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ARTICLE

Synthesis, Characterization, and Properties of Pentanitrobenzene $C_6H(NO_2)_5$

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Dedicated to Professor Jean'ne M. Shreeve on the Occasion of her 85th Birthday

Abstract. The synthesis of the polynitroaromatic compound pentanitrobenzene was re-examined by modern spectroscopic, structural and physicochemical methods. Originally prepared in 1979, this material could exhibit interesting properties as an oxygen-rich energetic building block. The energies of formation were calculated with the GAUSSIAN program package and the detonation parameters were predicted using the EXPLO5 computer code. The performance data were determined and compared to the common oxidizer ammonium perchlorate. The crystal structure of pentanitrobenzene was determined by X-ray crystallography, and those of 2,3,4,6-tetranitroaniline and styphnic acid (trinitroresorcinol) were re-determined.

Introduction

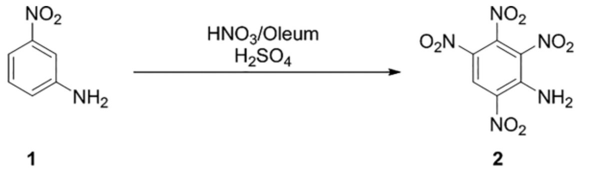
New high energy dense oxidizers (HEDOs) are an ongoing research topic in the synthesis and development of energetic materials. Efforts are being conducted to find environmentally friendly replacements for ammonium perchlorate (AP), which is often used as oxidizer in composite rocket propellants. The hazardous effects of AP include hypothyroidism and teratogenic properties as well as the formation of acidic and chlorine-containing gases during combustion. Further requirements for new HEDOs are insensitivity, high densities and high decomposition temperatures. As potential substitutes, the nitro salts ammonium nitrate (AN) and ammonium dinitramide (ADN) were investigated. However, they have some disadvantages such as low thermal stabilities and hygroscopicity.[1,2] Other possible alternatives were synthesized based on nitrocarbamates containing trinitroethyl moieties,[3] polynitrocarbamates[4] and dihydrazinium nitrates,[5] which often show promising calculated properties and sensitivity data.

The polynitro compound pentanitrobenzene, which is described and investigated in this work, is based on the benzene skeleton. Already several decades ago, the pernitro benzene, hexanitrobenzene, was described as a powerful oxidizer with high density, decomposition temperature and detonation velocity. However, this material decomposes in moist air, making further application difficult.[6] Similar to the synthesis of hexanitrobenzene, pentanitrobenzene was first prepared from the corresponding polynitroaniline derivative by *Nielsen* et al. in 1979;[7] characterization was achieved by ^1H NMR, mass spectrum and elemental analysis. A little later in 1990, the ^{13}C and ^{14}N NMR spectroscopic data followed without assignments.[8] Since then, no further reports with new information regarding pentanitrobenzene appeared. In this contribution we would like to re-investigate and study the properties of pentanitrobenzene.

Results and Discussion

Synthesis and Characterization

The precursor material of pentanitrobenzene is the aniline 2,3,4,6-tetranitroaniline (**2**). This can be prepared by a one-pot route starting from commercially available 3-nitroaniline (**1**) (Scheme 1).[9]



Scheme 1. Nitration of 3-nitroaniline (**1**) to 2,3,4,6-tetranitroaniline (**2**).

Relatively harsh conditions are required for a triple nitration of **1**. After a simple aqueous work-up, **2** was obtained as a dark yellow powder in good yield and also pure according to ^1H and ^{13}C NMR spectroscopy. As an alternative route with milder conditions in each reaction, **2** is also accessible by a four-step synthesis, which incorporates only single or double nitration. Since this route is more laborious (acetylation, nitration, de-acetylation, double-nitration[10]), more expensive and much slower than the one-pot synthesis, it is not considered further.

For the conversion into pentanitrobenzene (**3**), strong oxidizing conditions are essential in order to oxidize the remaining

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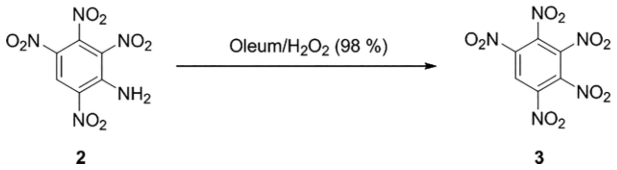
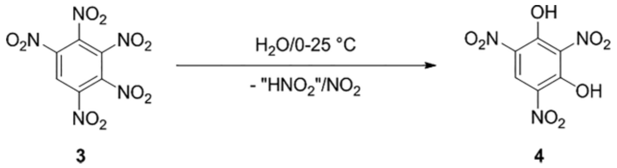
amino into a nitro group. The powerful oxidant peroxodisulfuric acid is generated in situ by using oleum and 98% hydrogen peroxide (Scheme 2).[7]



Scheme 2. Oxidation of 2,3,4,6-tetranitroaniline (**2**) to pentanitrobenzene (**3**).

