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SHORT COMMUNICATION

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Synthesis and Energetic Properties of 4-Diazo-2,6-dinitrophenol and 6-Diazo-3-hydroxy-2,4-dinitrophenol

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4-Amino-3,5-dinitroaniline (**3**) was synthesized by fluorine/amine exchange of 4-fluoro-3,5-dinitroaniline in ethanol. 4-Diazo-2,6-dinitrophenol (Iso-DDNP, **4**) was obtained after nitration in HNO_3 (100 %) and acetic anhydrid. 4-Amino-2,3,5-trinitrophenol (**7**) was obtained by nitration of *N*-(4-acetoxyphenyl)acetamide and deprotection of the amine. Further nitration resulted in 6-diazo-3-hydroxy-2,4-dinitrophenol (**8**). The thermal stability and sensitivity of **4** and **8** toward impact and friction was compared to commercially used DDNP (2-diazo-4,6-dinitrophenol). All target compounds were characterized by single-crystal X-ray diffraction, NMR and elemental analysis and DSC. The sensitivities were determined by BAM methods (drophammer and friction tester). The heats of formation were calculated by using CBS-4M electronic enthalpies and the atomization method. Various detonation parameters such as detonation velocity and pressure were computed by using the EXPLO5 computer code V6.01.

Introduction

Synthesis of energetic materials based on a benzene backbone has had a long tradition since the discovery of trinitrotoluene (TNT) in 1863.[1] Because of its important property as a melt-castable explosive it is still in use nowadays, even though it is highly toxic for the environment.[2] 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) was synthesized in 1888. It is a well-known insensitive explosive with a high melting point ($T_{melt} > 350$ °C) due to its strong intramolecular hydrogen bonds between alternation of amino and nitro groups.[3,4] This leads to a high density of ρ = 1.937 g cm^{-3} at 298 K, which was confirmed by its crystal structure[5] in 1965. For many applications, TATB shows a meager performance and is too insensitive to detonate, therefore alternatives with a better performance, less toxic properties and lower sensitivities towards external stimuli like impact, friction and electrostatic discharge, are desired. Originally, our research goals had been the synthesis of 4-amino-2,3,5,6-tetranitrophenol and 1,4-diamino-2,3,5,6-tetranitrobenzene. In order to obtain the latter, 4-amino-3,5-dinitroaniline (**3**) seemed to be a promising starting material. Its synthesis was already mentioned by Chu and Griffiths.[6] They reported on the nitration of *N*,*N*′-bis-(phenylsulfonyl)-*p*-phenylenediamine and received three different *C*-nitrated dinitro isomers, which were separated by column chromatography after the cleavage of the sulfonamide in concentrated sulfuric acid. However, for synthesis in larger scales, this reaction is useless, and a proper synthesis had to be developed. Alternatively, the substitution of the chlorine atom or the methoxy group of 4-chloro-2,6-dinitroaniline,[7] as well as its 4-methoxy derivative,[8] failed. Even the use of ammonia in high-pressure vessels did not result in any notable conversion. Finally, **3** could be synthesized by fluorine/amine exchange of 4-fluoro-3,5-dinitroaniline in ethanol. A further approach was the nitration of 4-aminophenol; however, all nitration attempts finally resulted in the formation of highly energetic diazophenols. These species represent a very interesting group of energetic zwitterionic molecules. A paper discussing the increased-valence bond structure of DDNP, as opposed to the zwitterionic approach, was published in 2003.[10] The mechanism of formation of *ortho*-diazophenols was described in detail by Atkins and Wilson in 1986.[9] Most compounds containing a nitro group in *ortho* position to a nitramine functionality eliminate nitric acid during the nitration reaction or boiling process in organic solvents. Including a cyclic transition state, this rearrangement results in the formation of *ortho*-diazophenols. DDNP (2-diazo-4,6-dinitrophenol) was synthesized for the first time by Griess in 1858.[11] It is an extremely sensitive primary explosive, which is commercially used in stab detonators.[12] Sensitization of lead azide using DDNP as an energetic additive was intensively studied by Spear and Elischer in 1982.[13] This study provides a comparison (e.g. sensitivities, thermal behavior) of the two title diazophenols to DDNP. While the synthesis of DDNP by oxidation of the primary aromatic amine of picramic acid (2-amino-4,6-dinitrophenol) has been published,[14] the formation of *para*-diazophenols is only rarely described.[9]

