Full Paper

An Energetic *N*-Oxide and *N*-Amino Heterocycle and its Transformation to 1,2,3,4-Tetrazine-1-oxide

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Abstract: This study reports the preparation of 1-amino-1,2,3-triazole-3-oxide (DPX2) and its transformation to 1,2,3,4-tetrazine-1-oxide. DPX-2 provides insight into a novel *N*-oxide/*N*-amino high-nitrogen system, being the first energetic material in this class. The ability of this material to undergo a nitrene insertion forming 1,2,3,4-tetrazine-1-oxide was also studied, and evidence for this material, the first non-benzoannulated 1,2,3,4-tetrazine-1-oxide, is presented. The existence of both of these materials opens new strategies in energetic materials design. DPX2 was characterized chemically (Infrared, Raman, NMR, X-ray) and as a high explosive in terms of energetic performances (detonation velocity, pressure, etc.) and sensitivities (impact, friction, electrostatic). DPX-2 was found to possess good thermal stability and moderate sensitivities, indicating the viability of *N*-amino *N*-oxides as a strategy for the preparation of new energetic materials.

Keywords: Energetic materials · Explosives · HEDM · N-oxides · N-amines

1 Introduction

In the field of energetic materials chemistry a major challenge is to prepare extremely high performance materials, while maintaining stability towards destructive stimuli. These metastable materials offer unique insights into the factors affecting molecular stability [1,2] as a result of their lying on the borderline of existence and non-existence. Efforts such as these require a unique mix of theory and experimental work in order to fulfil practical requirements; how much energy can be packed into a molecule before it becomes too unstable for practical use [3]. Beyond this area, energetic materials research is also actively focused on novel energetic compounds and strategies for creating materials that possess reduced toxicological or environmental footprints.

At the forefront of energetics research are new synthetic strategies to impart unique energetic qualities to a molecule. Within energetic materials design, there are two broad categories of strategies to incorporate energetic properties in a molecule: conventional fuel/oxidizer strategies seen in explosives such as TNT (2,4,6-trinitrotoluene) or PETN (pentaerythritol tetranitrate) and high heat of formation compounds (ring strain, high-nitrogen content). While high heat of formation compounds display unique properties, increasing energy content by increasing nitrogen content can lead to explosive sensitivity and decrease in thermal stability. This can be seen when 1,1'-azobis(1,2,3-triazole) [4] and 1,1'-azobis(tetrazole) [3] are compared; the former can easily be handled, and the latter, despite only two CH groups being replaced by N, often spontaneously detonates during handling and while displaying an onset of decomposition over 100 °C lower in temperature. Additionally, highly strained compounds such as 1,3,3-trinitroazetidine or octanitrocubane have exceedingly long syntheses [5].

Strategies have been developed to stabilize high heats of formation compounds [6,7]. This can be achieved by tailoring both molecular shape as well as the addition of electron withdrawing substituents [8]. Perhaps the most striking effect of removal of electron density from a nitrogen system increasing stability is through N-oxidation. 1,2,3,4-tetrazine-1,3-dioxide heterocycles are stable class of energetic compounds, often decomposing over 200 °C [9], while only one, thermally labile, unoxidized 1,2,3,4-tetrazine ring system is known [10]. Beyond the stabilization of a nitrogen system by *N*-oxide, the zwitterionic nature of this

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D. G. Piercey, D. E. Chavez, S. Heimsch, C. Kirst, T. M. Klapötke, J. Stierstorfer

functional group leads to strong dipoles and intermolecular interactions, which are known to stabilize energetic materials. 2,6-Diamino-3,5-dinitro-1,4,-pyrazine-1-oxide is an example of such an explosive [11], and our recent work with nitrotetrazole, azidotetrazole, and bistetrazole oxides also confirm the ability of *N*-oxides to stabilize energetic nitrogen heterocycles [12–14].

