2,4,6-Trinitropyridine and Related Compounds, Synthesis and Characterization

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2,4,6-Trinitropyridin und analoge Verbindungen, Synthese und Charakterisierung

Eine eingehende Untersuchung der Bildung von Trinitropyridin-1oxid aus Dinitroethanol wies den Weg zum bisher unbekannten 2,4,6-Trinitropyridin. Damit wurden Nitropyridine zugänglich, die durch direkte Nitrierung nicht zu erhalten waren; diese Substanzen konnten durch analytische Methoden und ihre spektralen Daten (IR, UV/VIS und NMR) charakterisiert werden. Erste Ergebnisse aus der Untersuchung ihrer physikalischen, thermischen und explosiven Eigenschaften werden mitgeteilt.

Summary

A detailed study of the formation of trinitropyridine-1-oxide from dinitroethanol led to the hitherto unknown 2,4,6-trinitropyridine. Thus, nitropyridines become accessible which cannot be obtained by direct nitration. The novel substances were characterized by analytical methods and their spectral data (UV, IR, NMR). First results from the research of their physical, thermical and explosive properties are presented.

1. Introduction

Within the class of polynitroaromatic compounds only representatives of the benzene series as the symmetric substances 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT) – preferred because of their stability – found application as explosives. Analogous nitro compounds from the series of N-heterocyclic aromatics (pyridine, diazine, triazine) have not been described until now. But it should be mentioned that dinitropyridines – depending on their substituents – may also represent high explosives, as does PYX (dinitrodipicrylpyridine), described by Coburn⁽¹⁾.

Despite of the reduced stability (increasing with the number of hetero-atoms) of such nitro compounds interesting energetic properties may be expected of the basic compound 2,4,6trinitropyridine (TNPy):

- a good thermal stability due to the aromatic structure and the symmetric arrangement of the nitro groups,
- a satisfying at least acceptable chemical stability. The sensitivity towards bases and nucleophiles is typical for trinitroaromatic compounds (TNT!) and had to be taken into account for TNPy, too,
- a more favorable oxygen balance than for TNT and TNB and therefore a higher energy content,
- a higher density than have TNT and TNB.

For the known 2,4,6-trinitropyridine-1-oxide $(\text{TNPyOx})^{(2,3)}$ the same stability could not be expected, but instead of this a higher density and a more favorable oxygen balance. So both compounds could be classified as candidate explosives: TNPy as a more stable, TNPyOx as a more energetic substance.

2,4,6-Trinitropyridine et composés analogues, synthèse et caractérisation

Une étude détaillée de la formation de trinitropyridine-1-oxide à partir de dinitroéthanol a conduit à la 2,4,6-trinitropyridine inconnue jusqu'à présent. Par cette voie des nitropyridines deviennent accessibles alors qu'elles ne peuvent être obtenues par nitration directe. Les substances nouvelles sont caracterisées par des méthodes analytiques et par spectroscopie (IR, UV/VIS und RMN). On présente les premiers résultats de l'examen de leurs propriétés physiques, thermiques et explosives.

2. The Nitration of Pyridine

During the synthesis of polynitroaromatic compounds one has to meet the fundamental problem that any nitro group introduced into the ring system will render the further nitrations more difficult by its substituent effect. So benzene already needs energetical conditions to yield 1,3-dinitrobenzene, while the trinitration realizable under drastic terms is normally replaced by the decarboxylation of trinitrobenzoic acid. This carbonic acid is derived from TNT, the good availability of which is based upon the activating effect of the methyl group in toluene compensating the desactivating effect of the nitro groups.

Pyridine with its reduced electron density at the carbon atoms can only be nitrated with still more difficulties. It resembles 1,3-dinitrobenzene with regard to its reactivity and, therefore, only 3-nitropyridine is directly accessible. On the other hand pyridine-1-oxide – easy to prepare from pyridine – represents an activated compound because of its increased electron density at the carbon atoms and can be nitrated to 4-nitropyridine-1-oxide. By subsequent reduction with PCl₃ 4-nitropyridine is obtained. Higher nitrated pyridine derivatives are neither directly accessible, nor via pyridine-1-oxide.