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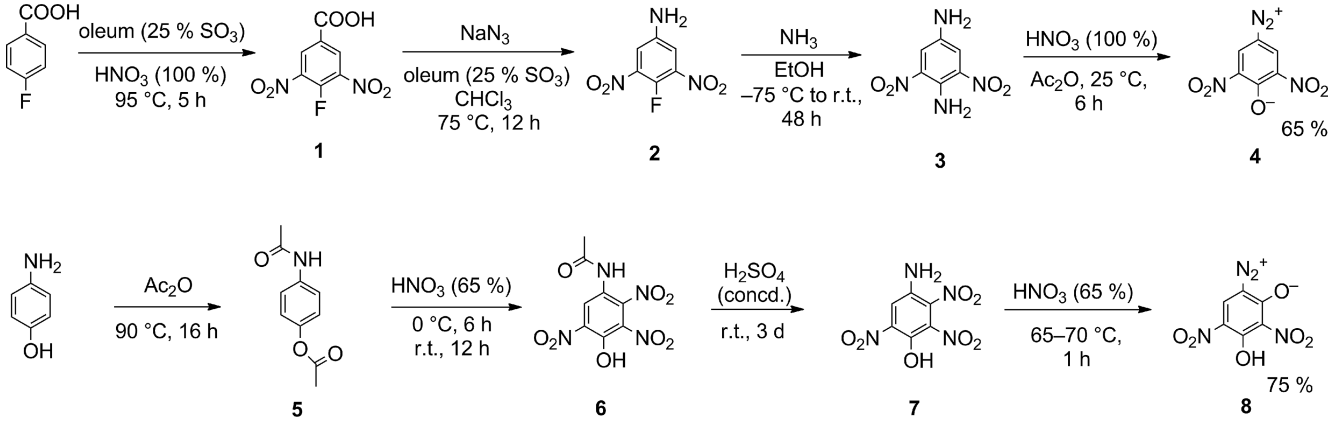
Results and Discussion

An overall synthetic protocol is displayed in Scheme 1. 4-Fluoro-3,5-dinitroaniline (**2**) was synthesized as described by Nielsen et al.[15] Compound **3** was obtained by reaction of **2** with ammonia in ethanol. Any further attempts to synthesize a tri- or tetranitro derivative of 1,4-diaminobenzene by various nitration conditions resulted in the formation of 4-diazo-2,6-dinitrophenol (**4**). Even if the amine in C1 position was protected with an acetyl or methylsulfonyl group, no other product but **4** was obtained, indicating that the protection group was cleaved quickly in nitrating media. Compound **5** was easily synthesized by using acetic anhydride both as acetylating reagent and solvent. Nitration of **5** by using 65% nitric acid yielded compound **6** in moderate quantities. To obtain compound **7** in high purity, **6** must be stirred in concentrated sulfuric acid for at least 3 d, which indicates that the amide cleavage of **6** works only very slowly. Compound **7** could easily purified by recrystallization from benzene. Further nitration attempts of **7** always resulted in decomposition or the formation of compound **8**, which is 6-diazo-3-hydroxy-2,4-dinitrophenol.

All target compounds and intermediates were characterized extensively. Single crystals of **3**, **4**, **7** and **8** could be grown from organic solvents (**3** and **8** from acetone; **4** from ethanol; **7** from benzene) and their structures determined by low-temperature X-ray diffraction (details are given in the Supporting Information). Figures 1 and 2 show the molecular structures of **3**, **4**, **7** and **8**. They crystallize in the monoclinic or orthorhombic crystal system in common space groups (**3**: $P2_1/c$; **4**: $P2_12_12_1$; **7** and **8**: *Pbca*).

The X-ray densities at 173 K increase with the number of nitro groups [1.742 (**3**) < 1.824 (**4**) < 1.837 (**8**) < 1.839 g cm^{-3} (**7**)]. In the case of **3** a nearly planar system is formed. Both nitro groups lie within the ring plane fixed by the intermolecular hydrogen bonds N1–H···O1 and N1–H···O4.

Proton-coupled ^{15}N NMR spectra of compounds **4**, **7** and **8** were recorded and are displayed in Figure 3. All four nitrogen atoms of **4** could be assigned. N_α is the only nitro-



Scheme 1. Synthesis protocol of compounds **1**–**8**.