Beyond *N*-oxides, *N*-amines have also demonstrated utility in energetic materials; the additional catenated nitrogen atom increases the heat of formation and the NH$_2$ unit is available for intermolecular interactions [15,16]. Molecules containing both *N*-oxides and *N*-amines on the same ring could be very high performing explosives [17–20]. Unfortunately the synthetic paths to *N*-amines and *N*-oxides often preclude them being on the same molecule, let alone the same heterocycle,

In this work, we prepare the first energetic molecule containing both an *N*-oxide and *N*-amine on the same heterocyclic ring. The simplest route to this unique material is the hypofluorous acid oxidation of 1-amino-1,2,3-triazole giving 1-amino-1,2,3-triazole-3-oxide. We also report the ring expansion of a derivative of this species giving a 1,2,3,4-tetrazine-1-oxide.

## 2 Experimental

2.1 Synthesis

The first route to the preparation of the new energetic material 1-amino-1,2,3-triazole-3-oxide (DPX2) (**1**) was a hypofluorous acid oxidation of 1-amino-1,2,3-triazole. An unoptimized procedure found that one equivalent of hypofluorous acid [21] at −23 °C produced DPX2. (Scheme 1) At higher temperatures the reaction of the hypofluorous acid appears to occur increasingly at the amine as opposed to the ring, resulting in loss of the amino group and formation of 1,2,3-triazole as identified by NMR and mass spectrometry. When increased equivalents of hypofluorous acid were used, oxidized and deaminated products were formed including triazole-1-oxide, as well as other unidentified oxidation products. After purification and recrystallization from nitromethane DPX2 was obtained as colorless crystals suitable for X-ray measurement.

With DPX2 in hand we sought new routes to produce the material. In an alternate route, 1-(benzyloxy)-1,2,3-triazole [22] was aminated with tosylhydroxylamine (THA) producing 1-amino-3-(benzyloxy)-1,2,3-triazolium tosylate. This molecule was reduced without purification with hydrogen (Pd/C catalyst) giving the target compound (Scheme 2) after column chromatography. DPX2 was isolated in poor yield from this method as a result of many unidentified side reactions during amination as determined by the presence of a multitude of unidentified peaks in the NMR spectra.
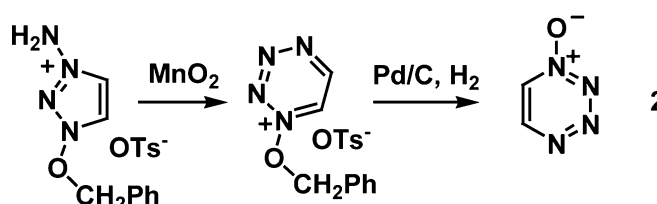
In attempting to purify the 1-amino-3-(benzyloxy)-1,2,3-triazolium tosylate to obtain a crystal structure we observed loss of the NH$_2$ protons by NMR, a shift in the re-
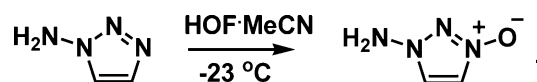
Scheme 1. Synthesis of DPX2 by oxidation.
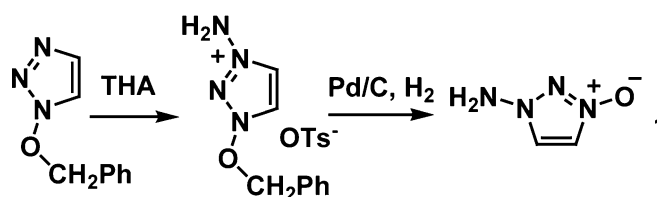
Scheme 2. Synthesis of DPX2 from 1-benzyloxy-1,2,3-triazole.

Scheme 3. Inadvertent formation of a 1,2,3,4-tetrazine-1-oxide.

maining two protons and additional shifts in the carbon spectrum to 129.2 and 119.4 ppm after hydrogenation of the recrystallized product. Mass spec (DEI$^+$) indicated that the produced material was two *m/z* lighter than the amino oxide DPX2. We suspected spontaneous nitrene formation and ring expansion, forming the previously unknown 1,2,3,4-tetrazine-1-oxide (**2**) and this was verified by reacting 1-amino-3-(benzyloxy)-1,2,3-triazolium tosylate with common nitrene-forming reagent manganese dioxide. With FAB$^+$ MS, we observed the cation molecular weight decrease from 191.1 to 189.2, indicating the presence of the 1-benzyloxy-1,2,3,4-tetrazenium cation. (Scheme 3) After H$_2$/ Pd reduction we obtained a material identical to the previous and have tentatively assigned it to be 1,2,3,4-tetrazine-1-oxide (Scheme 3). Unfortunately, we were unable to crystallize this material.

