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Synthesis and Initiation Capabilities of Energetic Diazodinitrophenols

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Abstract. The diazophenols 3-amino-6-diazo-2,4-dinitrophenol (**4**) and 3-chloro-6-diazo-2,5-dinitrophenol (**8**) were synthesized and comprehensively characterized. The regio-selectivity of nitration reactions with *N*,*N*′-(1,4-phenylene)dimethanesulfonamide (**1**) and *N*,*N*′-(1,4-phenylene)diacetamide (**6**) was investigated in detail. The purity of the products was confirmed via low temperature X-ray diffraction, multinuclear NMR spectroscopy, and elemental analysis. Moreover, the capability of **4** and **8** to initiate **RDX** (1,3,5-trinitro-1,3,5-triazinane) was tested, together with the two other recently presented diazophenols 4-diazo-2,6-dinitrophenol (***iso*-DDNP**) and 3-hydroxy-**DDNP** (**HODDNP**). The tests revealed superior properties of **HODDNP** compared to **DDNP** and the other tested diazophenols regarding its ability to initiate **RDX**.

Introduction

The current and the future scope of research in the field of energetic materials is the performance improvement of primary and secondary explosives in general.[1,2] In addition it is a common task to use heavy metal free compounds which are mostly more environmentally benign.[3,4]

The main difference between primary and secondary explosives is the unique ability of the former class to undergo the so called deflagration-to-detonation transition (DDT), meaning the acceleration of a subsonic heat based energy transfer of the decomposition reaction into a supersonic shockwave, even in an unconfined state. High performance primary explosives like lead azide (**LA**) detonate virtually immediately when exposed to heat even in the smallest quantities. Unfortunately, lead azide is a highly toxic compound and liberates hydrazoic acid in moist air due to the reaction with carbon dioxide, leading to the development of more environmentally benign primary explosives like copper(I) 5-nitrotetrazolate (**DBX-1**),[5] or dipotassium 1,1′-dinitramino-5,5′-bitetrazolate.[6] Another option are metal-free primary explosives like 1-(5-tetrazolyl)-3-guanyltetrazene hydrate (tetrazene), 2-diazo-4,6-dinitrophenol (**DDNP**), or 2,4,6-triazido-1,3,5-triazine (**TAT**), but practically most of them only undergo a DDT when confined and even then rather large amounts (several hundred milligrams) are necessary for the reliable initiation of a secondary explosive, rendering them unserviceable for small initiation devices. As a result of this and their high sensitivities toward mechanical stimuli they are usually utilized either in (environmentally benign) percussion caps,[7] or as sensitizers in detonators. For example, the addition of 2% tetrazene to **LA** lowers the stab initiation energy from 1000 mJ to 3 mJ.[8] However, **TAT** is currently under investigation as **LA** replacement in the NOL-130 stab mix employed in the M55 stab detonator,[9] owing to its better initiation capability than **LA**.[10] Unfortunately, it suffers from the major drawback of a high volatility due to the non-ionic structure with only weak intermolecular interactions. The recently presented,[11] and herein further investigated, 6-diazo-3-hydroxy-2,4-dinitrophenol (**HODDNP**) and 4-diazo-2,6-dinitrophenol (***iso*-DDNP**) offer the zwitterionic nature of **DDNP** coupled with a higher density. **HODDNP** with its additional hydroxy group in comparison to **DDNP** is a non-volatile metal-free primary explosive with superior initiation capability than **DDNP** itself.

Furthermore two diazophenols, namely 6-diazo-3-amino-2,4-dinitrophenol (**4**) and 3-chloro-6-diazo-2,5-dinitrophenol (**8**) were synthesized. During the synthesis of **4** the regio-selectivity of the nitrations using *N*,*N*′-(1,4-phenylene)dimethanesulfonamide (**1**) and *N*,*N*′-(1,4-phenylene)diacetamide (**6**) as starting materials was investigated and confirmed by single-crystal X-ray diffraction and NMR spectroscopy. The nitration of *N*,*N*′-(1,4-phenylene)dibenzenesulfonamide resulting in the formation of three regio-isomers was already described by *K.-Y. Chu* and *J. Griffiths*.[12] The use of the methanesulfonyl protection group resulted in two advantages described herein. Additionally, the initiation capability of these two compounds (**4** and **8**) was also tested in combination with **RDX**.

Results and Discussion

Synthesis

A synthesis protocol is displayed in Scheme 1.

The first step was the protection of the free amines resulting either in the formation of *N*,*N*′-(1,4-phenylene)dimethane sulfonamide (**1**) or *N*,*N*′-(1,4-phenylene)diacetamide (**6**). After that the regio-selectivity toward the nitration of **1** and **6** was

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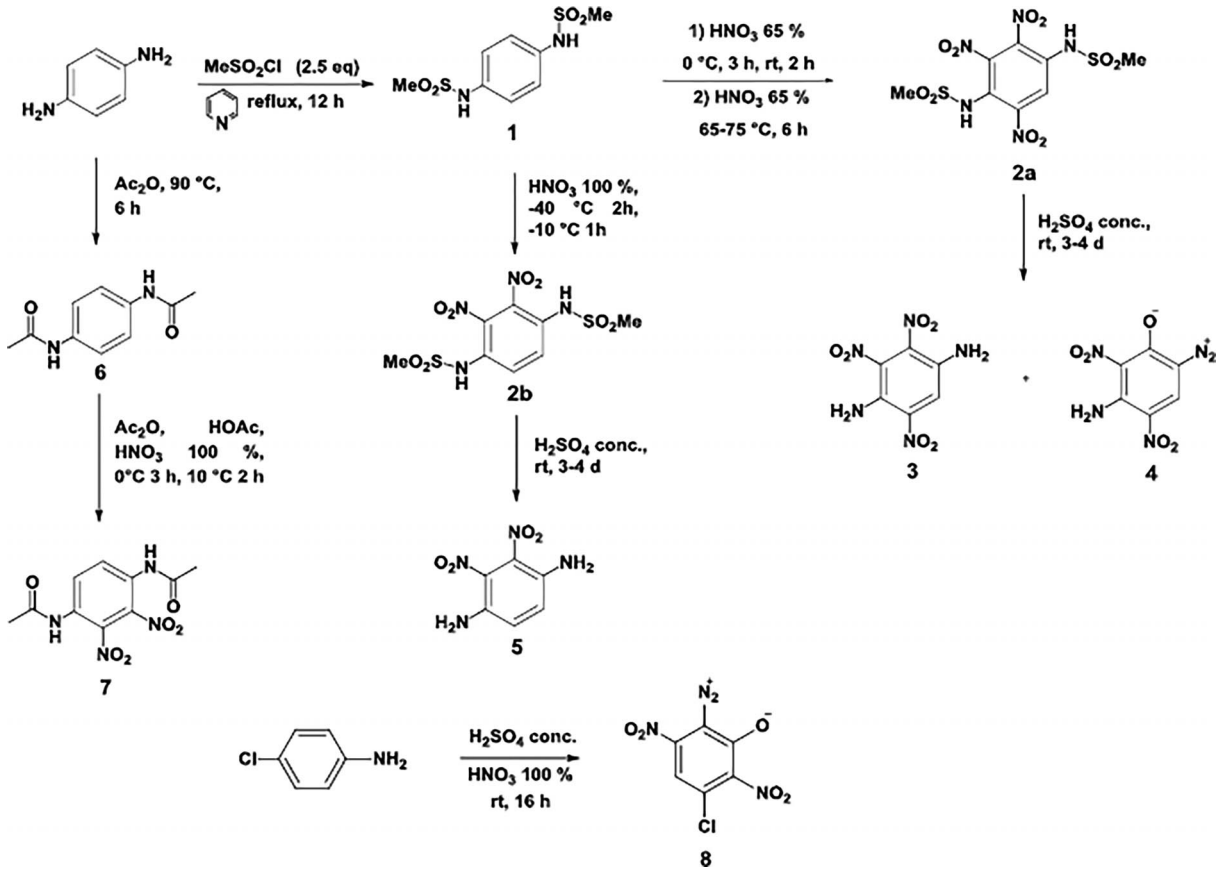