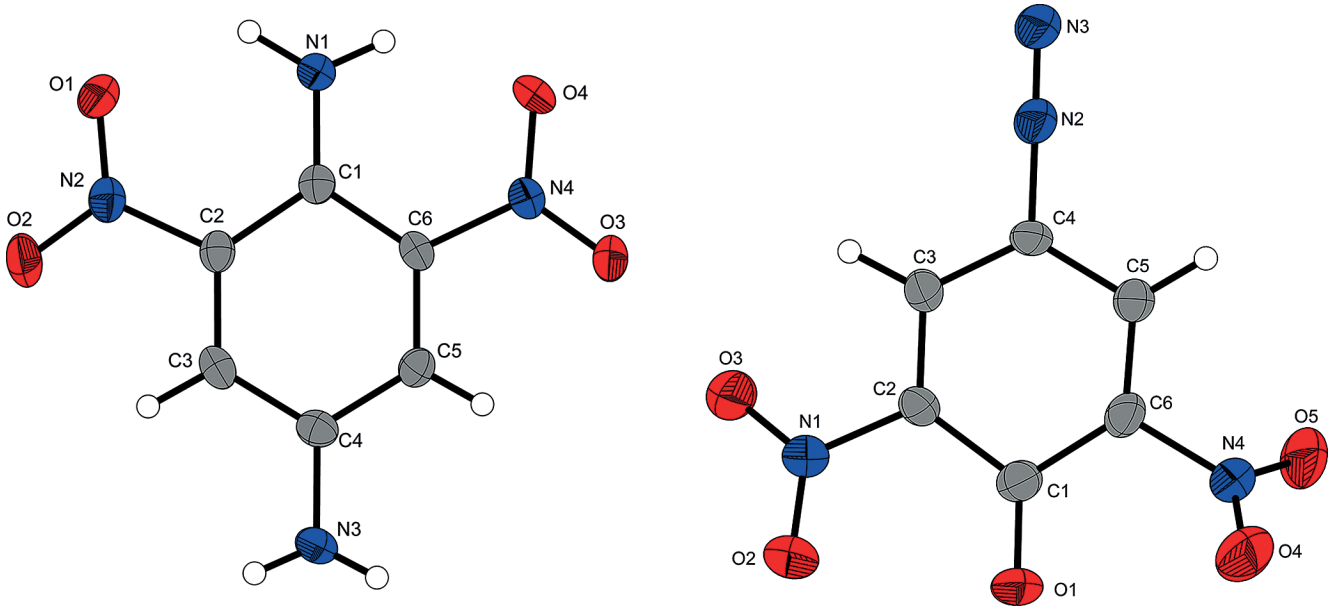


Figure 1. Molecular structure of **3** (left) and 4-diazo-2,6-dinitrophenol (**4**, right). Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level.