After extraction with dichloromethane and recrystallization from cold dichloromethane, pale yellow crystalline needles of **3** were obtained in good yield and were shown to be pure according to ^{1}H and ^{13}C NMR spectroscopy.

In moist environment, **3** decomposes by nucleophilic substitution of the nitro groups in *meta*-(3-)position to the CH carbon under formal elimination of nitrous acid. As was proven by X-ray diffraction, the hydrolysis product is 2,4,6-trinitro-3-hydroxyphenol (**4**), better known as trinitroresorcinol or styphnic acid (Scheme 3). At 25 °C solutions in polar solvents such as acetone, approximately 50% is decomposed after 3 d into **4**. Furthermore, already after storage at 0 °C of pure **3**, the odor of NO_2 is noticeable after some days.



Scheme 3. Hydrolysis of pentanitrobenzene (**3**) to styphnic acid (**4**).

NMR Spectroscopy

2,3,4,6-Tetranitroaniline (**2**) and pentanitrobenzene (**3**) were characterized by ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy, and for **3** the vibrational spectra (IR and Raman) were recorded. Most soluble are both **2** and **3** in [D$_6$]acetone, however, signals of decomposition were observed after 1 h. Therefore, more suitable solvents for **3** are $CDCl_3$ and CD_2Cl_2 despite lower solubility.

For **2**, in the ^{1}H NMR spectrum the two resonances attributed to the aromatic hydrogen (δ = 9.30 ppm) and amino hydrogen atoms (δ = 8.88 ppm) are observed as expected at lower field due to the electron-withdrawing nature of the neighboring nitro groups. The ^{13}C{^{1}H} NMR spectrum displays six resonances accordingly to the asymmetry with broadened signals for the CNO_2 carbon atoms. Accordingly, the ^{14}N NMR spectrum shows four resonances in a narrow range at –18 to –27 ppm with the NH_2 resonance detected at –294 ppm.

The ^{1}H NMR spectrum of **3** shows the singlet for the aromatic hydrogen atom at $\delta = 9.69$ ppm in [D$_6$]acetone, 9.21 ppm in CD_2Cl_2, and 9.12 ppm in $CDCl_3$. This indicates a further downfield shift upon introduction of the fifth nitro group compared to **2**. In the ^{13}C{^{1}H} and ^{13}C NMR spectra of **3** (Figure 1), the four expected resonances are detected according to the symmetry. Interestingly and as expected, the carbon atoms display broadening/coupling due to the attached nitro groups, and therefore require longer acquisition times to be observed. Two of the three nitro-bound carbon atoms display clear triplets due to coupling to ^{14}N [$^{1}J(^{13}\text{C},^{14}\text{N})$ = 14.1 and 14.3 Hz], as also already mentioned in the earlier report.[8] Based on the proton-coupled spectrum (insert Figure 1), a definite assignment of the *ortho*- and *meta*-carbon atoms (relative to the CH carbon atom) was established. The signal at δ = 140.3 ppm is now split into a doublet of triplets due to ad-