Scheme 1. Syntheses of diazophenols **4** and **8**.

intensively studied. **2a** was synthesized via a two-step nitration. In the first step an isomeric mixture of twice nitrated species was obtained. This was confirmed by CHN analysis. When the nitration is heated up to 65–75 °C the corresponding trinitro-derivative (**2a**) was obtained. **2a** could only be obtained when methansulfonyl chloride was used as protection group. When, for example, the benzenesulfonyl or the *p*-toluenylsulfonyl protection groups were used only the twice nitrated species were formed. Too harsh nitration conditions resulted in the cleavage of those protection groups or their nitration. *N*,*N*′-(2,3-dinitro-1,4-phenylene)dimethane sulfonamide (**2b**) or *N*,*N*′-(2,3-dinitro-1,4-phenylene)diacetamide (**7**) could also be synthesized selectively. Compound **2b** was synthesized using 100 % nitric acid at low temperatures and **7** by using acetylnitrate as nitrating reagent. The regio-selectivity was confirmed by crystallization of the protected (for compound **7**) and the deprotected product (for compound **5**). It was also confirmed that **2b** can be used as a more efficient starting material for **2a** achieving higher yields. In this case **2a** was synthesized by using 82.5 % nitric acid at a reaction temperature of 45 °C resulting in an enhanced yield of **2a** (70 %). The deprotection of **2a** resulted in the formation of two different compounds. As expected 1,4-diamino-2,3,5-trinitrobenzene (**3**) is formed. Additionally the highly sensitive primary explosive 3-amino-6-diazo-2,4-dinitrophenol (**4**) is formed. This even happens in all attempts to synthesize 1,4-diamino-2,3,5,6-tetranitrobenzene with **3** as starting material. The same behavior was observed when using 4-amino-2,3,6-trinitrophenol, resulting in the formation of **HODDNP**.[11] The mechanism how **3** is converted into **4** could not be determined certainly. After isolation of pure **3** and **4** DSC curves were recorded to determine their decomposition temperatures (displayed in Figure 1).

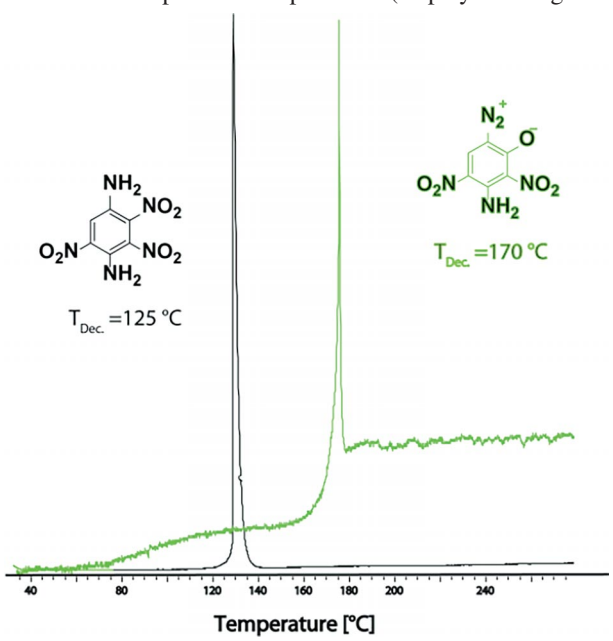

Figure 1. DSC curves of **3** and **4** (heating rate β = 5 K·min^{-1}).

Additionally, compounds **5** and **7** were crystallized from DMSO.

These two products differ dramatically in their thermal stability. Interesting to mention is the unexpected low thermal stability of **3** (125 °C). The literature known constitution isomer 1,3-diamino-2,4,6-trinitrobenzene for example is stable up to 286 °C.[13] Compound **4** however shows the typical thermal stability of 170 °C. The purity of **3** could only be confirmed by CHN elemental analysis, high resolution mass spectrometry and additionally by IR spectroscopy due to the conversion of **3** into **4** in organic polar solvents. The diazo vibration at 2195 cm^{-1} and the carbonyl vibration at 1593 cm^{-1} only appear in the IR spectrum of **4**. The N–H vibrations of the amino groups appear at 3365 cm^{-1} and 3474 cm^{-1}, whereas for **4** they are located at 3282 cm^{-1} and 3390 cm^{-1}. Finally, the nitration of 4-chloroaniline resulted in the formation of 2-diazo-5-chloro-3,6-dinitrophenol (**8**).

Crystal Structures

Suitable single crystal of compounds **2a**, **4**, **5**, **7**, and **8** were picked from the crystallization mixtures and mounted in Kel-F oil, transferred to the N_2 stream of an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection and data reduction was performed using the CRYSALISPRO software.[14] The solution and refinement of all structures were performed using the programs ^{sir}-92[15], SHELXS-97[16] and SHELXL-97[17] implemented in the WINGX software package[18] and finally checked with the PLATON software.[19] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined when possible. The absorptions were corrected with the SCALE3 ABSPACK multi-scan method.[20] Selected data of the measurements and the refinements are given in Table 1.

