA)[5] and ethylene dinitramine (EDNA)[6]] have impressive high densities, positive oxygen balances (except EDNA) and good detonation properties. However, the application of primary nitramines as energetic materials is limited due to their relatively low thermal stability (for DNU:[4c] $T_{\text{dec.}}$: 92 °C, for MDNA:[5] $T_{\text{dec.}}$: 98–101 °C). Thermal decomposition studies involving aliphatic primary nitramines have led to an understanding of the relationship between structure and thermostability, and to the suggestion of a decomposition mechanism for these compounds.[7a,b] Increasing the number of nitro groups in a molecule in order to obtain a more balanced and powerful explosive inevitably results in an increase in acidity and a decrease in thermal stability of the resulting compounds.[7]

Here we describe the synthesis of a new energetic pentaerythrityl tetranitramine (PETNA) **4** that is a colorless crystal at ambient temperature, thermally decomposes at 183 °C, and has high density. Also described are the chemical, thermal, and sensitivity properties of **4**, as well as some preliminary calculated detonation properties.

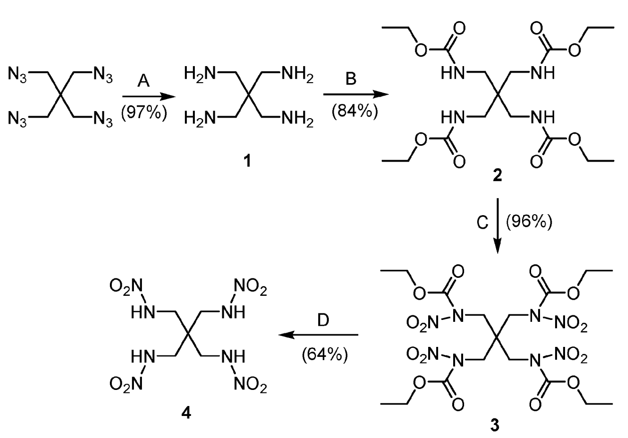
Pentaerythrityl tetranitramine (PETNA) **4** was prepared from pentaerythritol in overall good yields. Pentaerythrityl tetraurethane **2**, prepared from aqueous tetraamine **1**[8] and ethyl chloroformate, was nitrated using 100% nitric acid in trifluoroacetic anhydride to form tetranitrourethane **3**. The latter was converted into **4** by ammonolysis with aqueous ammonia at 90 °C (Scheme 1). Within two hours, the ester groups were removed and the water-soluble ammonium salt was formed. After hydrolysis with concentrated hydrochloric acid, tetranitramine **4** was extracted with ethyl acetate and obtained in good yield. The structure of **4** was verified by single-crystal X-ray diffraction analysis (Fig. 1).‡ Efforts to nitrate urethane **2** did not yield the tetranitro derivative **3** when treated with only 100% nitric acid.

Other successful syntheses of polynitramines **5** (77%), which was proved by single crystal X-ray diffraction analysis (Fig. 1), **6** (79%) and **7** (90%) by analogous nitration of polyurethane derivatives with concomitant retention of the pentaerythritol system resulted from extension of this reaction (Scheme 2).

The structures of all polynitramine derivatives **4–7** are supported by ^{1}H, ^{13}C and ^{15}N NMR spectroscopic data (Table 1).

The preparation of an asymmetric tetranitramine **11** was attempted by analogous nitration of the asymmetric tetraurethane **8** (Scheme 3; also see ESI†, Scheme S1). When the latter was nitrated with 100% nitric acid in trifluoroacetic anhydride, only a trinitro-substituted carbamate **9** was obtained as a colorless oil in a yield of 96%. Incomplete substitution of nitro groups results from steric hindrance of the three nitro urethane groups; this is significantly different from methylene bridged nitro urethane **3**. The reaction of the asymmetric nitramine **10** with excess hydrazine hydrate in ethanol provided a further approach to the trihydrazinium salt (see ESI†).