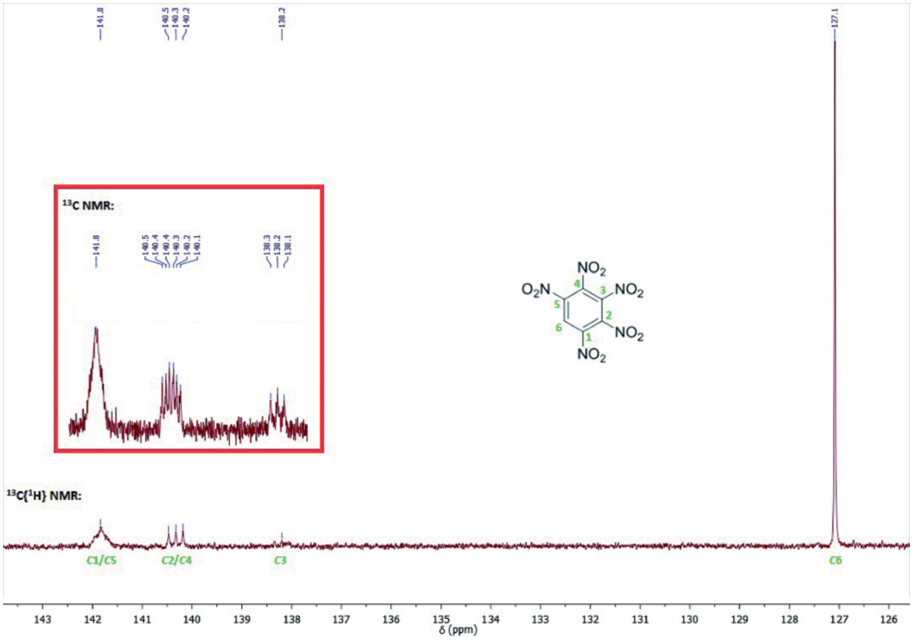


Figure 1. ^{13}C{^{1}H} and ^{13}C (red box) NMR spectrum of **3** in CD_2Cl_2.

Table 1. Crystal data, details of the structure determinations, and refinement of **2**–**4**.

	2	**3**	**4**
Formula	$C_6H_3N_5O_8$	$C_6HN_5O_{10}$	$C_6H_3N_3O_8{\cdot}2/3H_2O$
FW /g·mol^{-1}	273.13	303.10	257.12
T /K	103(2)	143(2)	143(2)
λ /Å	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	trigonal
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{3}c1$
Crystal size /mm	0.40 × 0.30 × 0.10	0.20 × 0.10 × 0.05	0.30 × 0.15 × 0.15
Crystal habit	colorless platelet	pale yellow block	pale yellow block
a /Å	7.1929(4)	8.1268(5)	12.5856(7)
b /Å	11.0332(6)	13.1290(8)	12.5856(7)
c /Å	12.0424(7)	20.3142(15)	9.9705(8)
α /°	90	88.676(5)	90
β /°	97.724(2)	79.512(6)	90
γ /°	90	81.601(5)	120
V /Å^3	947.02(9)	2108.4(2)	1367.71(19)
Z	4	8	2
$\rho_{calcd.}$ /g·cm^{-3}	1.916	1.910	1.873
μ	0.181	0.187	0.181
F(000)	552	1216	784
2Θ range /°	6.800–50.700	8.678–52.000	8.992–52.736
Index ranges	$-8 \le h \le 8$	$-9 \le h \le 10$	$-11 \le h \le 13$
	$-13 \le k \le 13$	$-14 \le k \le 16$	$-8 \le k \le 15$
	$-14 \le l \le 14$	$-25 \le l \le 24$	$-6 \le l \le 12$
Reflections collected	6864	17766	3061
Reflections unique	1728	8229	931
Parameters	180	757	91
GooF	1.073	1.052	1.081
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0460 / 0.0935	0.0490 / 0.0970	0.0402 / 0.0931
R_1 / wR_2 (all data)	0.0777 / 0.1033	0.0848 / 0.1130	0.0611 / 0.1117
Largest diff. peak / hole /e·Å^{-3}	0.291 / –0.267	0.276 / –0.255	0.241 / –0.242

ditional coupling to ^{1}H with $^3J(^{13}C,^1H)$ = 7.5 Hz, whereas that at δ = 141.8 ppm remains virtually unchanged. Because of the generally larger C–H coupling constant in benzenes at *meta* position compared to *ortho* position the assignment for **3** was made.

The ^{14}N NMR spectrum of **3** shows three signals at –33.5 ppm [*ortho*-(*C*1/*C*5)], –36.6 ppm [*meta*-(*C*2/*C*4)], and –37.2 ppm [*para*-(*C*3)] with the assignments. Definite distinction between those nitro groups at *ortho*-(*C*1/*C*5) and *meta*-(*C*2/*C*4) position is based on the ^{1}H-^{15}N-HMBC experiment, which shows one cross peak derived from the ^{1}H-^{15}N coupling to the *ortho*-(*C*1/*C*5) nitro group at –33.5 ppm.

Single Crystal Structure Analysis

Single crystals suitable for X-ray structure determination were obtained for the polynitrobenzenes **2**–**4** (Table 1).

Single crystals of **2** were obtained by recrystallization from dichloromethane. 2,3,4,6-Tetranitroaniline (**2**) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The calculated density is 1.916 g·cm^{-3} and the volume of the unit cell is 947.02(9) Å^3 at 103 K (Figure 2).