N,*N*′-(2,3,5-Trinitro-1,4-phenylene)dimethanesulfonamide (**2a**) could only obtained crystalline with inclusion of DMSO. The molecular unit consisting of one *N*,*N*′-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide and two dimethylsulfoxide molecules is shown in Figure 2. The compound crystallizes in the triclinic space group $P\bar{1}$ with a density of 1.597 g·cm^{-3} at –100 °C. As expected all nitro groups are twisted out of the ring plane.

The molecular unit of 3-amino-6-diazo-2,4-dinitrophenol (**4**) is depicted in Figure 3. The compound crystallizes in the orthorhombic space group *Pnma* with four molecules in the unit cell. Its density of 1.913 g·cm^{-3} at –100 °C is significantly higher than that of the recently published **HODDNP** (1.837 g·cm^{-3}).[11] The bond length N1–N2 of 1.098(3) Å clearly indicates a N≡N triple bond, whereas the C1–N1

Table 1. Crystallographic data and refinement parameters of compound **2a**, **4**, **5**, **7**, and **8**.

	2a	**4**	**5**	**7**	**8**
Formula	$C_{12}H_{21}N_5O_{12}S_4$	$C_6H_3N_5O_5$	$C_6H_6N_4O_4$	$C_{10}H_{10}N_4O_6$	$C_6HClN_4O_5$
FW /g·mol^{-1}	555.58	225.13	198.15	282.22	244.56
Crystal system	triclinic	orthorhombic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	*Pnma* (no. 62)	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)	*Pc* (no. 7)
Color / habit	colorless plate	orange block	yellow block	yellow needle	yellow rod
Size /mm	0.03 × 0.15 × 0.20	0.15 × 0.19 × 0.20	0.19 × 0.21 × 0.49	0.06 × 0.14 × 0.23	0.08 × 0.11 × 0.23
a /Å	10.1892(11)	16.2313(6)	12.2042(6)	7.7535(16)	6.5289(4)
b /Å	10.5895(9)	10.6548(4)	10.8478(4)	8.0847(11)	6.9889(4)
c /Å	11.6355(15)	4.5210(2)	7.2959(4)	10.7662(19)	9.7159(6)
α /°	97.918(9)	90	90	84.878(13)	90
β /°	104.484(10)	90	124.954(4)	70.272(17)	97.723(6)
γ /°	103.643(8)	90	90	75.493(15)	90
V /Å^3	1155.1(2)	781.87(5)	791.66(8)	615.0(2)	439.31(5)
Z	2	4	4	2	2
$\rho_{calcd.}$ /g·cm^{-3}	1.597	1.913	1.663	1.524	1.849
μ /mm^{-1}	0.479	0.170	0.142	0.128	0.450
F(000)	576	456	408	292	244
λ(Mo-$K_α$) /Å	0.71073	0.71073	0.71073	0.71073	0.71073
T /K	173	173	173	298	173
θ min-max /°	4.2, 26.0	4.6, 27.0	5.1, 26.5	4.3, 26.0	4.2, 26.0
Dataset h; k; l	–12:12; –13:13; –14:14	–17:20; –13:13; –5:5	–15:15; –13:13; –9: 9	–9:9; –9:9; –11:13	–8:8; –8:8; –11:11
Reflect. coll.	8374	5595	5627	4029	5976
Independ. refl.	4506	891	823	2385	1704
R_{int}	0.047	0.023	0.023	0.037	0.025
Reflection obs.	3236	822	742	1352	1662
No. parameters	316	88	76	221	149
R_1 (obs)	0.0868	0.0380	0.0303	0.0637	0.0212
wR_2 (all data)	0.1990	0.0947	0.0891	0.1770	0.0525
S	1.08	1.20	1.05	1.01	1.07
Resd. dens. /e Å^{-3}	–0.49, 1.63	–0.22, 0.27	–0.25, 0.19	0.22, 0.23	–0.13, 0.15
Device type	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan

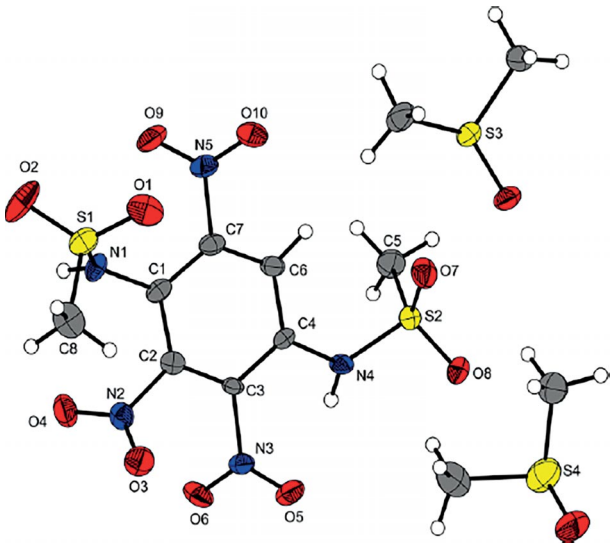

Figure 2. Molecular unit of **2a**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level. Selected bond lengths /Å: C7–N5 1.479 (7), C2–N2 1.471 (8), 1.471 (8), C1–N1 1.411 (9), C4–N4 1.381 (9), S1–N1 1.628 (6), S2–N4 1.645 (6), S1–O1 1.434 (7), S1–O2 1.428 (8), S2–S8 1.426 (5), S1–C8 = S2–C5 1.745 (8); Selected bond angles /°: C2–C3–N3 117.87 (6), C3–C2–N2 119.22 (6), C6–C7–N5 115.64 (6), C4–N4–S2 125.93 (5), C1–N1–S1 124.31 (5), O1–S1–N1 107.67 (3), O2–S1–N1 105.19 (4), C8–S1–N1 105.68, O2–S1–O1 121.04 (4), O7–S2–O8 120.02 (3), C5–S2–N4 107.09 (3), O8–S2–N4 104.27 (3), O7–S2–N4 107.66 (3); Selected torsion angles /°: C3–C2–N2–O3 57.3 (1), C2–C3–N3–O6 55.9 (1), C6–C7–N5–O10 46.9 (1), C2–C1–N1–S1 75.9 (1), C6–C4–N4–S2 9.4 (1).