Caution! The prepared compounds are all high-nitrogen species with potential sensitivity towards various stimuli. Although we had no problems during synthesis, proper protective equipment (Kevlar gloves and wrist protectors, face shield, ear protection, and thick leather coat) should be worn. Extra precautions should be taken when working on larger scale.

2.2 1-Amino-1,2,3-triazole-3-oxide (DPX2) (1) from 1-Amino-1,2,3-triazole

1-Amino-1,2,3-triazole (10.91 g) was dissolved in acetonitrile (250 mL) and cooled to −35 °C. Hypofluorous acid (285 mL, 0.45 м) in acetonitrile as prepared by the literature method was added slowly keeping the temperature below −23 °C. The reaction was kept at this temperature for 15 min before quenching with a saturated aqueous solution of sodium hydrogen carbonate. The reaction was allowed to warm and was evaporated to dryness. The solid residue obtained was extracted with copious amounts of ethanol and acetonitrile, and the combined extracts evaporated. The produced solid material was dissolved in water (100 mL), a small amount of sodium hydrogen carbonate (5 mL saturated solution) was added and the aqueous solution was extracted 15 times with ethyl acetate (50 mL). The organic extracts were discarded and the aqueous evaporated to dryness, followed by extraction with hot, dry, ethanol. The ethanol extract was evaporated to dryness and dissolved in water. To this was added dropwise an aqueous solution of silver nitrate in water until precipitation stopped, followed by filtration of the solid material through kieselgur. To the aqueous solution, saturated sodium chloride was added to precipitate any residual silver, followed by another kieselgur filtration. The aqueous filtrate was evaporated to dryness, extracted with hot ethanol, and recrystallized from nitromethane yielding 2.3 g (16.1%) of pure crystalline 1-amino-1,2,3-triazole-3-oxide (DPX2). MS (DEI$^+$) *m/z*: 100.1. ^{1}H NMR (DMSO-d_6): $\delta = 8.02$ (1 H, C−H), 7.51 (1 H, C−H), 6.91 (s, 2 H, NH$_2$). ^{13}C NMR (DMSO-d_6): $\delta = 127.5$ (s, C4), 118.9 (s, C5). IR: $\tilde{v} = 1620$ (w), 1518 (w), 1404 (s), 1224 (m), 1216 (m), 1073 (m), 990 (m), 820 (s), 769 (s) cm^{-1}. DSC (5 °C min^{-1}): 210 °C (T_{dec}); EA (C$_2$H$_2$N$_4$O, 100.08 g mol^{-1}) calcd. C 24.00, N 55.98, H 4.03%, found: C 24.27, N 55.69, H 3.80%. BAM Impact: 8.5 J; BAM friction: 192 N; ESD: 550 mJ.

2.3 1-Amino-1,2,3-triazole-3-oxide (DPX2) from 1-(Benzyloxy)-1,2,3-triazole

Freshly prepared pulverized ethyl O-*p*-tolylsulphonylacetohydroximate (1.8 g, 7.0 mmol) [23] was added to perchloric acid (32 mL, 60%) and stirred for two h under ambient conditions. This mixture was poured into a ice/water mixture (200 mL) and the ice was allowed to melt followed by the extraction with five portions (50 mL) of dichloromethane. The organic phases were dried with sodium sulfate and added to 1-(benzyloxy)-1,2,3-triazole (0.6 g, 3.4 mmol). This was stirred under ambient conditions for 3 d, precipitated ammonium tosylate was filtered, and the organic solution was evaporated yielding very crude 1-amino-3-(benzyloxy)-1,2,3-triazolium tosylate. MS (FAB$^+$) *m/z*: 191.2 (1-amino-3-(benzyloxy)-1,2,3-triazolium cation). ^{1}H NMR (DMSO-d_6), selected identifiable data: $\delta = 8.14$ (1 H, triazole C−H), 7.68 (1 H, triazole C−H), 5.42 (s, 2 H, benzyl CH$_2$). ^{13}C NMR (DMSO-d_6) selected identifiable data: $\delta = 132.8$ (s, triazole C), 120.1 (s, triazole C). Without further purification, this material was dissolved in ethanol (250 mL) and Pd/C (1 g, 5%) was added to the solution. The flask was sealed with a septa and a hydrogen balloon was inserted. This solution was stirred for 3 d, refreshing hydrogen as necessary. After filtration and evaporation, the crude material was purified by column chromatography (methanol:acetonitrile:benzene 3:4:4) yielding 10 mg (0.1 mmol, 3.2%) of 1-amino-1,2,3-triazole-3-oxide after recrystallization from nitromethane. The analytics are identical to those of the material prepared by the previous method.