The structure of 2,3,4,6-tetranitroaniline (**2**) consists of an almost completely planar benzene ring. The distance between N4 and C1 [1.318(4) Å] is quite short compared to the other C–N bond lengths [1.456(3)–1.478(3) Å], which is due to the electron-donating effect of the NH_2 group pushing electron density into the bond and thereby shortens the distance. In ac-

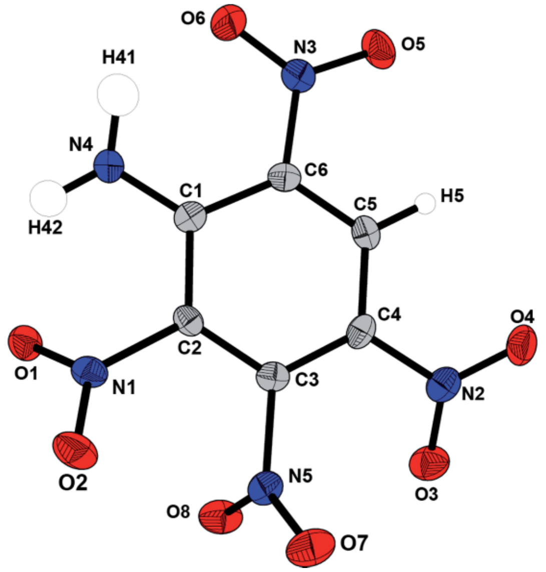


Figure 2. X-ray molecular structure of 2,3,4,6-tetranitroaniline (**2**). Selected bond lengths /Å: C2–C1 1.429(4), C6–C1 1.423(4), C3–C4 1.383(4), C4–C5 1.382(4), C3–C2 1.379(4), C6–C5 1.378(4), N4–C1 1.318(4), N2–C4 1.456(3), C3–N5 1.478(3), O7–N5 1.220(3), O8–N5 1.223(3), C5–H5 0.9500; Selected bond angles /°: C6–C1–C2 114.3(2), C3–C2–C1 122.7(2), C2–C3–C4 120.0(2), C5–C4–C3 119.7(2), C6–C5–C4 120.4(2), C5–C6–C1 122.6(2), N4–C1–C2 121.5(2); Selected torsion angles /°: C2–C3–N5–O8 64.9(3), C3–C2–N1–O2 41.0(3), C5–C6–N3–O5 –0.9(3), O3–N2–C4–C3 15.5(4).

cordance to this, the C–C bonds in direct vicinity to the amino group (C2–C1 and C6–C1) are longer than the other C–C bonds in the ring. The bond angles of the benzene ring have values between 114.3(2)° and 122.7(2)°, whereby the angle in direct vicinity to the amino group (C6–C1–C2) is the smallest. The nitro group (N5) in *meta* position to C1 is significantly twisted out of the plane by 64.9(3)°, since there is no "stabilization" possible by a neighboring hydrogen atom. The two nitro groups in *ortho* position to the carbon atom carrying the aromatic hydrogen atom (C5) are the most "stabilized", whereas the nitro moiety at C2 shows a distortion as well [41.0(3)°]. The distances between the weak intramolecular interacting hydrogen and oxygen atoms are 2.30 Å for O5–H5, 2.42 Å for O4–H5, 1.86 Å for O6–H41, and 2.02 Å for O1–H42.

A room temperature (298 K) determination of the crystal structure of 2,3,4,6-tetranitroaniline was reported in 1966 with a density of 1.86 g·cm^{-3}.[11]

Based on the crystal structure, the sensitivity towards moisture of **2** (as also is the case for **3**) could be explained. Due to the strong twist of the N5-nitro group, the molecule is labile towards nucleophilic attack at this position, provided that the free rotation is restricted in solution as well. This assumption was confirmed by treating 2,3,4,6-tetranitroaniline (**2**) in refluxing water/acetone resulting in 3-amino-picric acid,[9] which agrees with the observations from the NMR experiments in [D$_6$]acetone of **2**.

Single crystals of **3** were obtained by recrystallization from cold dichloromethane. Pentanitrobenzene (**3**) crystallizes in the triclinic space group $P\bar{1}$ with eight molecules per unit cell and four molecules per asymmetric unit. The molecules in the asymmetric unit are slightly different to each other regarding their bond lengths, bond angles and torsion angles which is presumably due to intra- and intermolecular interactions of the nitro groups. The calculated density of **3** is 1.910 g·cm^{-3} and the volume of the unit cell is 2108.4(2) Å^3 at 143 K. Figure 3 shows one of the four molecules of the asymmetric unit.