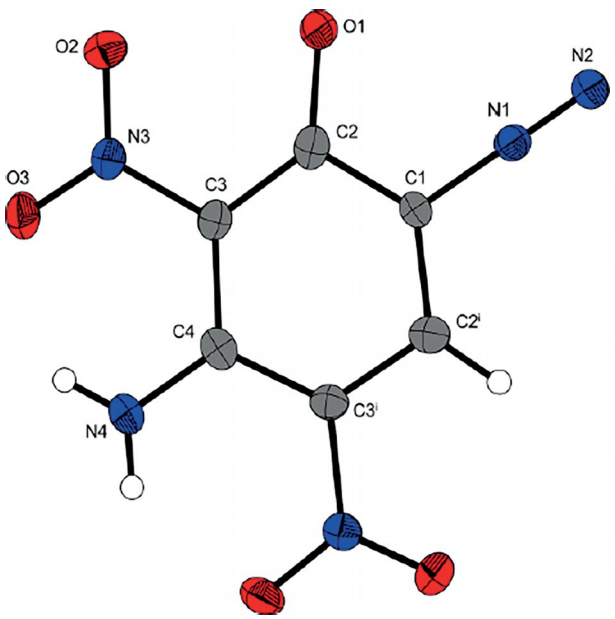

Figure 3. Molecular unit of **4**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level. Selected bond lengths /Å: C1–N1 1.367 (3), N1–N2 1.098 (3), C2–O1 1.324 (4), C3–N3 1.441 (2), N3–O3 1.235 (2), C4–N4 1.321 (3), O3–N4 2.59 (1); Selected bond angles /°: C1–N1–N2 177.7 (3), N3–O3–O2 121.3, O3–N3–O2 121.3; Selected torsion angles (°): C2–C3–N3–O2 11.8 (2), C3–C4–N4–H 2.9 (2.9).

[1.367(3) Å] and C2–O1 [1.324(4) Å] bonds are also significantly shorter than typical C–N (1.47 Å) and C–O (1.43 Å) single bonds.

1,4-Diamino-2,3-dinitrobenzene (**5**), depicted in Figure 4, crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell. Its density at –100 °C is 1.663 g·cm^{-3} which is slightly lower than that of 1,3-diamino-2,4-dinitrobenzene (1.74 g·cm^{-3} at 298 K)[21] and 1,2-diamino-4,5-dinitrobenzene (1.725 g·cm^{-3} at –100 °C).[22] The molecular unit is shown in Figure 4.

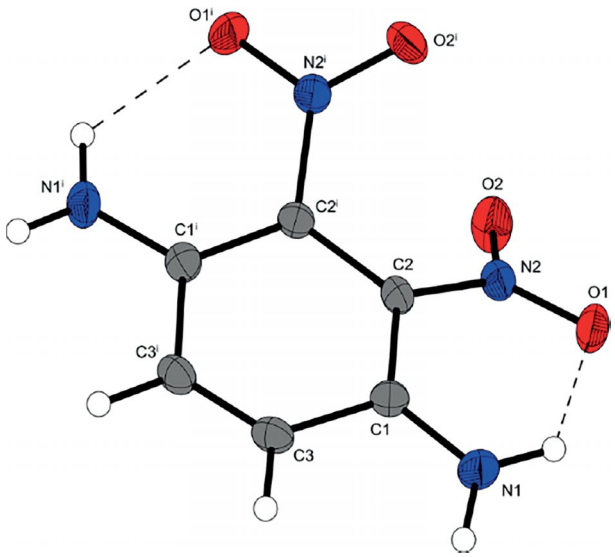

Figure 4. Molecular unit of **5**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level. Selected bond lengths /Å: C1–N1 1.332 (2), C2–N2 1.411 (2), N2–O1 1.254 (2), N2–O2 1.239 (2); Selected bond angles /°: O1–N2–O2 120.8 (2). Selected torsion angles /°: C2–C2i–N2–O2 15.1 (2), C2–C1–N1–H1B 6.8 (2);.

The twice N-protected *N*,*N*′-(2,3-dinitrophenyl)1,4-diacetamide (**7**) crystallizes in the triclinic pace group $P\bar{1}$ with two molecular units (Figure 5) in the unit cell. Its density (1.524 g·cm^{-3}) is significantly lower than that of **5**.

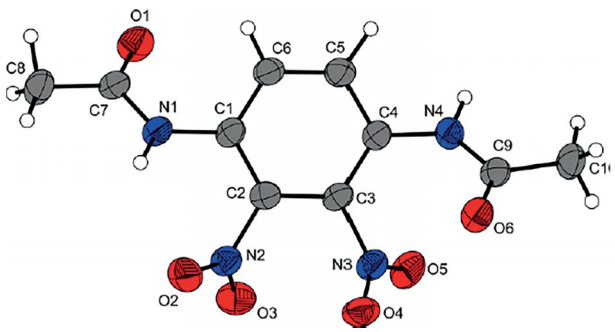

Figure 5. Molecular unit of **7**. Selected bond lengths /Å: C1–N1 1.423 (4), C2–N2 1.464 (4), C3–N3 1.475 (4), C4–N4 1.411 (4), N2–O2 1.217 (3), N2–O3 1.222 (3), N3–O4 1.215 (3), N3–O5 1.221 (3), C7–O1 1.219 (4), C9–O6 1.223 (4). Selected bond angles /°: N1–C1–O1 122.3 (3), O2–N2–O3 123.8 (3), O4–N3–O5 125.5 (3), N4–C9–O6 122.4 (3). Selected torsion angles /°: C3–C4–N4–C9 50.2 (5), C6–C1–N1–C7 42.9 (5), C4–C3–N3–O5 51.5 (5), C3–C2–N2 O3 48.5 (4).

2-Diazo-5-chloro-3,6-dinitrophenol (**8**), depicted in Figure 6, crystallizes in the monoclinic space group *Pc* with two molecules in the unit cell. Its density at –100 °C is 1.849 g·cm^{-3} which interestingly is lower than that of **4** (1.913 g·cm^{-3}). The diazo bond N2–N9 [1.111(2) Å] is again in the range of a N≡N triple bond, whereas the C4–N5 bond length is significantly shorter [1.234(2) Å] than the C–O bond observed in structure of **4**.

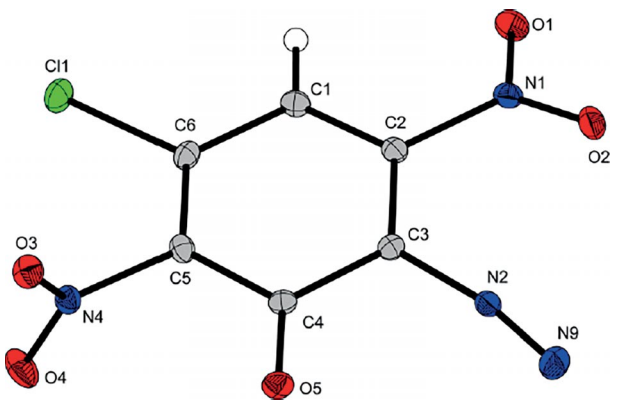

Figure 6. Molecular unit of **8**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level. Selected bond lengths /Å: C3–N2 1.354 (2), N2–N9 1.111 (2), C4–O5 1.234 (2), C5–N4 1.465 (2), N4–O3 1.221 (2), N4–O4 1.220 (2), C6–Cl1 1.714 (2), C2–N1 1.470 (2), N1–O1 1.228 (2), N1–O2 1.219 (2). Selected bond angles /°: C3–N2–N9 168.3 (2), O2–N1–O1 125.0 (2), O3–N4–O4 125.1 (2). Selected torsion angles /°: C4–C3–N2–N9 0.7 (1), C4–C5–N4–O3 77.4 (2), C3–C2–N1–O2 12.8 (2).