3. Trinitropyridines by Cyclization

Trinitropyridine-1-oxide (TNPyOx) 1 was recognized as product of the acid hydrolysis of potassium aci-2,2-dinitroethanol 2 by Gundermann and Alles^(2, 3), sixty years after Duden and Ponndorf⁽⁴⁾ had described its formation without being able to identify it.

Bagal⁽⁵⁾ and al. made evident that this multi-step reaction which strongly depends on the pH-value, proceeds via potassium aci-2,2,4,4-tetranitro-1-butanol 3 and 1,1,3,3,5,5-hexanitropentane 4 to give TNPyOx at pH = 2, whereas at pH = 4 the reaction stops at compound 3 (Klager⁽⁶⁾ and al.). However the subsequent reaction of TNPyOx 1 with PCl₃/POCl₃ – analogous to the above mentioned reduction of 4-nitropyridine-1-oxide – did not result in the formation of the symmet-



ric trinitropyridine 7 but of 2,6-dichloro-4-nitropyridine 5 and when reacted with HCl of the corresponding N-oxide 6 resp. Thus, a typical behavior of the trinitropyridine-1-oxide Ibecomes evident: when reducing the N-oxide function one has to take into account nucleophilic substitutions of the nitro groups in 2- and 6-position (Scheme 1).

4. Synthesis of 2,4,6-Trinitropyridine 7

When TNPyOx 1 obtained according to the classical preparation⁽⁴⁾ is submitted to a detailed analysis, one will observe a second substance in an amount of 3-5% beside TNPyOx 1. This by-product will scarcely be recognized by TLC if one does not make use of the well known ability of polynitroaromatic compounds to form strongly colored charge transfer complexes. Thus it became visible as red spot on chromatograms exposed to NH₃ vapors and had to be considered as a polynitropyridine. Despite of its small amount we were able to isolate and identify this compound as 2,4,6-trinitropyridine 7.

Synthesis of TNPyOx 1 according to Refs. 2 and 4 provides a raw product with a content of only 86% 1 which must be recrystallized. By the use of 2 N phosphoric acid the yield of 1 is doubled and the purity of the product markedly improved (>95%). This substance can be used for further reactions and needs no recrystallization (Scheme 2).

The conversion of TNPyOx 1 to TNPy 7 was realized by reduction with sodium nitrite in acid medium with satisfying yield (43%). The enhanced reactivity of the nitro groups in 2- and 6-position of TNPyOx 1 against nucleophilic substitution made possible the synthesis of further derivatives: Thus, by action of sodium azide is obtained 2,6-diazido-4-nitropyridine-1-oxide (DAzNPyOx) 8, a sensitive explosive, and of aniline the mono-substituted derivative 9. The formation of 9 is probably due to its poor solubility.

5. Physical Properties

Pycnometric determination of the density gave the results presented in Table 1. Heat of explosion Q was measured in a calorimetric bomb under conditions of propellant combustion and may give a first information about the energy content of an explosive. Compared with other nitroaromatics, the nitropyridines exhibit superior results and TNPyOx the highest value because of its favorable oxygen balance.

Table 1. Density d and Heat of Explosion Q

Co	mpound	TNPy	TNPyOx	TNT	TNB
d	[g/cm ³]	1.77	1.86	1.64	1.68
Q	[J/g]	4173	5291	4521	4898

6. Spectral Characterization

In Figs. 1–3 are shown the IR-spectra of the above mentioned novel nitro compounds. As can be seen from the UV spectra (Table 2), the maximum absorption of TNPy 7, TNPyOx 1, and DAzNPyOx 8, appears in the UV region (<400 nm). In the presence of NH₃ the trinitro compounds 1 and 7 give red colored solutions by complex formation with two distinct absorption maxima at 430 nm and 530 nm.

As expected, in the ¹H-NMR spectra was found a chemical shift of the signals of the H-3-atoms of TNPy 7 and TNPyOx I in a similar order of magnitude (Table 3). The ¹³C-NMR spectra exhibit remarkable shifts of the signals C-2/C-6 and C-4 to lower, C-3/C-5 to higher field referred to unsubstituted pyridine. These results together with the striking spread of the signals of the carbon atoms carrying nitro groups – due to



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quadrupole effects – confirm the assumed structure of both compounds.