The ^{15}N NMR spectra[9] of the polynitramines measured in [D$_6$]DMSO show two or four resonances for nitrogen of NO$_2$ and NH (see ESI†). In the spectra, a typical chemical shift for NO$_2$ is observed between −23.1 and −17.8 ppm. The nitrogen signals from NH are found between −207.6 and −195.7 ppm at higher field than the starting material of polynitrourethane (between −167.8 and −173.0 ppm) and lower field than



Scheme 1 Synthesis of pentaerythrityl tetranitramine (PETNA) **4**; A: H$_2$–Pd/C, B: ClCOOCH$_2$CH$_3$, C: 100% HNO$_3$–(CF$_3$CO)$_2$O, D: 28% aq. NH$_3$–36% HCl.

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† Electronic supplementary information (ESI) available: The experimental procedures, analytical data, and NMR spectra of products. CCDC 737611 (**4**) and 737612 (**5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b916909a

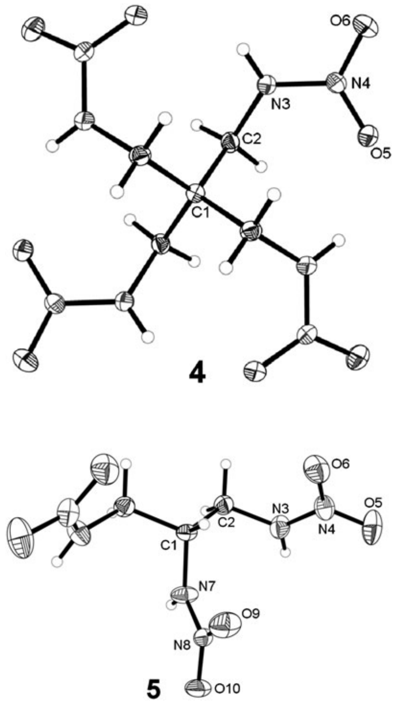
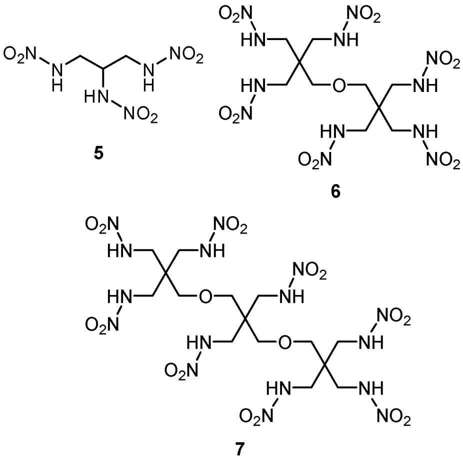
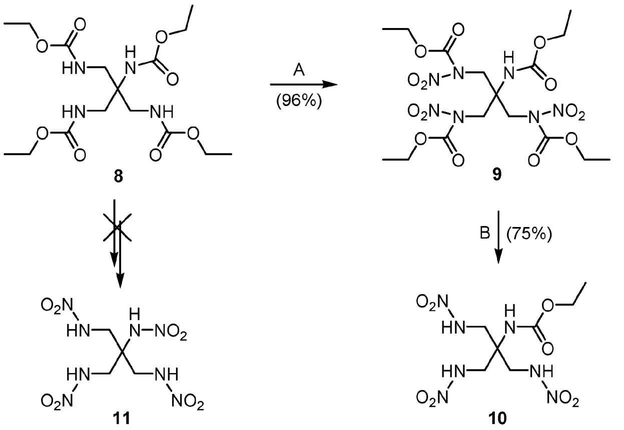


Fig. 1 Molecular structures (thermal ellipsoids represent 50% probability) of **4** (top) and **5** (bottom). Selected bond lengths [Å] and angles [°]: **4**: C1–C2 1.5417(12), C2–N3 1.4598(16), N3–N4 1.3327(15), N4–O6 1.2263(15), N4–O5 1.2379(14), C1–C2–N3 114.39(9), C2–N3–N4 122.37(10); **5**: C(1)–C(2) 1.5318(17), C2–N3 1.4463(18), N3–N4 1.3262(18), N4–O6 1.2230(17), N4–O5 1.2279(19), C1–C2–N3 113.74(12), C2–N3–N4 121.61(12).