Initiation Capability Testing and Energetic Properties

The capability of the compounds to undergo a DDT was tested with some basic heating methods. First, a small amount (approx. 5 mg) of **HODDNP**, ***iso*-DDNP**, **4**, or **8** was heated on a spatula using a lighter, without direct flame contact. Typical for metal-free primary explosives the compounds only deflagrated upon reaching their corresponding ignition temperatures due to the missing confinement, similar to tetrazene and **DDNP**. Rapid heating by touching a small amount of the compounds with a hot needle or a hot spatula thus also only resulted in a deflagration. To investigate the capability of the compounds to nevertheless initiate a secondary explosive the commonly used **RDX** (200 mg) was loaded into an aluminum tube (58.0 mm × 7.2 mm, inner diameter 6.5 mm) glued to the center of a copper witness plate (50 mm × 50 mm × 1 mm) and slightly pressed manually. Varying amounts of those diazophenols were loaded onto the **RDX** and also slightly pressed manually. For the ignition a commercial type A electrical igniter was used on top, with a direct contact of the fusehead to the primary explosive. The isolator casing of the igniter was clamped with the metal tube (see Figure 7 for a schematic). The whole setup was placed in a wooden box and covered with slightly wet sand. While ***iso*-DDNP**, **4**, and **8** (50 mg of each) were not able to initiate **RDX**, similar to **DDNP** itself (also 50 mg), **HODDNP** on the other hand was able to initiate **RDX**. Figure 7 (top right) shows the test results of **HODDNP** together with the witness plate of a lead azide (50 mg) test sample. The plates clearly reveal that not only did 25 mg of **HODDNP** result in a full detonation of **RDX** but even a small amount of only 10 mg were able to detonate the secondary

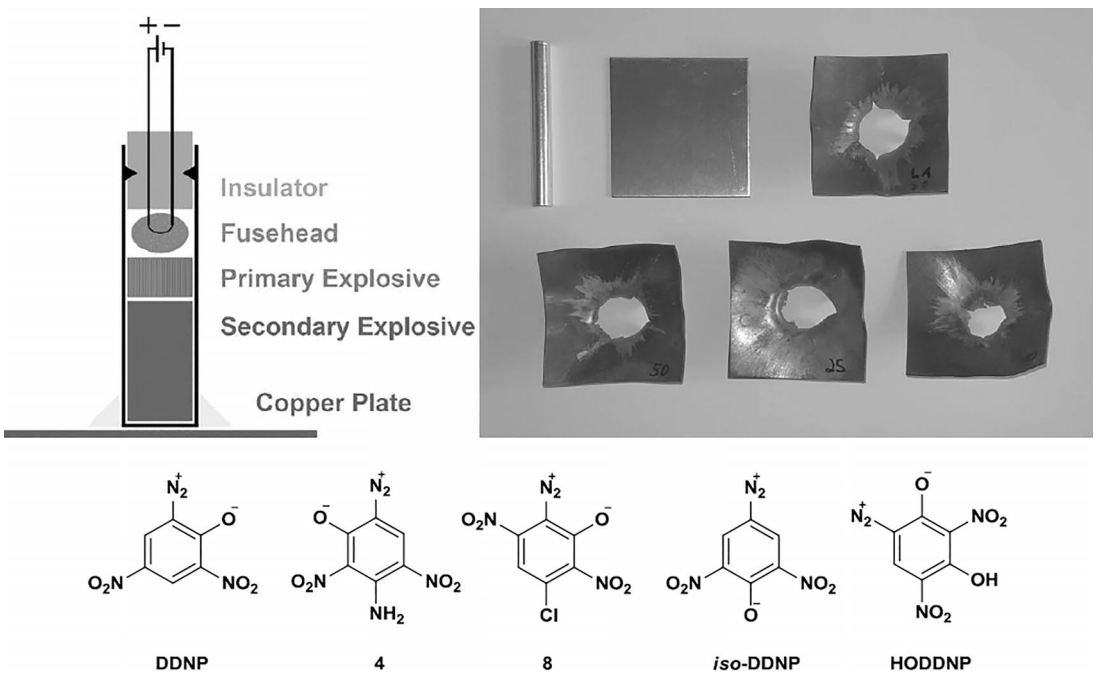

Figure 7. Schematic test setup (top left), tested primary explosives (row below) and results of the initiation capability test of **HODDNP** (top right): Upper row: aluminum tube, copper plate, copper plate of the lead azide (50 mg) benchmark; lower row: copper plates of the tests with **HODDNP** (50, 25, 10 mg); each test performed with 200 mg RDX as secondary explosive.

explosive. **DDNP** itself, ***iso*-DDNP**, **4**, and **8** only resulted in a (partial) deflagration of the output charge, with merely a small dent in the copper plate, or no damage at all. In the case of a detonation the aluminum tube is completely shattered into very small pieces, while in the case of a deflagration it is usually only torn open. Typically, in the case of the latter about half of the RDX load can still remain in the bottom of the tube with no visible changes to it.

Furthermore the thermal stability of **HODDNP** was tested by isoperibolic long term measurement in an open glass vessel using a Systag Flexy TSC equipped with a Radex V5 measuring cell, revealing that the compound is stable for at least 60 h at 75 °C. Moreover, storage of this compound in an oven at 100 °C for 60 h does not result in any mass lost or change in the chemical composition. This was proven by CHN elemental analysis and ^{1}H NMR spectroscopy. In addition, **HODDNP** is stable when stored under water, which is important for shipping security reasons. After suspending it in 30 mL of water the suspension was allowed to stand for a few days at ambient temperature until the water evaporated. The chemical composition was subsequently again confirmed by CHN elemental analysis and ^{1}H NMR spectroscopy as unchanged and pure.

Conclusions

The regio-selective nitration of double protected *p*-phenylene-1,4-diamine was investigated. The methanesulfonyl protection group seems to be superior in comparison to the acetyl group because it allows the phenyl ring to be nitrated three times and the cleavage of that group works straight forward.