2.4 1,2,3,4-Tetrazine-1-oxide from 1-(Benzyloxy)-1,2,3-triazole

Freshly prepared pulverized ethyl O-*p*-tolylsulphonylacetohydroximate (1.8 g, 7.0 mmol) was added to perchloric acid (32 mL, 60%) and stirred for 2 h under ambient conditions. This mixture was poured into a ice/water mixture (200 mL) and the ice was allowed to melt followed by the extraction with five portions (50 mL) of dichloromethane. The organic phases were dried with sodium sulfate and added to 1-(benzyloxy)-1,2,3-triazole (0.6 g, 3.4 mmol). This was stirred under ambient conditions for 3 d, precipitated ammonium tosylate was filtered, and the organic solution evaporated yielding very crude 1-amino-3-(benzyloxy)-1,2,3-triazolium tosylate. MS (FAB$^+$) *m/z*: 191.2 (1-amino-3-(benzyloxy)-1,2,3-triazolium cation). ^{1}H NMR (DMSO-d_6), selected identifiable data: $\delta = 8.14$ (1 H, triazole C−H), 7.68 (1 H, triazole C−H), 5.42 (s, 2 H, benzyl CH$_2$). ^{13}C NMR (DMSO-d_6) selected identifiable data: $\delta = 132.8$ (s, triazole C), 120.1 (s, triazole C). Without further purification, this material was dissolved in acetonitrile (250 mL), and activated manganese dioxide (25 g) was added. The solution was stirred overnight, followed by filtration and evaporation of the filtrate, yielding crude 1-(benzyloxy)-1,2,3,4-tetrazenium tosylate. MS (FAB$^+$) *m/z*: 189.2 (1-(benzyloxy)-1,2,3,4-tetrazenium cation). This material was dissolved in ethanol (250 mL), Pd/C (1 g 5%) was added, and the mixture was stirred in a hydrogen atmosphere for 3 d (refilling the hydrogen balloon when necessary). After filtration and evaporation, a mixture of the product 1,2,3,4-tetrazine-1-oxide and tosylate was obtained as an oily solid. Extensive characterization of this material was prevented by difficulty in purification and scaling. MS (DEI$^+$) *m/z*: 97.9 (1,2,3,4-tetrazine-1-oxide). ^{1}H NMR (DMSO-d_6): $\delta = 7.69$ (1 H, tetrazine C−H), 7.50 (1 H, tetrazine C−H). ^{13}C NMR (DMSO-d_6): $\delta = 131.8$ (s, tetrazine C), 118.5 (s, tetrazine C) ppm.

D. G. Piercey, D. E. Chavez, S. Heimsch, C. Kirst, T. M. Klapötke, J. Stierstorfer

Table 1. Crystallographic details of 1-amino-1,2,3-triazole-3-oxide.

	DPX2
Formula	$C_2H_4N_4O$
Formula weight [g mol^{-1}]	100.08
Temperature [K]	173
Crystal system	orthorhombic
Space group	Pnma
a [nm]	0.55802
b [nm]	0.59907
c [nm]	1.26603
α [°]	90
β [°]	90
γ [°]	90
Volume [nm]	0.42323
Vormula Z	4
Space group Z	4
Density calcd. [g cm^{-3}]	1.571
R_1/wR_2 [all data]	0.0494/0.0832
R_1/wR_2 [$I > 2\sigma(I)$]	0.0327/0.0746
S	1.059

3 Results and Discussion

3.1 X-ray Structure

The structure of 1-amino-1,2,3-triazole-3-oxide was determined with an Oxford Xcaliber3 diffractometer with a Spellman generator (voltage 50 kV, 40 mA current) and a KappaCCD detector at 173 K. The data collection and reduction was performed using the CrysAlis Pro software [24,25]. The structure was solved using the SIR-92 program [26], refined with SHELXL-97 [27], and finally checked with PLATON software [28]. The hydrogen atoms were located and refined. Relevant data and parameters of the X-ray measurement and refinement are given in Table 1.