The structure of pentanitrobenzene (**3**) consists of an almost completely planar benzene ring, similar as observed for **2**. The respective bonds (C1–C2 and C4–C5, C2–C3 and C4–C3, C5–C6 and C1–C6) have each the same or a very similar bond length. The shortest C–C bond lengths [1.378(4) Å and 1.377(4) Å] are observed for the carbon atom carrying the hydrogen atom (C6). The C–N bond lengths are in the typical range of C–N single bonds. The bond angles in the ring are alternating between around 119° and 121°. Regarding the torsion angles, it is obvious that the nitro groups in *meta* position to C6 (N2 and N4) are strongly twisted out of the plane with –74.5(3)° (Figure 4). The N3-nitro group is with –42.9(3)° slightly twisted as well, whereas the nitro groups in *ortho*-position to C6 are almost unaffected. Similar as in **2**, this is due to weak stabilizing interactions between the aromatic hydrogen atom and the oxygen atoms of the adjacent nitro moieties. The distance between O1 and H6 is 2.37 Å and the distance between O10 and H6 is 2.47 Å.

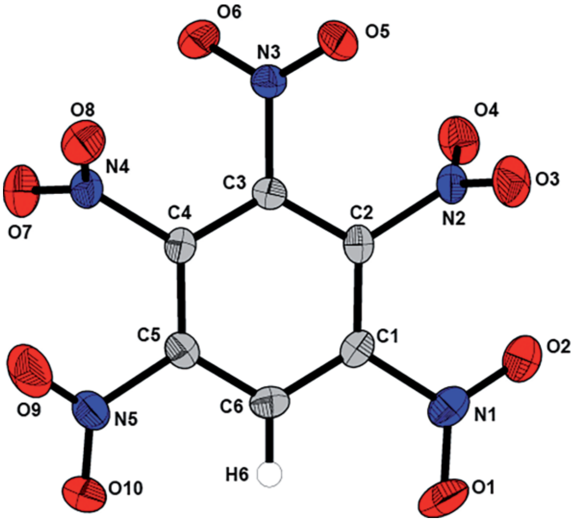


Figure 3. X-ray molecular structure of pentanitrobenzene (**3**). Selected bond lengths /Å: C1–C2 1.388(4), C4–C5 1.388(4), C2–C3 1.384(4), C4–C3 1.383(3), C5–C6 1.378(4), C1–C6 1.377(4), N1–C1 1.481(3), N1–O1 1.216(3), N1–O2 1.223(3), C6–H6 0.9500; Selected bond angles /°: C1–C6–C5 119.0(2), C6–C5–C4 121.3(2), C3–C4–C5 118.7(2), C4–C3–C2 120.9(2), C3–C2–C1 119.0(2), C6–C1–C2 121.1(2), O1–N1–C1 116.9(2), O1–N1–O2 125.7(2); Selected torsion angles /°: O2–N1–C1–C2 –8.3(4), O4–N2–C2–C3 –74.5(3), O6–N3–C3–C4 –42.9(3).

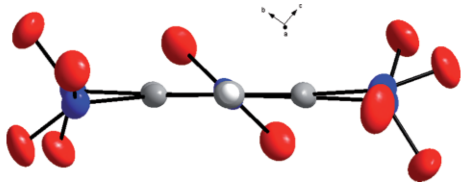


Figure 4. View along the *x,y* axis and the benzene plane showing the twist of the NO$_2$ groups in the structure of pentanitrobenzene (**3**).

Also in this case, the sensitivity of **3** towards nucleophilic attack can be explained due to the distortion of the N2- and N4-nitro groups, as was similarly described for **2**. Accordingly, **3** is also sensitive to moisture regioselectively at the *meta* positions to C6. This was proven by reacting **3** in cold water yielding the corresponding dihydroxy product, styphnic acid (**4**), in addition to observations during NMR experiments of **3**.

Single crystals of **4** were obtained from aqueous solution at 5 °C. Styphnic acid (**4**) crystallizes in the trigonal space group $P\bar{3}c1$ with two molecules per unit cell and with two-thirds equivalents of crystal water. The calculated density is 1.873 g·cm^{-3} and the volume of the unit cell is 1367.71(19) Å^3 at 143 K (Figure 5).