Scheme 2 New polynitramines.



Scheme 3 Attempt to synthesize asymmetric tetranitramine **11**; A: 100% HNO_3–$(CF_3CO)_2O$, B: 28% aq. NH_3–36% HCl.

polyurethane with respect to the electronegativity effect (see ^{15}N NMR spectra for polynitrourethane in the ESI†).

The thermal behavior of **4–7**, which have decomposition temperatures between 181 and 185 °C (PETN: 160 °C, NG: 50–60 °C), was investigated using differential scanning calorimetry (Table 2). Only tris(nitramino)propane (**5**) shows a melting point (133 °C). Calculation of the heats of formation for polynitramines **4** and **5** was accomplished by using the Gaussian 03 suite of programs.[10] The geometric optimizations of the structures and frequency analyses were carried out by using the B3LYP functional with the 6–31 + G** basis set, and zero-point energies were calculated at the MP2/6–311 + + G** level.

All of the polynitramines exhibit negative heats of formation with **4** and **5** having the least negative −0.193 and 1.450 kJ g^{-1} (PETN: −1.590 kJ g^{-1}, NG: −1.548 kJ g^{-1}). The detonation parameters [pressures (*P*) and velocities (*D*)] were calculated using the CHEETAH 5.0 computer program.[13] The program is based on the traditional Chapman–Jouget thermodynamic detonation theory. For **4** and **5** the calculated detonation pressures are 31.59 and 35.62 GPa (PETN: 31.39 GPa, NG: 25.3 GPa). Detonation velocities are 8657 and 8933 m s^{-1}, respectively (PETN: 8564 m s^{-1}, NG: 7700 m s^{-1}). The impact sensitivity was tested according to BAM methods (BAM Fallhammer).[14] In Table 1, there is a range in impact sensitivities from the sensitive **4** (6 J) to **5** (20 J) and finally to the insensitive compound **6** (>40 J) and **7** (>40 J). The sensitivity of these polynitramino compounds is greatly reduced compared to PETN (2.9 J) and NG (0.2 J).

Table 1 Selected physical data of polynitramine compounds **4**, **5**, **6** and **7**[a]

4: colorless crystal; ^1H NMR: δ = 3.63 (s, 8H), 12.02 (s, 4H, NH); ^{13}C NMR: δ = 42.2, 46.4; ^{15}N NMR: δ = −207.6, −23.1.

5: white crystal; ^1H NMR: δ = 3.49 (dd, ^2J = 14.7 Hz, ^3J = 8.3 Hz, 2H), 3.74 (dd, ^2J = 14.7 Hz, ^3J = 4.5 Hz, 2H), 4.47 (m, 1H), 12.20 (s, 3H, NH); ^{13}C NMR: δ = 44.4, 51.4; ^{15}N NMR: δ = −202.1, −195.7, −19.6, −18.5.

6: white crystal; ^1H NMR: δ = 3.27 (s, 4H), 3.60 (s, 12H), 11.80 (br s, 6H, NH); ^{13}C NMR: δ = 44.0, 46.1, 70.5; ^{15}N NMR: δ = −202.3, −18.0.

7: white solid; ^1H NMR: δ = 3.26 (s, 4H), 3.60 (s, 16H), 11.94 (br s, 8H, NH); ^{13}C NMR: δ = 43.7, 44.9, 45.7, 46.0, 70.5; ^{15}N NMR: δ = −202.1, −201.9, −18.0, −17.8.