When a hot solution of DPX2 in nitromethane is allowed to cool, crystals suitable for X-ray measurement are obtained (Figure 1). DPX2 crystallizes in the orthorhombic space group Pnma with four formula units in the unit cell and a density of 1.571 g cm^{-3}.
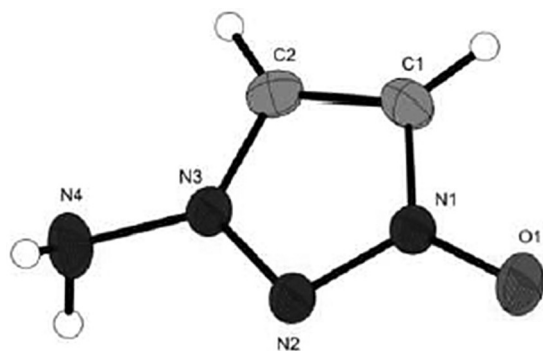
Figure 1. Molecular unit of DPX2.

3.2 NMR Spectroscopy

3.2.1 ^{1}H NMR

In DPX2 the two CH protons occur at $\delta = 8.02$ and 7.51 ppm respectively. The NH$_2$ protons occur at $\delta = 6.91$ ppm. In 1,2,3,4-tetrazine-1-oxide the two CH protons have shifted to 7.69 and 7.50 ppm

3.2.2 ^{13}C NMR

In DPX2 the two carbon resonances appear at $\delta = 127.5$ and 118.9 ppm. In 1,2,3,4-tetrazine-1-oxide these resonances have now shifted to 131.8 and 118.5 ppm. Between non-ring-inserted (aminotriazole) and ring inserted (tetrazine) there is the greater shift in the downfield resonances, suggesting the assignments that this carbon is not the one next to the N-oxide, which stays relatively constant between both compounds.

3.3 Differential Scanning Calorimetry (DSC)

For determination of the decomposition temperature of DPX2, a differential scanning calorimetry (DSC) experiment was run at a heating rate of 5 °C min^{-1}. Exothermic decomposition occurred beginning at 210 °C. This implies the ability of the new energetic moiety N-amino N-oxides to be capable of forming thermally stable energetic materials.

3.4 Explosive Properties

3.4.1 Experimental Sensitivities

For initial safety testing, impact, friction, and electrostatic discharge sensitivities were determined. Impact sensitivity was carried out according to STANAG 4489 [29] and modified according to instruction [30] on a BAM drophammer [31,32]. Friction sensitivity was carried out in accordance with STANAG 4487 [33] and modified according to instruction [34]. Sensitivity towards electrostatic discharge (ESD) was determined [35,36] on a small scale electric spark tester ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package" [37]. DPX2 possesses an impact sensitivity of 8.5 J, a friction sensitivity of 192 N, and an electrostatic sensitivity of 0.550 J. According to the UN Recommendations on the Transport of Dangerous Goods, DPX2 is classified as sensitive [38]. The average impact and friction sensitivities of this material point to the potential utility of N-amino N-oxides in new energetic materials.

3.5 Detonation Parameters

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.05) [39]. The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous

Table 2. CBS-4M results.

	Point group	El. state	$-H^{298}$/a.u.	NIMAG
1	C_{2h}		-372.209008	0
H		$^{2}A_{1g}$	0.500991	0
C			37.786156	0
N		$^{4}A_{1g}$	54.522462	0
O			74.991202	0

Table 3. Literature values for atomic $\Delta_f H^{\circ 298}$ [kJ mol^{-1}].

	NIST[20]
H	218.13
C	717.20
N	473.11
O	249.53

Table 4. Enthalpies of the gas-phase species M.

M	M	$\Delta_f H^{\circ}$(g,M) [kJ mol^{-1}]
1	$C_2H_4N_4O$	$+372.2$

Table 5. Solid state energies of formation ($\Delta_f U^{\circ}$).