Styphnic acid (**4**) is a highly symmetric molecule with an almost planar benzene ring. The C–C bonds directly adjacent to the carbon atoms C2 bound to the hydroxyl groups are slightly longer than the C1–C3 bonds. A similar effect was observed for the bonds adjacent to the electron-donating amino group in the aniline **2**. The bond angles in the benzene ring range from 116.6 to 124.1°, whereby the smallest angles are located at C2. The N1-nitro and the hydroxyl groups are almost planar to the benzene ring. The N2-nitro group in *para* position to the unsubstituted carbon atom C3 is twisted out of the plane by around 64.9°. Moreover, the compound contains

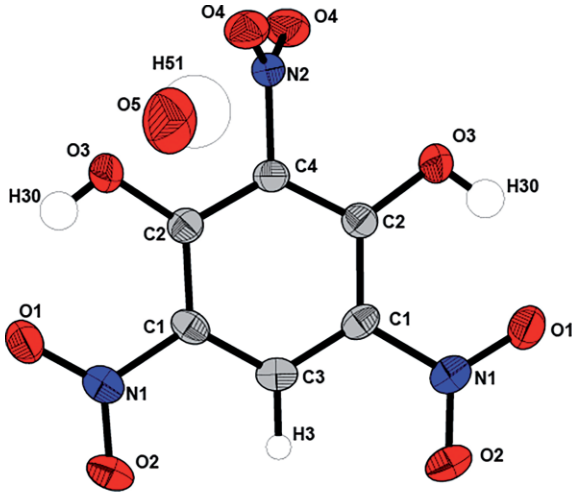


Figure 5. X-ray molecular structure of styphnic acid (**4**) with two-thirds of crystal water. Selected bond lengths /Å: C1–C2 1.404(3), C4–C2 1.389(2), C1–C3 1.379(2), N1–C1 1.450(3), N2–C4 1.467(4), N1–O1 1.240(2), N1–O2 1.224(2), N2–O4 1.2231(19), C3–H3 1.01(3), O3–C2 1.331(2), O3–H30 0.84(3); Selected bond angles /°: C1–C3–C1 119.8(3), C2–C4–C2 124.1(3), C3–C1–C2 121.5(2), C4–C2–C1 116.57(19), C2–C1–N1 120.47(18), O1–N1–C1 118.14(17); Selected torsion angles /°: O1–N1–C1–C2 2.118(31), C1–C2–O3–H30 –0.906(26), C2–C4–N2–O4 64.853(22).

two-thirds equivalents of crystal water (O5 and H51), which is disordered.

The crystal structure of styphnic acid containing two-thirds of crystal water at room temperature (298 K) with a density of 1.84 g·cm^{-1} was described in 1982, after an initial report from 1931.[12] Now, with this low-temperature data set, there is an improved quality styphnic acid crystal structure available.

Thermal Stabilities and Energetic Properties

The physical properties of pentanitrobenzene (**3**) were determined or calculated and compared with those of ammonium perchlorate (AP) (Table 2).

The thermal stability was investigated by differential thermal analysis (DTA) with a temperature range of 15–400 °C and a heating rate of 5 K·min^{-1}. It was found that pentanitrobenzene (**3**) melts at 143 °C before decomposition occurs at 220 °C. Sensitivity measurements against impact, friction and electrostatic discharge show that **3** is sensitive against these stimuli (IS = 5 J, FS = 96 N, ESD = 63 mJ). Furthermore, **3** has a positive oxygen balance regarding the formation of carbon monoxide and an oxygen content comparable with that of AP. The detonation velocity is significantly higher than in the common oxidizer ammonium perchlorate (AP) and the calculated density approaching that of AP. The specific impulse for the neat compound as well as with aluminum is higher than for AP. However, mixed with 15 % aluminum and 14 % binder, the oxygen balance seems not to be sufficient to obtain a higher specific impulse than in compositions with AP. Lower binder content might be more adequate for an optimal combustion behavior.

Table 2. Physical and sensitivity data of **3** in comparison with AP.

	3	AP
Formula	$C_6HN_5O_{10}$	NH_4ClO_4
FW /g·mol^{-1}	303.10	117.49
T_m /°C $^{a)}$	143	–
T_{dec} /°C $^{a)}$	220	240
IS /J $^{b)}$	5	20
FS /N $^{b)}$	96	360
ESD /mJ $^{b)}$	63	–
ρ /g·cm^{-3} $^{c)}$	1.91	1.95
O /% $^{d)}$	52.8	54.5
Ω_{CO} /% $^{e)}$	18.5	+34.0
Ω_{CO2} /% $^{e)}$	–13.2	+34.0
$\Delta_f H_m$ /kJ·mol^{-1} $^{f)}$	66.4	–295.8
V_{det} /m s^{-1} $^{g)}$	9090	6368
I_{sp} /s $^{h)}$	251	157
I_{sp} /s (15 % Al) $^{h)}$	259	235
I_{sp} /s (15 % Al, 14 % binder) $^{h)}$	234	261

a) Onset melting T_m and decomposition point T_{dec} from DTA measurements, heating rate 5 K·min^{-1}. b) Sensitivity towards Impact IS, Friction FS and electrostatic discharge ESD. c) Recalculated X-ray density at room temperature. d) Oxygen content. e) Oxygen balance assuming formation of CO and CO_2. f) Energy of formation calculated by the CBS-4M method using Gaussian 09[13]. g) Predicted detonation velocity. h) Specific impulse I_{sp} of the neat compound and compositions with aluminum or aluminum and binder (6 % polybutadiene acrylic acid, 6 % polybutadiene acrylonitrile, and 2 % bisphenol A ether) using the EXPLO5 (Version 6.03) program package (70 kbar, isobaric combustion, equilibrium expansion).[14]