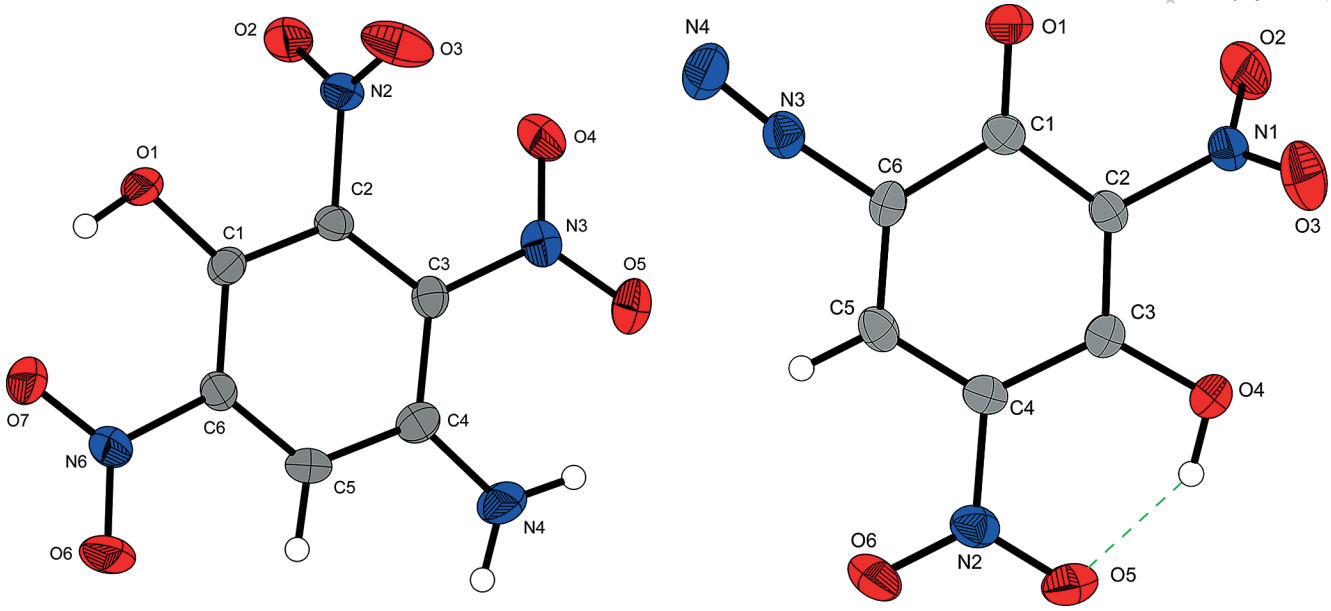


Figure 2. Molecular structure of 4-amino-2,3,6-trinitrophenol (**7**, left) and 6-diazo-3-hydroxy-2,4-dinitrophenol (**8**, right).

gen atom, which shows a singlet at δ = –21.7 ppm. The N_δ and N_β signals appear as doublets at δ = –17.2 ($^3J_{N,H}$ = 2.9 Hz) and –19.9 ppm ($^4J_{N,H}$ = 1.2 Hz). Even the nitrogen-proton coupling ($^3J_{N,H}$ = 2.4 Hz) of the amine could be observed. In the ^{15}N NMR spectrum of compound **7** three signals could be detected. N_β of the diazo group shows a singlet at δ = –45.0 ppm. N_α shows a first-order triplet at δ = –139.3 ppm (t, $^3J_{N,H}$ = 2.4 Hz). In contrast, for N_γ a deceptively simple triplet is observed. In fact the ^{15}N NMR signal of N_γ represents the X part of an AA′X spectrum, from which $N = |^3J_{N,H} + {}^5J_{N,H}| = 3.0$ Hz is determined. The coupling constant $^5J_{N,H}$ is expected to be very small, and thus the value of N observed corresponds roughly to $^3J_{N,H}$. In the ^{15}N NMR spectrum of compound **8** four signals could be observed. N_β of the diazo group shows a singlet at δ = –33.2 ppm. N_α shows a doublet at δ = –134.9 ppm ($^3J_{N,H}$ = 1.8 Hz). N_γ appears as singlet and N_δ as and as doublet ($^3J_{N,H}$ = 2.8 Hz).

Energetic properties of compounds **4** and **8** in comparison to DDNP are displayed in Table 1. The impact sensitivity of all three compounds is 1 J, typically for primary explosives. *Therefore handling of these compounds should be carried out only with proper safety measures!* Interestingly, compounds **4** and **8** are also very sensitive toward friction