[a] ^1H, ^{13}C and ^{15}N NMR (CH_3NO_2 as external standard) spectra were recorded (using $[D_6]$DMSO as solvent) at 300.1 MHz, 75.5 MHz and 50.7 MHz, respectively. The data for all compounds are summarized in the ESI.†

Table 2 Physical properties of polynitramines **4** and **5** comparing with PETN, NG and RDX

Compd	T_d[a]/°C	Density[b]/g cm^{-3}	$\Delta_f H^\circ_{298}$[c]/kJ mol^{-1} (kJ g^{-1})	P[d]/GPa	D[e]/m s^{-1}	IS[f]/J	OP[g] (%)
4	183	1.778	−60.3 (−0.193)	31.59	8657	6	41
5	183[h]	1.753[i]	324.9 (1.450)	35.62	8933	20	43
PETN[j]	160	1.778	−502.8 (−1.590)	31.39	8564	2.9	61
NG[k]	50–60	1.60	−351.5 (−1.548)	25.3	7700	0.2	63
RDX[j]	230	1.816	92.6 (0.42)	35.17	8977	7.4	43

[a] Thermal decomposition temperature under nitrogen gas (DSC, 10 °C min^{-1}). [b] Gas pycnometer (25 °C). [c] Heat of formation (using 83.68 kJ mol^{-1} for the enthalpy of sublimation for each compound; calculated *via* Gaussian 03). [d] Calculated detonation pressure (CHEETAH 5.0). [e] Calculated detonation velocity (CHEETAH 5.0). [f] Impact sensitivity (BAM Fallhammer). [g] OP = oxygen percent. [h] **5** has melting point at 133 °C. [i] Determined by X-ray crystallography (20 °C). [j] PETN = pentaerythrityl tetranitrate, RDX = 1,3,5-trinitro-1,3,5-triazacyclohexane, ref. 3*c* and 11. [k] NG = nitroglycerine, ref. 11 and 12.

Safety precautions: while we have experienced no difficulties with the shock instability of polyazide and polynitramino compounds, manipulations must be carried out in a hood behind a safety shield. Leather gloves must be worn.

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Notes and references

‡ *Crystallographic data* compound **4**: $C_5H_{12}N_8O_8$, M_r = 312.23, tetragonal, $I\bar{4}$, $a = b$ = 9.6543(11) Å, c = 6.3283(9) Å, $\alpha = \beta = \gamma$ = 90°, V = 589.83(13) Å^3, Z = 2, ρ_{calcd} = 1.758 g cm^{-3}, T = 293(2) K, μ = 0.163 mm^{-1}, F(000) = 324, R_1 = 0.0256 for 610 observed ($I > 2\sigma I$) reflections and 0.0258 for all 615 reflections (R_{int} = 0.0180), goodness-of-fit = 1.113, 48 parameters. **5**: $C_3H_8N_6O_6$, M_r = 224.15, orthorhombic, *Pnma*, a = 6.7812(7) Å, b = 13.9258(13) Å, c = 8.9932(9) Å, $\alpha = \beta = \gamma$ = 90°, V = 849.26(15) Å^3, Z = 4, ρ_{calcd} = 1.753 g m^{-3}, T = 293(2) K μ = 0.166 mm^{-1}, F(000) = 464, R_1 = 0.0354 for 808 observed ($I > 2\sigma I$) reflections and 0.0394 for all 911 reflections (R_{int} = 0.0169), goodness-of-fit = 1.069, 76 parameters.

1 (*a*) Y.-H. Joo and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2009, **48**, 564; (*b*) Y.-H. Joo and J. M. Shreeve, *Chem.–Eur. J.*, 2009, **15**, 3198; (*c*) J. Stierstorfer, K. R. Tarantik and T. M. Klapötke, *Chem.–Eur. J.*, 2009, **14**, 5775; (*d*) H. Gao, Y. Huang, C. Ye, B. Twamley and J. M. Shreeve, *Chem.–Eur. J.*, 2008, **14**, 5596; (*e*) T. M. Klapötke, J. Stierstorfer and A. U. Wallek, *Chem. Mater.*, 2008, **20**, 4519; (*f*) H. Xue, H. Gao, B. Twamley and J. M. Shreeve, *Chem. Mater.*, 2007, **19**, 1731.