Conclusions

The polynitrobenzene pentanitrobenzene (**3**) can be prepared now via a two-step route and is now fully characterized. The starting material 3-nitroaniline (**1**) is easily available and inexpensive. Important experimental and calculated properties such as sensitivities, thermal stability, and energetic parameters were determined and discussed. Pentanitrobenzene exhibits a relatively high decomposition temperature, detonation velocity, density and specific impulse for the neat compound. The molecular structure of **3** in the crystalline state was determined and discussed. Furthermore, the crystal structures of 2,3,4,6-tetranitroaniline (**2**) and styphnic acid/trinitroresorcinol (**4**) were improved by low-temperature X-ray crystallography. Unfortunately, the moisture sensitivity of pentanitrobenzene (**3**) restricts some further applications and chemistry, but additional studies as a synthetic building block from freshly prepared material will be subject of future studies.

Experimental Section

General: Solvents were dried and purified with standard methods. The starting material 3-nitroaniline (**1**) is commercially available and used without further purification. Raman spectra were recorded in a glass tube with a Bruker MultiRAM FT-Raman spectrometer with a Klaastech DENICAFC LC-3/40 laser (Nd:YAG, 1064 nm, up to 1000 mW) in the range of 4000–400 cm^{-1}. IR spectra were recorded with a Perkin–Elmer Spectrum BX-FTIR spectrometer coupled with a Smiths ATR DuraSample IRII device. Measurements were recorded in the range of 4000–650 cm^{-1}. All Raman and IR spectra were measured at ambient temperature and their intensities are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m), "weak" (w) and "very weak" (vw). NMR spectra were recorded with JEOL Eclipse and Bruker TR 400 MHz spectrometers at 25 °C. Chemical shifts were determined in relation to external standards Me_4Si (^1H, 399.8 MHz; ^{13}C, 100.5 MHz); $MeNO_2$ (^{14}N, 28.9 MHz) and are given in parts per million (ppm). Elemental analyses (CHN) were obtained with a Vario EL Elemental Analyzer.

The sensitivity data were acquired by measurements with a BAM drophammer and a BAM friction tester.[1] Melting and decomposition points were determined by differential thermal analysis (DTA) using an OZM Research DTA 552-Ex instrument with Meavy 2.1.2 software. The samples (3–15 mg) were measured in open glass tubes (diameter 4 mm, length about 47 mm) at a heating rate of 5 $K\cdot min^{-1}$ in the range of 15–400 °C. The temperatures are given as onset temperatures.

Crystal Structure Determination: The crystal structure data were obtained with an Oxford Xcalibur CCD Diffractometer with a KappaCCD detector at low temperature (143 K and 103 K). Mo-K_α radiation ($\lambda = 0.71073$ Å) was delivered by a Spellman generator (voltage 50 kV, current 40 mA). Data collection and reduction were performed using the CRYSALIS CCD[15] and CRYSALIS RED[16] software, respectively. The structures were solved by SIR92/SIR97[17] (direct methods) and refined using the SHELX-97[18] software, both implemented in the program package WinGX22.[19] Finally, all structures were checked using the PLATON software.[20] Structures displayed with ORTEP plots are drawn with thermal ellipsoids at 50 % probability level.

The theoretical calculations were achieved by using the Gaussian 09 program package[13] and were visualized by using GaussView 5.08.[21] Optimizations and frequency analyses were performed at the B3LYP level of theory (Becke's B3 three parameter hybrid functional by using the LYP correlation functional) with a cc-pVDZ basis set. After correcting the optimized structures with zero-point vibrational energies, the enthalpies and free energies were calculated on the CBS-4M (complete basis set) level of theory.[22] The detonation parameters were obtained by using the EXPLO5 (V6.03) program package.[14,23]

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-1866511 (for **2**), CCDC-1866506 (for **3**), and CCDC-1866507 (for **4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

CAUTION! The benzene derivatives **2**–**4** are energetic materials and show sensitivities in the range of secondary explosives! They should be handled with caution during synthesis or manipulation and additional protective equipment (leather jacket, face shield, ear protection, Kevlar gloves) is strongly recommended.