	$\Delta_f H^{\circ}$(s) [kJ mol^{-1}]	M [g mol^{-1}]	$\Delta_f U^{\circ}$(s) [kJ kg^{-1}]
1	286.1	100.08	2969.7

detonation products and Cowan-Fickett's equation of state for solid carbon [40]. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique. Enthalpies of formation were calculated using the CBS-4M quantum chemical method [41] with Gaussian09 A.02 [42]. Gas phase enthalpies were transformed to solid state enthalpies by Trouton's rule [43] (Table 2, Table 3, Table 4, and Table 5). The detonation parameters calculated with the EXPLO5 program using the experimentally determined density (X-ray) are summarized in Table 6. DPX2 has a detonation velocity of 8117 m s^{-1} and a detonation pressure of 24.9 GPa. While these values are insufficient for practical use, this first member of the new energetic motif, *N*-amino *N*-oxides does illustrate the ability of *N*-amino *N*-oxides to be capable of forming highly-performing and stable energetic materials.

4 Conclusions

We have synthesized 1-amino-1,2,3-triazole-3-oxide (DPX2) by two routes, the higher yielding being the direct oxidation of 1-amino-1,2,3-triazole with hypofluorous acid. This is the first energetic material making containing both *N*-

Table 6. Energetic properties of DPX2.

	DPX2
Formula	$C_2H_4N_4O$
FW [g mol^{-1}]	$C_2H_4N_4O$
IS[a)] [J]	8.5 J
FS[b)] [N]	192 N
ESD[c)] [J]	0.500 J
N[d)] [%]	55.98
Ω[e)] [%]	-41.71
T_{Dec}[f)] [$^{\circ}$C]	210
ρ[g)]/g cm^{-3}	1.571
$\Delta_f U^{\circ}$[i)] [kJ kg^{-1}]	2969.7
Calculated values by EXPLO5 (Explo5.04)	
$\Delta_{Ex}U^{\circ}$[j)] [kJ kg^{-1}]	5576
T_{det}[k)] [K]	3524
P_{CJ}[l)] [GPa]	249
V_{Det}[m)] [m s^{-1}]	8117
V_o[n)] [L kg^{-1}]	753

a) BAM Drophammer. b) BAM impact. c) Electrical Spark Sensitivity. d) Nitrogen content. e) Oxygen balance. f) Decomposition temperature from DSC (5 $^{\circ}$C min^{-1}). g) Density from X-ray diffraction. h) Calculated molar enthalpy of formation. i) Energy of formation. j) Total energy of detonation. k) Explosion temperature. l) Detonation pressure. m) Detonation velocity. n) Volume of detonation products.

amino and *N*-oxide functionalities on the same heterocyclic ring. This material was characterized chemically and with respect to its sensitivity to impact, spark, and friction, and energetic properties were computed with the EXPLO5 program. DPX2 was found to be a high performing energetic material with no undo sensitivities toward mechanical or thermal stimuli. While its performances are insufficient for practical use, these results illustrate the ability of *N*-amino *N*-oxide heterocycles to be a potentially interesting energetic motif for the design of next-generation energetic materials. Additionally, we have shown the ability of the *O*-benzylated version of this compound to be capable of undergoing ring expansion to 1,2,3,4-tetrazine-1-oxide offering further utility of this class of compounds.

Symbols and Abbreviations

D	Detonation velocity [m s^{-1}]
δ	Chemical shift [ppm]
$\Delta_f H$	Heat of formation [kJ mol^{-1}]
$\Delta_f U$	Energy of formation [kJ kg^{-1}]
$\Delta_E U^{\circ}$	Energy of explosion [kJ kg^{-1}]
EA	Elemental analysis
ESD	Electrostatic discharge [J]
FS	Friction Sensitivity [N]
FW	Formula weight [g mol^{-1}]
IS	Impact sensitivity [N]
N	Nitrogen content [%]
NMR	Nuclear magnetic resonance
Ω	Oxygen balance [%]

Full Paper

D. G. Piercey, D. E. Chavez, S. Heimsch, C. Kirst, T. M. Klapötke, J. Stierstorfer

p_{CJ}	Detonation pressure [GPa]
PETN	Pentaerythritol tetranitrate
RDX	Hexogen
T_{dec}	Decomposition temperature [°C]
T_E	Explosion temperature [°C]

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