The yields for *N*,*N*′-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide (**2a**) could be improved by two steps by first nitrating *N*,*N*′-(1,4-phenylene)dimethanesulfonamide twice in C2 and C3 position and then in C5 position with 82.5 % HNO_3 at 45 °C.

The capability of the synthesized diazophenols (**4**, **8**, **HODDNP** and ***iso*-DDNP**) to initiate **RDX** was tested and compared to **DDNP**. **HODDNP** shows superior properties as **RDX** initiator in comparison to **DDNP**. It is thermally stable for a prolonged time (100 °C for 60 h), stable in water and obtainable via a low cost straight forward synthesis.

Experimental Section

General: NMR spectra were recorded with the spectrometers JEOL Eclipse 270, Eclipse 400, JEOL ECX 400 and Bruker Avance III 400. The measurements were conducted in regular glass NMR tubes (Ø 5 mm) and, if not stated otherwise, at 25 °C. Tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{15}N) were used as external standards. As an additional internal standard the reference values of the partially deuterated solvent impurity (^{1}H) and the fully deuterated solvent (^{13}C) were used.[23] Infrared (IR) spectra were recorded with a PerkinElmer BX FT IR spectrometer equipped with a Smiths DuraSamplIR II diamond ATR unit using pure samples. Transmittance values are qualitatively described as "strong" (s), "medium" (m) and "weak" (w). The determination of the carbon, hydrogen, and nitrogen contents (EA analysis) was carried out by combustion analysis using an Elementar Vario EL. Differential scanning calorimetry was conducted with a Linseis DSC-PT10 in closed aluminum pans, equipped with a hole (Ø 0.1 mm) for gas release, and at a heating rate of 5 K·min^{-1}. Melting points were checked with a Büchi Melting Point B-540 apparatus in open glass capillaries.

The sensitivities to impact (IS) and friction (FS) were determined according to BAM[24] standards using a BAM drop hammer (100 cm maximum drop height; 1, 5 and 10 kg weights; compound contained between two steel cylinders held together by a steel ring) and a BAM friction apparatus (5 to 360 N range).[25] The compounds were sieved to determine the grain size (< 100 µm, 100 to 500 µm, > 500 µm).

***N*,*N*′-(1,4-Phenylene)dimethanesulfonamide (1):** *P*-Phenylene-diamine (36.2 g, 335 mmol) was dissolved in pyridine (350 mL). The solution was cooled down to 0 °C and methanesulfonylchloride (57.0 mL, 781 mmol) was added slowly. After 1 h the cooling was removed and the suspension was stirred at ambient temperature for about 3 h. Subsequently, the suspension was refluxed for at least 16 h. After that the solution was poured onto crushed ice (1 kg) and filtered. The precipitate was washed with large amounts of 2 M hydrochloric acid and water. **2** was obtained as a cocoa-colored powder (84.8 g, 96 %). $C_8H_{12}N_2O_4S_2$ (264.32 g·mol^{-1}): found (calcd.): C 36.49 (36.35), H 4.75 (4.58), N 10.89 (10.60), S 24.40 (24.26) %. **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 2.91 (s, 6 H, CH_3), 7.15 (s, 4 H, $CH_{arom.}$), 9.58 (br. s, 2 H, NH); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 39.6 (2C, CH_3), 122.2 (4C, CH), 135.1 (2C, C–N) ppm.

***N*,*N*′-(2,3,5-Trinitro-1,4-phenylene)dimethanesulfonamide (2a):** Nitric acid (65 %, 200 mL) was cooled to 0 °C. **1** (25 g, 95 mmol) was added portion wise so that the temperature did not exceed 5 °C. The solution was stirred at 0 °C for 6 h. After that the solution was further stirred at ambient temperature for about 12 h. The formed yellow precipitate is a mixture of isomeric *N*,*N*′-(dinitro-1,4-phenylene)dimethanesulfonamide and **2a**. The suspension was poured onto crushed ice (1 kg) and filtered. After washing with large amounts of water the crude solid was dried in an oven at 60 °C for about 12 h. Then, nitric acid (65 %, 250 mL) was heated up to 65–70 °C. The crude material isolated before was added slowly, resulting in the release of huge amounts of nitrous fumes. The suspension was stirred until no such fumes occurred anymore (typically four to 5 h). After that the suspension was poured onto crushed ice (500 g). The bright yellow solid was filtered off and washed only with small amounts of ice water to remove the acid. The obtained **2a** was dried in an oven at 60 °C for 12 h. **2a** was further purified. The yellow solid was refluxed in glacial acetic acid overnight. Subsequently the suspension was filtered directly after cooling down to ambient temperature and pure **2a** was obtained (12 g, 32 %). DSC (5 °C·min^{-1}): $T_{dec.}$ = 230 °C. $C_8H_9N_5O_{10}S_2$ (399.31 g·mol^{-1}): found (calcd.): C 24.18 (24.06), H 2.35 (2.27), N 17.79 (17.54), S 16.30 (16.06) %. **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 3.05 (s, 3 H, CH_3), 3.23 (s, 3 H, CH_3), 8.37 (s, 1 H, $CH_{arom.}$). Note: The N–H protons could not be observed. **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 41.6 (1C, CH_3), 42.5 (1C, CH_3), 118.8 (1C, C-H), 124.0, 133.1, 138.2, 143.8, 149.5. **^{15}N NMR** ([D$_6$]DMSO, 75 °C, 25 °C): δ = –18.5 (d, $^{3}J_{N-H}$ = 2.8 Hz, 1 N, NO_2), –23.7 (s, 1N, NO_2), –24.1 (d, $^{4}J_{N-H}$ = 2.8 Hz, 1N, NO_2), –262.3 (d, $^{3}J_{N-H}$ = 0.8 Hz, 1N, NH-SO_2Me), –281.6 (s, 1N, NH-SO_2Me) ppm.

Alternative Synthesis of 2a using 2b as Starting Material: Nitric acid (65 %, 20 mL) was mixed with nitric acid (100 %, 20 mL) under cooling. **2b** (4.5 g, 13 mmol) was added slowly. After 1 h the suspension was heated to 45 °C and the temperature was held for 16 h. The suspension was filtered through a borosilicate glass filter (pore size 3) after cooling down to ambient temperature. The precipitate was washed first with water, then with ethanol and diethyl ether. **2a** was

thus obtained as a pale yellow powder (3.6 g, 70 %). Analytics for **2a** see above.