7. Thermal Properties

After recrystallization or when a sufficiently pure product has been prepared, TNPyOx I is stable up to $170 \,^{\circ}$ C and decomposes on further heating without melting, as can be seen from the DTA/TG-registrations (Figs. 4–7). DAzNPyOx 8 deflagrates already at $100 \,^{\circ}$ C.

Table 2. Ultraviolet/Visible Absorption Spectra of 2,4,6-Trinitropyridine and Related Compounds, λ_{max} and $\log \epsilon_{max}$ are given

TNPy 7	TNPyOx 1	DANPyOx 8
(a) 209 nm (4.45) 282 nm (3.57)	200 nm (4.32) 259 nm* (3.77) 308 nm (4.03)	208 nm* (4.12) 238 nm (4.29) 283 nm* (4.05) 354 nm (3.77)
(b) 440 nm (4.33) 540 nm (4.00)	430 nm (4.18) 525 nm (4.03)	spectrum is not affected by addition of NH ₃

* absorption band with small intensity.

(a) solutions in 100% acetonitrile. (b) solutions in 95% actonitrile/ 5% water, containing NH_3 in a concentration of 1 M/l.

Figure 1. Infrared spectrum of 2,4,6-trinitropyridine (0.5 wt% in KBr).

Figure 2. Infrared spectrum of 2,6diazido-4-nitropyridine-1-oxide (0.5 wt% in KBr).

Figure 3. Infrared spectrum of 2,4,dinitro-6-(N-phenyl-amino)-pyridine-1-oxide (0.5 wt% in KBr). Infrared spectra: transmittance (0-100%) versus wavelength (2.5-16.7 µm).

Cable 3. ¹ H- and ¹³ C-NMR Spectra of 2,4,6-Trinitropyridine, 2,4,6-
Trinitropyridine-1-oxide and Related Compounds in Acetone-d ₆ ;
chemical shifts are reported in parts per million (δ) relative to an
nternal tetramethylsilane reference).

H-3	C-2/C-6	C-3/C-5	C-4
9.37	156.7	118.8	160.5
9.32	154.3	118.7	142.9
7.25	150.6	124.4	136.3
7.28	-	-	-
	H-3 9.37 9.32 7.25 7.28	H-3 C-2/C-6 9.37 156.7 9.32 154.3 7.25 150.6 7.28 -	H-3 C-2/C-6 C-3/C-5 9.37 156.7 118.8 9.32 154.3 118.7 7.25 150.6 124.4 7.28 - -

TNPy 7 on the other hand reveals a better thermal stability. It melts at 163 °C without any decomposition. The similarity with TNB is striking: both compounds exhibit a slow weight loss above 200 °C. By DSC was found for TNPy 7 a heat of fusion of 22 kJ/mol, which clearly exceeds the corresponding value (15.5 kJ/mol) of TNB: the nitrogen atom in the pyridine ring obviously leads to enhanced intermolecular interactions in the solid state.

Note to the DTA/TG traces (s. p. 28):

Heating rate: 6 K/min, atmosphere: nitrogenDTA:100 μV (fullscale) except TNPyOx: 200 μVTG1:100 mg (full scale)

TG2: 10 mg (full scale)



Figure 4. DTA/TG trace for 2,4,6-trinitropyridine-1-oxide (sample 8.3 mg).

8. Explosive Properties

The here described nitropyridines represent high explosives whereby oxygen balance and element composition prove to be advantageous. This becomes evident when the theoretical maximum detonation velocities D are calculated with Rothstein's formula⁽⁷⁾ (Table 4).

Table 4. Detonation Velocities D (calc.) and Oxygen Balance (O.B.)

Compound	TNPy	TNPyOx	DAzNPyOx	TNT	TNB
D [m/s]	8161	8369	8532	6666	7277
O.B. [%]	-37.4	-27.8	-57.6	-73.9	-56.3



Figure 5. DTA/TG trace for 2,6-diazido-4-nitropyridine-1-oxide (sample 9.7 mg).