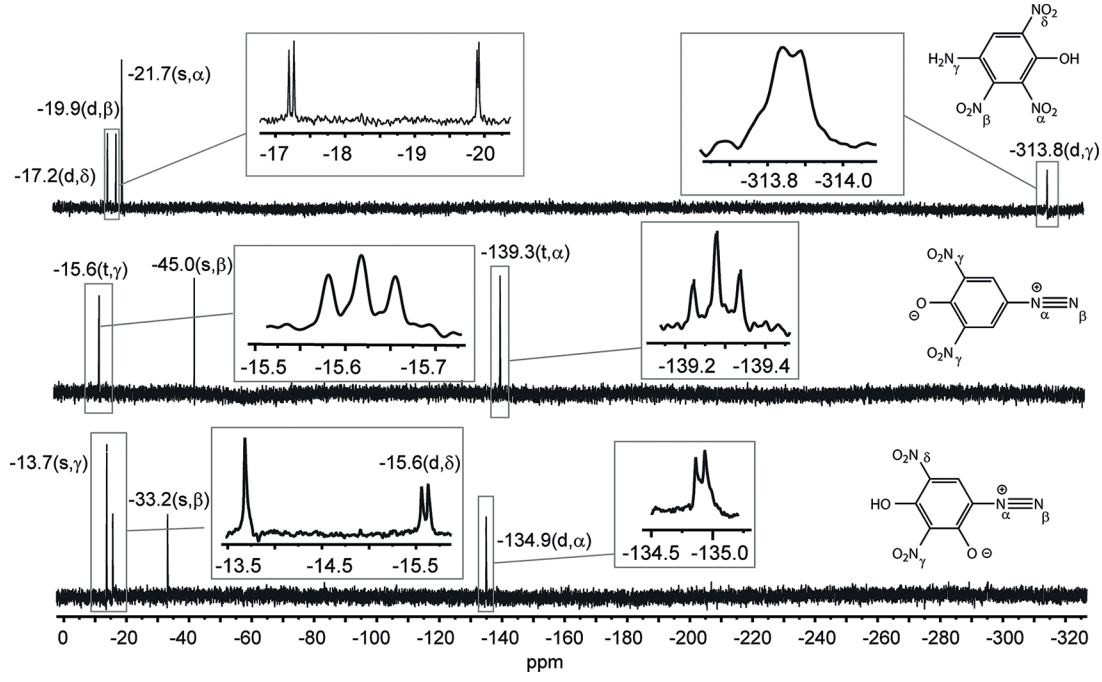


Figure 3. ^{15}N NMR spectra of **4** (top), **7** (center) and **8** (bottom).

but slightly less than DDNP, what makes them safer for handling. In addition they are slightly better (ca. 10–12 °C) in thermal stability. Due to the higher densities of **4** and **8** in comparison to DDNP higher detonation parameters were calculated by using the EXPLO5 V6.01 computer code. Statistically, detonation pressure and velocity of **4** and **8** are ca. 5% higher than those of DDNP. An empirical confirmation of these values has to be further researched in order to determine the relevance, as well as the benefits of those compounds. For selected applications like initiation of secondary explosives, these advantages could surpass the detriment of an increased number of synthetic steps to produce **4** and **8**.

Table 1. Energetic properties of compounds **4** and **8** in comparison to DDNP.

	4	**8**	DDNP[a]
Empirical formula	$C_6H_2N_4O_5$	$C_6H_2N_4O_6$	$C_6H_2N_4O_5$
Formula mass	210.10	226.10	210.10
IS [J][b]	1 (< 100 μm)	1 (< 100 μm)	1 (< 100–500 μm)
FS [N][c]	40 (< 100 μm)	16 (< 100 μm)	5 (< 100–500 μm)
N [%][d]	26.67	24.78	26.67
$T_{dec.}$ [°C][e]	168	170	158[16]
ρ [g cm^{-3}][f]	1.790[g]	1.803[g]	1.727[16]
$\Delta_f H_m°$ [kJ mol^{-1}][h]	184.1	–42.0	142.4[16]
$\Delta_f U°$ [kJ kg^{-1}][i]	941.0	–120.0	742.6[16]
Ω [%][j]	–60.9	–49.5	–60.9
EXPLO 6.01 values:[k]			
$-\Delta_{Ex}U°$ [kJ kg^{-1}][l]	5241	4755	5009
T_{det} [K][m]	3816	3579	3737
P_{CJ} [kbar][n]	269	263	241
V_{det} [m s^{-1}][o]	7978	7900	7685
V_o [L kg^{-1}][p]	620	627	632

[a] A DDNP sample of high purity was provided by another group member.[16] [b] Impact sensitivity (BAM drophammer, 1 of 6). [c] Friction sensitivity (BAM friction tester 1 of 6). [d] Nitrogen content. [e] Decomposition temperature from DSC (β = 5 °C). [f] From X-ray diffraction. [g] Density at 298 K was calculated by using the formula $\rho_{298\ K} = \rho_T/1 + \alpha_V(298 - T_0)$ with $\alpha_V = 1.50 \times 10^{-4}$ K^{-1} (α_V is the volume coefficient of thermal expansion; V = volume) and T_0 = 173 K.[8,17] [h] Calculated (CBS-4M) heat of formation. [i] Energy of formation. [j] Oxygen balance. [k] Values have been calculated by using room-temperature densities. [l] Energy of explosion. [m] Explosion temperature. [n] Detonation pressure. [o] Detonation velocity. [p] Assuming only gaseous products.