***N,N′*-(2,3-Dinitro-1,4-phenylene)dimethanesulfonamide (2b):** Nitric acid (100 %, 150 mL) was cooled down to –40 °C. Afterwards **1** (20.0 g, 75.7 mmol) was added slowly so that the temperature did not exceed –30 °C. The dark solution was stirred at –40 °C for 2 h. The solution was warmed up to –10 °C and further stirred for 1 h. Then it was poured onto crushed ice and **2b** precipitated as a brownish powder. **2b** was filtered and washed with ice water to get rid of nitric acid. (14.9 g, 56 %) $C_8H_{10}N_4O_8S_2$ (354.32 g·mol^{-1}): found (calcd.): C 27.20 (27.12), H 2.55 (2.84), N 15.74 (15.81), S 18.22 (18.10) %. **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 3.17 (s, 3 H, CH_3), 7.88 (s, 2 H, C–$H_{arom.}$), 10.30 (br. s, 2 H, N–H); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 41.3 (2C, CH_3), 128.6 (2C, C–H), 131.3 (2C, C–$NH_{sulfonamide}$), 139.2 (2C, C–NO_2) ppm.

1,4-Diamino-2,3,5-trinitrobenzene (3): 2a (10 g, 25 mmol) was suspended in concentrated sulfuric acid (250 mL) at 0 °C and water (10 mL) was added very slowly so that the temperature did not exceed 15 °C. The suspension was stirred until a dark red solution was obtained (typically 24–48 h!!). The solution was filtered using a very fine borosilica consisting suction strainer (pore size 4) to get rid of traces of **2a**. The clear filtrate was slowly poured onto large amounts of crushed ice (about 1 kg) so that the temperature did not rise significantly. **3** was obtained as a dark purple powder (1.8 g 30 %). DSC (5 K·min^{-1}): $T_{dec.}$ = 125 °C. $C_6H_5N_5O_6$ (243.13 g·mol^{-1}): found (calcd.): C 29.77 (29.64), H 2.07 (2.07), N 28.91 (28.80) %. **HRMS** (%, error in mmu): 243.0231 (–0.9). **MS** [DEI+,(%)]: 243.1 (100), 197.1 [M–HNO_2 (2)], 151.1 [197.1-NO_2(58)], 105.1 [151.1-NO_2(23)]. **IR** (ATR): $\tilde{\nu}$ = 3474 (m), 3365 (s), 3090 (w), 1549 (s), 1528 (s), 1427 (m), 1390 (w), 1348 (m), 1253 (vs), 885 (s), 809 (s), 766 (m), 743 (m) cm^{-1}. Good NMR spectroscopic data could not be obtained so far. It is proposed that **3** decomposes to **4** in any organic solvent.

When the mother liquor of **3** is stored in the fridge at 4 °C for at least 24 h compound **4** slowly started to precipitate. This also happens when the solution during the deprotection exceeds 30 °C.

3-Amino-6-diazo-2,4-dinitrophenol (4): DSC (5 K·min^{-1}): $T_{dec.}$ = 170 °C. $C_6H_3N_5O_5$ (225.13 g·mol^{-1}) found (calcd.): C 31.94 (32.01), H 1.40 (1.34), N 30.87 (31.11) %. **^{1}H NMR** ([D$_6$]DMSO, 75 °C, 25 °C): δ = 8.69 (br. s, 2 H, NH_2), 9.32 (s, 1 H, CH_{arom}). **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 87.3 (1C, C–N_2), 123.7, 125.1, 137.2, 147.0, 163.9 (1C, C–O). **^{15}N NMR** ([D$_6$]DMSO, 25 °C): δ = –15.0 (s, 1N, NO_2), –16.4 (d $^3J_{N–H}$ = 2.8 Hz, 1N, NO_2), –37.5 (s, 1N, N_2, N_β), –137.1 (d, $^3J_{N–H}$ = 3.2 Hz, 1N, N_2, N_α), –288.7 (s, 1N, NH_2) ppm. **IR** (ATR): $\tilde{\nu}$ = 3390 (m), 3282 (m), 3076 (w), 2195 (s), 1593 (vs), 1557 (s), 1520 (m), 1477 (m), 1368 (m), 1311 (m), 1277 (s), 1242 (s), 1162 (m), 1128 (m), 1033 (m), 929 (m), 887 (m), 781 (m), 755 (m), 570 (s) cm^{-1}. **Sensitivities** (grain size < 100 µm): IS 1 J, FS 28 N.

1,4-Diamino-2,3-dinitrobenzene (5): 2b (10.0 g, 28.2 mmol) was dissolved in concentrated sulfuric acid (150 mL) and water (5 mL) was added slowly. The dark solution was stirred at ambient temperature for at least 3 d. Afterwards the solution was poured onto crushed ice (1 kg). **5** precipitated as a dark reddish powder (3.8 g, 68 %). $C_6H_6N_4O_4$ (198.14 g·mol^{-1}). **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 7.13 (s, 2 H, C-$H_{arom.}$), 7.19 (br. s, 2 H, NH_2); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 123.1 (2C, C–NH_2), 128.2 (2C, C–$H_{arom.}$) 139.8 (2C, C–NO_2) ppm.

***N,N′*-(1,4-Phenylene)diacetamide (6):** *P*-phenylenediamine (10 g, 93 mmol) was dissolved in acetic anhydride (100 mL) at ambient temperature. The slurry was boiled at 90 °C for 6 h. Afterwards the mixture was poured onto ice water (500 g) and stirred until the acetic anhydride was completely hydrolyzed. After filtration the solid was washed with large amounts of water and 2 M HCl to remove the acetic acid. After drying at 60 °C for 12 h, **6** was obtained as a colorless powder. (12.5 g 70 %). $C_{10}H_{12}N_2O_2$ (192.21 g·mol^{-1}): found (calcd.): C 62.68 (62.49), H 6.50 (6.29), N 14.74 (14.57) %. **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 2.02 (s, 6 H, CH_3), 7.49 (s, 4 H, C–$H_{arom.}$), 9.85 (br. s, 2 H, N–$H_{acetamide}$); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 24.3 (s, 2C, CH_3), 119.9 (s, 4C, C–$H_{arom.}$), 135.1 (s, 2C, C–N–$H_{acetamide}$), 168.4 (s, 2C, C=O) ppm.