Figure 6. DTA/TG trace for 2,4,6-trinitropyridine (sample 8.0 mg).

The sensitivity to impact was determined by a drop-weight test, sensitivity to friction by the BAM-friction apparatus. The two pyridine-1-oxides exhibited a pronounced sensitivity, especially the diazido compound 8. TNPy 7, on the other hand is not sensitive to friction and has a sensitivity to impact – depending on its granulometry – in the order of cyclonite RDX (Table 5).

Table 5. Friction and Impact Sensitivity

Compound	TNPy	TNPyOx	DAzNPyOx	TNT	TNB
Sensitivity to impact [Nm] Friction [kp]	4.5–6.5 > 36	1.5–3.0 16	<1.5 10	15 > 36	7.5 > 36



Figure 7. DTA/TG trace for 1,3,5-trinitrobenzene (sample 8.0 mg).

9. Experimental

2,4,6-Trinitropyridine-1-oxide (TNPyOx) 1

Potassium aci-2,2-dinitroethanol 2 (17.4 g, 0.1 mole) was added to 200 ml of 2 N phosphoric acid. The coloration of the originally yellow solution deepens and after 30 min the separation of crystals of *I* begins. The mixture was allowed to stand for 2 h. The solid was filtered, washed and dried: yield 3.3 g (43%) of yellow crystals containing 3–5% of TNPy 7 as byproduct. Since several recrystallizations from different solvents did not remove TNPy, TNPyOx was used in this quality for further reactions. TNPyOx does not exhibit a fusion point, but decomposes above 170 °C.

2,4,6-Trinitropyridine (TNPy) 7

TNPyOx 1 (16.1 g, 0.07 mole) is suspended with vigorous stirring in 700 ml of 2 N sulfuric acid and heated to 100 °C. Very slowly (1 drop/10 s) an aqueous solution (10 wt%) of sodium nitrite is added until a clear yellow solution is formed (consumption ca. 300 ml). After cooling to room temperature 5 g of pure 7 had separated in form of yellow needles with a fusion point of 162 °C. By extraction with methylene chloride a further amount of 1.8 g is obtained. Total yield: 46%.

C_5H_2N	I_4O_6 (214.1):		
calc.	28.05% C	0.94% H	26.17% N
found	28.04	1.22	26.13

2,6-Diazido-4-nitropyridine-1-oxide (DAzNPyOx) 8

To a stirred solution of TNPyOx 1 (2.3 g, 0.01 mole) in 35 ml of acetone is added sodium azide (4.14 g, 0.06 mole) and the suspension heated to reflux. After 90 min a yellow solid is precipitated by cooling and subsequent addition of 20 ml of water, filtered, washed with water/acetone (3:1) and dried at 40 °C in vacuo: 1.23 g (55%) fine yellow crystals decomposing – after recrystallization from acetone – above 100 °C.

C_5H_2N	N ₈ O ₃ (222.1):		
calc.	27.03% C	0.91% H	50.45% N
found	26.92	0.82	50,32

2,4-Dinitro-6-(N-phenyl-amino)-pyridine-1-oxide 9

TNPyOx 1 (0.92 g, 0.04 mole) is added to a mixture of 20 ml of acetone and 60 ml of ether and heated to 40 °C. After rapid addition of aniline (0.91 ml, 0.1 mole) dissolved in ether (10 ml) to the yellow suspension a clear brown solution is formed. Orange crystals begin to separate and are filtered after 15 min, washed with few acetone and dried at 60 °C in vacuo: 0.77 g (60%) small orange crystals; decomposition point above 170 °C.

$-C_{11}H_{8}I$	N₄O ₅ (276.0):		
calc.	47.83% C	2.92% H	20.28% N
found	47.58	2.83	19.81

10. References

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Addendum

During completion of this publication we got to know that Zeng Minxiu and Lang Hengyan presented TNPy and other nitropyridines at the 1st International Symposium on Pyrotechnics and Explosives (ISPE), Beijing, October 12–15, 1987.

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