Conclusions

From this experimental study the following conclusions can be drawn: 4-Amino-3,5-dinitroaniline (**3**) can be synthesized in three steps in high purity and on large scales (> 20 g). 4-Amino-2,3,6-trinitrophenol (**7**) can also be synthesized by a three-step protocol in good yields. Unfortunately, **7** is only stable up to 119 °C and therefore not of interest for any explosive-based applications. Further nitration of compounds **3** and **7** resulted in the formation of the very sensitive diazophenol derivatives **4** (diazo-2,6-dinitrophenol) and **8** (6-diazo-3-hydroxy-2,4-dinitrophenol). The molecular structures of **3**, **4**, **7** and **8** were determined by single-crystal X-ray diffraction. The sensitivities of **4** and **8** are in the range of DDNP's values, while the thermal stability and calculated performance are slightly better from a statistical point of view.

Experimental Section

4-Fluoro-3,5-dinitrobenzoic Acid (1): To oleum (25% SO_3 by weight, 175 mL) was added nitric acid (100%, 50 mL) under cooling. 4-Fluorobenzoic acid (25.0 g, 178 mmol) was dissolved in this solution portionwise. After complete dissolution, the mixture was heated slowly to 95 °C. This temperature was kept for 5 h. Compound **1** slowly started to precipitate. After cooling, the suspension was poured onto crushed ice (600 g). The product was filtered and washed three times with of ice-cold water (3 × 100 mL) to remove the acid. Compound **1** was obtained as a bright-shining colorless powder (32 g, 78%). $C_7H_3FN_2O_6$ (230.11): calcd. C 36.54, H 1.31, N 12.17; found C 36.58, H 1.24, N 12.44. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 8.94 [d, ^4J(H,F) = 6.3 Hz, 2 H, CH], 11.59 (br. s, 1 H, COOH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 127.4 (d, $^4J_{C,F}$ = 5.8 Hz, 1 C, *C*-COOH), 131.6 (s, 2 C, C-H), 139.2 (d, $^2J_{C,F}$ = 6.7 Hz, 2 C, C-NO$_2$), 152.0 (d, $^1J_{C,F}$ = 283.7 Hz, 1 C, C-F), 162.8 (s, 1 C, COOH) ppm. ^{19}F NMR (376.5 MHz, [D$_6$]acetone): δ = –121.0 (t, $^4J_{H,F}$ = 6.5 Hz, 1 F) ppm.

4-Fluoro-3,5-dinitroaniline (2): Compound **1** (10 g, 43.5 mmol) was dissolved in oleum (25% SO_3 by weight, 25 mL). Afterwards, chloroform (40 mL) was added. Then the suspension was heated to 45 °C, and sodium azide (4.80 g, 73.8 mmol) was added portionwise so that the temperature did not exceed 55 °C. After that, the suspension was stirred for 1 h and then heated to reflux (75 °C) for 16 h. After cooling, the mixture was poured onto crushed ice (500 g), and **2** precipitated as a yellow-brownish powder (7.7 g, 88%). $C_6H_4FN_3O_4$ (201.11): calcd. C 35.83, H , N 20.89; found C 35.68, H 2.20, N 20.96. ^{1}H NMR (400.2 MHz, [D$_6$]acetone): δ = 5.40 (br. s, 2 H, NH$_2$), 7.63 (d, $^4J_{H,F}$ = 5.5 Hz, 2 H, C-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 121.3 (d, $^3J_{C,F}$ = 27.8 Hz, 2 C, C-H), 134.9 (d, $^4J_{C,F}$ = 7.7 Hz, 1 C, C-NH$_2$), 139.1 (s, 2 C, C-NO$_2$), 149.5 (d, $^1J_{C,F}$ = 237.7 Hz, 1 C, C-F) ppm. ^{19}F NMR (376.5 MHz, [D$_6$]acetone): δ = –147.5 (t, $^4J_{H,F}$ = 4.3 Hz, 1 F) ppm. ^{14}N NMR (29.0 MHz, [D$_6$]acetone): δ = –14 (s, 2 N, NO$_2$), –308 (br. s, 1 N, NH$_2$) ppm.