2 (*a*) R. P. Singh, R. D. Verma, D. T. Meshri and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2006, **45**, 3584; (*b*) G. Steinhauser and T. M. Klapötke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3330; (*c*) R. P. Singh, H. Gao, D. T. Meshri and J. M. Shreeve, in *High Energy Density Materials*, ed. T. M. Klapötke, Springer, Berlin, Heidelberg, 2007, vol. 37; (*d*) T. M. Klapötke, in *High Energy Density Materials*, ed. T. M. Klapötke, Springer, Berlin, Heidelberg, 2007, p. 85.

3 (*a*) M. Göbel and T. M. Klapötke, *Adv. Funct. Mater.*, 2009, **19**, 347; (*b*) Y. Huang, H. Gao, B. Twamley and J. M. Shreeve, *Chem.–Eur. J.*, 2009, **15**, 917; (*c*) D. E. Chavez, M. A. Hiskey, D. L. Naud and D. Parrish, *Angew. Chem., Int. Ed.*, 2008, **47**, 8307; (*d*) W.-G. Liu, S. V. Zybin, S. Dasgupta, T. M. Klapötke and W. A. Goddard, *J. Am. Chem. Soc.*, 2009, **131**, 7490; (*e*) T. M. Klapötke, P. Mayer, C. M. Sabate, J. M. Welch and N. Wiegand, *Inorg. Chem.*, 2008, **47**, 6014; (*f*) T. M. Klapötke, C. M. Sabate and M. Rasp, *Dalton Trans.*, 2009, 1825; (*g*) M. Göbel, B. H. Tchitchanov, J. S. Murray, P. Politzer and T. M. Klapötke, *Nat. Chem.*, 2009, **1**, 229.

4 (*a*) P. Goede, N. Wingborg, H. Bergman and N. V. Latypov, *Propellants, Explos., Pyrotech.*, 2001, **26**, 17; (*b*) C. Ye, H. Gao, B. Twamley and J. M. Shreeve, *New J. Chem.*, 2008, **32**, 317; (*c*) D. B. Lempert and I. N. Zyuzin, *Propellants, Explos., Pyrotech.*, 2007, **32**, 360.

5 R. C. Brian and A. H. Lamberton, *J. Chem. Soc.*, 1949, 1633.

6 W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and C. E. Maxwell III, *J. Am. Chem. Soc.*, 1950, **72**, 3132.

7 (*a*) R. S. Stepanov, A. M. Astachov and L. A. Kruglyakova, *29th International Annual ICT-Conference*, 1998, 128/1–128/7; (*b*) A. M. Astachov, R. R. Stepanov, L. A. Kruglyakova and Y. V. Kekin, *31th International Annual ICT-Conference*, 2000, 13/1–13/10; (*c*) Y. Lee, P. Goede, N. Latypov and H. Östmark, *36th International Annual ICT-Conference*, 2005, 124/1–124/9.

8 W. Hayes, H. M. Osborn, S. D. Osborne, R. A. Rastall and B. Romagnoli, *Tetrahedron*, 2003, **59**, 7983, the method of hydrogenation of azide was modified. See ESI†.

9 S. Berger, S. Braun and H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, Band 2, ^{15}N-NMR-Spektroskopie, Georg Thieme Verlag, Stuttgart, New York, 1992, pp. 36.

10 M. J. Frisch *et al.*, *GAUSSIAN 03 (Revision D.01)*, see ESI†.

11 (*a*) H. H. Klause, in *Energetic Materials*, ed. U. Teipel, VCH, Weinheim, 2005, p. 1; (*b*) R. Meyer, J. Köhler and A. Homburg, in *Explosives*, Wiley-VCH, Weinheim, 2007.

12 T. M. Klapötke, A. Penger, S. Scheutzow and L. Vejs, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2994.

13 S. Bastea, L. E. Fried, K. R. Glaesemann, W. M. Howard, P. C. Souers and P. A. Vitello, *CHEETAH 5.0 User's Manual*, Lawrence Livermore National Laboratory, 2007.

14 (*a*) www.bam.de; (*b*) A portion of polynitramine (20 mg) was subjected to a drop-hammer test using a 5 or 10 kg weight dropped. (Insensitive > 40 J; less sensitive ≥ 35 J; sensitive ≥ 4 J; very sensitive ≤ 3 J).