2,3,4,6-Tetranitroaniline (2):[9] A solution of 3-nitroaniline (**1**) (4.00 g, 29.0 mmol) in sulfuric acid (40 mL, 96 %) was heated to 60–65 °C. A mixture of nitric acid (4.5 mL, 99.5 %) and oleum (13 mL, 20–25 wt% SO_3) was added dropwise to the solution keeping the temperature below 80 °C. The reaction mixture was allowed to cool to room temperature and stirred for 45 h at ambient temperature before pouring on crushed ice. The precipitating yellow solid (3.59 g, 45 %) was filtered, washed with cold water and dried in vacuo for 10 h. **^1H NMR** ([D_6]acetone): δ = 9.30 (s, 1 H, C*H*), 8.88 (s, 2 H, N*H*$_2$); **$^{13}C\{^1H\}$ NMR** ([D_6]acetone): δ = 143.6 (*C*NH_2), 142.8/133.5/130.3/126.4 (br., *C*NO_2), 129.1 (s, *C*H). **^{14}N NMR** ([D_6]acetone): δ = –19/–24/–25/–26 (*N*O_2), –294 (*N*H_2) ppm.

Pentanitrobenzene (3):[7] 2,3,4,6-Tetranitroaniline (**2**) (500 mg, 1.83 mmol) was dissolved in oleum (25.0 mL, 20–25 wt% SO_3) and the solution was cooled to 5 °C. H_2O_2 (2.70 mL, 98 %) was added dropwise keeping the temperature below 25 °C. The suspension was stirred for 24 h at 25–30 °C and for 1 h at 0 °C. Afterwards, the reaction mixture was extracted with DCM (5 × 50 mL) and the solvent was evaporated. The resulting yellow solid was recrystallized from cold DCM (15 mL) to afford pale yellow crystalline needles (295 mg, 53 %) which were filtered, washed with ice-cold DCM and dried in vacuo for 5 h. **^1H NMR** ($CDCl_3$): δ = 9.12 (s, 1 H, C*H*). **^1H NMR** (CD_2Cl_2): δ = 9.21 (s, 1 H, C*H*). **^1H NMR** ([D_6]acetone): δ = 9.69 (s, 1 H, C*H*). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$): δ = 141.4 (br., *ortho-C* rel. to CH), 139.8 [t, ^1J(C-^{14}N) = 14.3 Hz, *meta-C* rel. to CH], 137.8 [t, ^1J(C-^{14}N) = 14.1 Hz, *para-C* rel. to CH], 125.9 (s, *C*H). **^{13}C NMR** (CD_2Cl_2): δ = 141.8 (br., *ortho-C* rel. to CH), 140.3 [dt, ^1J(C-H) = 7.5, ^1J(C-^{14}N) = 14.3 Hz, *meta-C* rel. to CH], 138.2 [t, ^1J(C-^{14}N) = 14.1 Hz, *para-C* rel. to CH], 127.1 [d, ^1J(C-H) = 183.5 Hz, *C*H]. **^{14}N NMR** (CD_2Cl_2): δ = –33.5 (*ortho-N*O_2 rel. to CH), –36.6 (*meta-N*O_2 rel. to CH), –37.2 (*para-N*O_2 rel. to CH) ppm. **IR** (ATR): $\tilde{\nu}$ = 3080 (w, νCH), 1606 (w), 1555 (vs, νNO_2), 1393 (w), 1325 (vs, νNO_2), 1307 (m), 1167 (w), 926 (m), 890 (s), 832 (w), 817 (m), 804 (m), 789 (w), 769 (w), 725 (m), 716 (w) cm^{-1}. **Raman** (502 mW): $\tilde{\nu}$ = 3083 (w), 1610 (w), 1593 (w), 1569 (m), 1360 (s), 1338 (m), 1201 (w), 833 (vs) cm^{-1}. $C_6HN_5O_{10}$ (303.10 $g\cdot mol^{-1}$): calcd.: C 23.78, H 0.33, N 23.11 %; found: C 23.84, H 0.47, N 22.82 %. Melting point: 143 °C; Dec. point: 220 °C. Sensitivities (BAM): IS:5 J, FS: 96 N, ESD: 63 mJ (grain size 100–500 µm).

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Keywords: Energetic materials; Oxidizer; Polynitrobenzenes; NMR spectroscopy; X-ray diffraction

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