4-Amino-3,5-dinitroaniline (3): Ethanol (300 mL) was placed into a three-neck flask and cooled to –75 °C by using a CO_2/ethanol cooling bath. Then gaseous ammonia was bubbled through the mixture for ca. 30 min. Then **2** (20.0 g, 99.5 mmol) was suspended in this solution. The color of the suspension turned deep red relatively quickly. The temperature was kept at –45 °C for at least 6 h, and then the suspension was further stirred at ambient temperature for ca. 2 d. After removal of the ethanol, the dark brown precipitate was washed several times with ice-cold water to remove the ammonium fluoride. Compound **3** was obtained as a "dark red-black" powder (17.4 g, 88%). $C_6H_6N_4O_4$ (198.14): calcd. C 36.37, H 3.05, N 28.28; found C 36.48, H 2.98, N 27.96. ^{1}H NMR (400.2 MHz, [D$_6$]DMSO): δ = 5.40 (br. s, 2 H, NH$_2$), 7.85 (br. s, 2 H, NH$_2$), 7.89 (s, 2 H, C-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 119.5 (s, 2 C, C-H), 134.3 (s, 1 C, C-NH$_2$), 135.3 (s, 2 C, C-NH$_2$), 137.6 (s, 2 C, C-NO$_2$) ppm. IR (ATR): $\tilde{\nu}$ = 3443, 3361, 3298, 3099, 1614, 1578, 1521, 1506, 1420, 1251, 1231, 1114, 1022, 988, 896, 878, 803, 766 (m) cm^{-1}.

4-Diazo-2,6-dinitrophenol (4): Acetic anhydride (10 mL) was cooled to –10 °C, and nitric acid (100%, 1 mL) was added slowly. After stirring for 1 h, **3** (500 mg, 2.52 mmol) was added. The solution was stirred at 0 °C for 3 h and further at ambient temperature for

16 h. As soon as 24 °C was reached, **4** started to precipitate slowly from the solution. Afterwards, the suspension was poured onto crushed ice (50 g). A beige precipitate of **4** (344 mg, 65%) was obtained. It was filtered and washed with cold water and twice with ice-cold ethanol (20 mL). DSC (5 °C min^{-1}): $T_{dec.}$ = 168 °C. $C_6H_2N_4O_5$ (210.10): calcd. C 34.30, H 0.96, N 26.67; found C 34.40, H 0.89, N 26.52. ^{1}H NMR (400.2 MHz, [D$_6$]acetone/[D$_6$]-DMSO, 5:1): δ = 9.01 (s, 2 H, C-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone/[D$_6$]DMSO, 5:1): δ = 80.9 (s, 1 C, C-N$_2$) 132.6 (s, 2 C, C-H), 143.9 (s, 2 C, C-NO$_2$), 161.8 (s, 1 C, C-O) ppm. ^{15}N NMR (40.6 MHz, [D$_6$]DMSO): δ = –15.6 (t, N = $|^3J_{N,H} + {}^5J_{N,H}|$ = 3.0 Hz, 2 N, NO$_2$), –45.0 (s, 1 N, N$_2$), –139.3 (t, $^3J_{N,H}$ = 2.4 Hz, 1 N, N$_2$) ppm. IR (ATR): $\tilde{\nu}$ = 3033, 2204, 2186, 1639, 1616, 1522, 1504, 1355, 1339, 1291, 1168, 1086, 938, 908, 900, 783, 706 cm^{-1}.

***N*-(4-Acetoxyphenyl)acetamide (5):** 4-Aminophenol (35 g, 320.7 mmol) was dissolved in acetic anhydride (250 mL). Afterwards the solution was stirred until a precipitate formed (typically after 20–25 min). The suspension was heated to 95 °C for 16 h. Then the suspension was poured on crushed ice (1 kg) and stirred until all acetic anhydride was hydrolyzed. Compound **5** was obtained as a white crystalline powder (50 g, 81%). $C_{10}H_{11}NO_3$ (193.20): calcd. C 62.17, H 5.74, N 7.25; found C 62.01, H 5.80, N 6.96.

***N*-(4-Hydroxy-3,5,6-trinitrophenyl)acetamide (6):** Compound **5** (12 g, 62.1 mmol) was dissolved in nitric acid (100 mL, 65%) at 0 °C. This temperature was kept for 5 h, and then the solution's temperature was slowly risen to ambient temperature (6–8 h) and stirring continued for further 12 h. A yellow precipitate was formed. The suspension was poured on crushed ice (500 g). After the ice was molten, the suspension was filtered and washed with only small amounts of ice-cold water to remove the nitric acid. Compound **6** was obtained as a bright-shining yellow powder (10 g, 56%). $C_8H_6N_4O_8$ (286.16): calcd. C 33.58, H 2.11, N 19.58; found C 33.41, H 2.30, N 19.76. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.19 (s, 3 H, CH$_3$), 8.84 (s, 1 H, C-H), 9.58 (br. s, 1 H, N-H), 11.08 (br. s, 1 H, OH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 22.6 (s, 1 C, CH$_3$) 123.3 (s, 1 C, C-NH), 124.7 (s, 1 C, C-H), 135.8 (s, 1 C, C-NO$_2$), 137.5 (s, 1 C, C-NO$_2$), 139.7 (s, 1 C, C-NO$_2$), 143.4 (s, 1 C, C-OH), 169.2 (s, 1 C, C=O) ppm.