***N,N′*-(2,3-Dinitro-1,4-phenylene)diacetamide (7):** In a two necked 250 mL flask equipped with a thermometer nitric acid (99.5 %, 10 mL) was added dropwise to Ac_2O (100 mL, 1.06 mol) at 0 °C. The temperature should not rise above 10 °C. After that glacial acetic acid (10.0 mL, 175 mmol) was added. The solution was stirred at 0 °C for at least 1 h. In the next step **6** (8.0 g 42 mmol) was added slowly so that the temperature did not exceed 10 °C, resulting in a solution after several minutes. After 1 h the temperature was risen to ambient temperature using a water bath. The formed suspension was further stirred at ambient temperature for 4 h. The suspension was poured onto crushed ice (600 g). After stirring for 1 h the precipitate was filtered off, washed with large amounts of cold water to remove traces of acid and then dried in an oven at 60 °C for 12 h. **7** was obtained as a white-yellow powder (10.5 g, 89 %). $C_{10}H_{10}N_4O_6$ (282.22 g·mol^{-1}): found (calcd.): C 42.58 (42.56), H 3.42 (3.57), N 19.74 (19.85) %. **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 2.06 (s, 6 H, CH_3), 7.78 (s, 2 H, C–$H_{arom.}$), 10.38 (br. s, 2 H, N–$H_{acetamide}$). **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 23.4 (s, 2C, CH_3), 128.7 (s, 2C, C–$H_{arom.}$), 130.8 (s, 2C, C–N–$H_{acetamide}$), 138.3 (s, 2C, C–NO_2), 169.7 (s, 2C, C=O). **^{15}N NMR** ([D$_6$]DMSO, 25 °C): δ = –17.8 (t, N = $I^4J_{N,H}$ + $^5J_{N,H}$I = 0.6 Hz, 2N, NO_2), –257.1 (d, $^1J_{N–H}$ = 92.0 Hz, 2N, N–$H_{acetamide}$). **^{15}N{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = –17.8 (s, 2N, NO_2), –257.1 (s, 2N, N-$H_{acetamide}$) ppm.

2-Diazo-5-chloro-3,6-dinitrophenol (8): 4-Chloroaniline (3.0 g, 24 mmol) was dissolved in concentrated sulfuric acid (30 mL) at ambient temperature. Nitric acid (100 %, 3.5 mL) was added slowly so that the temperature did not exceed 40 °C. The formed suspension was further stirred at ambient temperature for 12–16 h and then poured onto crushed ice (250 g). A powder was formed which was filtered off and washed with small amounts of ice-water to remove traces of acid. After drying at ambient temperature **8** was obtained as a brilliant yellow powder (3.1 g 53 %). DSC (5 K·min^{-1}): $T_{dec.}$ = 165 °C; $C_6HClN_4O_5$ (244.55 g·mol^{-1}): found (calcd.): C 29.51 (29.47), H 0.58 (0.41), N 22.76 (22.91) %. **^{1}H NMR** ([D$_6$]acetone, 25 °C): δ = 7.50 (s, 1 H, C-$H_{arom.}$). **^{13}C{^{1}H} NMR** ([D$_6$]acetone, 25 °C): δ = 86.0 (s, 1C, C–N_2), 113.1 (s, 1C, C–$H_{arom.}$), 134.9 (s, 1C, C–Cl), 143.1 (s, 1C, C–NO_2), 148.0 (s, 1C, C–NO_2), 164.9 (s, 1C, C–O). **Sensitivities** (grain size < 100 µm): IS 1 J, FS 12 N.

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-1425273 (**2a**), CCDC-1425274 (**4**), CCDC-1425276 (**5**), CCDC-1425275 (**7**), and CCDC-1425272 (**8**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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References

[1] T. M. Klapötke, *Chemie der hochenergetischen Materialien*, 1st ed., Walter de Gruyter, Berlin, **2009**, p. 6.
[2] T. M. Klapötke, *Chemie der hochenergetischen Materialien*, 1st ed., Walter de Gruyter, Berlin, **2009**, p. 26.
[3] T. M. Klapötke, N. Mehta, *Propellants Explos. Pyrotech.* **2014**, *39*, 7–8.
[4] J. A. Steevens, B. M. Duke, G. R. Lotufo, T. S. Bridges, *Environ. Toxicol. Chem.* **2002**, *21*, 1475–1482.
[5] J. W. Fronabarger, M. D. Williams, W. B. Sanborn, J. G. Bragg, D. A. Parrish, M. Bichay, *Propellants Explos. Pyrotech.* **2011**, *36*, 541–550.
[6] D. Fischer, T. M. Klapötke, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172–8175.
[7] U. Brede, R. Hagel, K. H. Redecker, W. Weuter, *Propellants Explos. Pyrotech.* **1996**, *21*, 113–117.
[8] R. J. Spear, P. P. Elischer, *Aust. J. Chem.* **1982**, *35*, 1–13.
[9] N. Mehta, R. Damavarapu, S. Cheng, T. Dolch, J. Rivera, R. Duddu, K. Yang, 36th *International Pyrotechnics Seminar*, Rotterdam, The Netherlands, August 22–28, **2009**.
[10] S. R. Ahmad, M. Cartwright, *Laser Ignition of Energetic Materials*, John Wiley & Sons, Chichester, **2015**.
[11] T. M. Klapötke, A. Preimesser, J. Stierstorfer, *Eur. J. Org. Chem.* **2015**, 4311–4315.
[12] K.-Y. Chu, J. Griffiths, *J. Chem. Soc. Perkin Trans. 1* **1978**, 406–408.
[13] J. P. Agrawal *High Energy Materials*, 1st Edition, Wiley-VCH, Weinheim, **2010**, p. 85.
[14] *CrysAlisPRO*, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, UK, **2009**.
[15] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[16] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[17] G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structure, University of Göttingen, Göttingen, Germany, **1994**.
[18] L. J. Farrugia, WinGX Suite for Small-Molecule Single-Crystal Crystallography, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[19] *PLATON*, A Multipurpose Crystallographic Tool, A. L. Spek, Utrecht, The Netherlands, **1998**; A. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
[20] *SCALE3 ABSPACK – An Oxford Diffraction Program* (1.0.4, gui: 1.03), Oxford Diffraction Ltd, Oxford, UK, **2005**.
[21] T. Zhou, D.-F. Han, Y.-J. Hu, *Acta Crystallogr., Sect. E* **2008**, *64*, o840.
[22] O. Siri, P. Braunstein, *New J. Chem.* **2005**, *29*, 75–79.
[23] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
[24] Bundesanstalt für Materialforschung und -prüfung, http://www.bam.de (accessed June 6, 2015).
[25] a) M. Sućeska, *Test Methods for Explosives*, Springer, New York – Berlin - Heidelberg, **1995**; b) NATO Standardization Agreement 4489, September 17, **1999**; c) WIWeB-Standardarbeitsanweisung 4–5.1.02, November 8, **2002**; d) NATO Standardization Agreement 4487, August 22, **2002**; e) WIWeB-Standardarbeitsanweisung 4–5.1.03, November 8, **2002**; f) Reichel & Partner GmbH, http://www.reichel-partner.de (accessed June 6, 2015).

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