4-Amino-2,3,6-trinitrophenol (7): Compound **6** (11.0 g, 38.4 mmol) was dissolved in concentrated sulfuric acid (100 mL) at 0 °C. The yellow solution was stirred at ambient temperature in an open flask for at least 3 d. Afterwards it was poured onto crushed ice (400 g), and a deep dark-reddish powder precipitated. After filtration and subsequent washing with ice-cold water, **7** was obtained as a dark powder (7.14 g, 76%). DSC (5 °C min^{-1}): $T_{dec.}$ = 119 °C. $C_6H_4N_4O_7$ (244.12): calcd. C 29.52, H 1.65, N 22.95; found C 29.40, H 1.39, N 23.10. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 6.60 (br. s, 2 H, NH$_2$), 8.13 (s, 1 H, C-H), 9.82 (br. s, 1 H, O-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 117.7 (s, 1 C, C-H) 127.1 (s, 1 C, C-NH$_2$), 135.1 (s, 1 C, C-NO$_2$), 136.7 (s, 1 C, C-NO$_2$), 138.6 (s, 1 C, C-NO$_2$), 140.9 (s, 1 C, C-OH) ppm. ^{15}N NMR (40.6 MHz, [D$_6$]-acetone): δ = –17.2 (d, $^3J_{N,H}$ = 2.9 Hz, 1 N, NO$_2$), –19.9 (d, $^4J_{N,H}$ = 1.2 Hz, 1 N, NO$_2$), –21.7 (s, 1 N, NO$_2$), –313.8 (d, $^3J_{N,H}$ = 2.4 Hz, 1 N, NH$_2$) ppm. IR (ATR): $\tilde{\nu}$ = 3500, 3385, 3286, 3095, 1602, 1577, 1544, 1508, 1479, 1430, 1372, 1340, 1320, 1262, 1240, 1154, 1043, 903, 893, 806, 758, 736 cm^{-1}.

6-Diazo-3-hydroxy-2,4-dinitrophenol (8): Compound **7** (1.00 g, 4.10 mmol) was dissolved in nitric acid (15 mL, 65%) at 65 °C. The solution was stirred at 65–70 °C for 2 h. Afterwards it was poured onto crushed ice (100 g). After a few minutes, **8** precipitated as a bright yellow powder (695 mg, 75%). DSC (5 °C min^{-1}): $T_{dec.}$ = 170 °C. $C_6H_2N_4O_6$ (226.10): calcd. C 31.87, H 0.89, N 24.28; found C 31.96, H 1.05, N 24.51. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 9.28 (s, 1 H, C-H), 11.37 (br. s, 1 H, O-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 90.9 (s, 1 C, C-N$_2$) 123.8 (s, 1 C, C-NO$_2$), 132.3 (s, 1 C, C-NO$_2$), 133.7 (s, 1 C, C-H), 154.1 (s, 1 C, C-OH), 164.6 (s, 1 C, C-O) ppm. ^{15}N NMR (40.6 MHz, [D$_6$]DMSO): δ = –13.7 (s, 1 N, NO$_2$), –15.6 (d, $^3J_{N,H}$ = 2.8 Hz, 1 N, NO$_2$), –33.2 (s, 1 N, N$_2$), –134.9 (d, $^3J_{N,H}$ = 1.8 Hz, 1 N, N$_2$) ppm. IR (ATR): $\tilde{\nu}$ = 3075, 2192, 1638, 1606, 1516, 1492, 1449, 1368, 1304, 1215, 1172, 1084, 932, 915, 798, 770, 743, 706 cm^{-1}.

CCDC-1057558 (for **3**), -1057560 (for **4**), -1057559 (for **7**), and -1057561 (for **8**) contain 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.

Supporting Information (see footnote on the first page of this article): X-ray diffraction data; general methods; calculation of heat of formation; ^{1}H and ^{13}C NMR spectra.

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