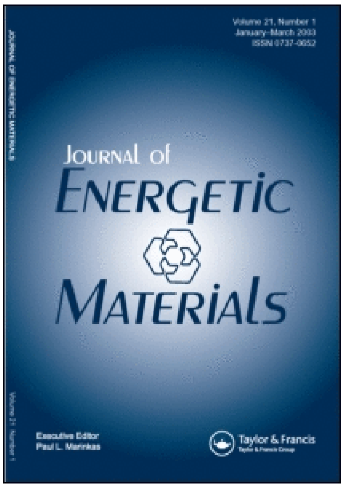

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NEW ENERGETIC MATERIALS FROM TRIAZOLES AND TETRAZINES

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ABSTRACT

Nitrotriazoles and tetrazines - among them compounds without nitro groups - are multi-purpose energetic materials. We found examples for all classes of explosives: primary explosives, IHE, and gas generators. By reaction with methazonic acid 3-amino-5-nitro-1,2,4-triazole (ANTA) could be converted into a new explosive with theoretically improved performance, a bitriazolyl compound. Starting with 3,6-diamino-1,2,4,5-tetrazine three compounds of differing explosive behaviour were prepared. Physical data and small scale explosive properties of the new substances are published.

INTRODUCTION

The nitration of heteroaromatic six-membered rings normally encounters difficulties because of the reduced reactivity of the parent compounds, attributed to their electron

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deficient structure. By introducing activating substituents like the amino or hydroxy group the electrophilic substitution is favoured. So, several dinitrated and trinitrated pyridine derivatives have been prepared, some of them (aminodinitropyridines e.g.) even in a one-step reaction. Otherwise, energetic derivatives of five-menbered heterocycles are accessible by nitration without problems (trinitroimidazole e.g.), since the conditions for a nitration are now more favourable. Nevertheless, 1,2,4-triazole itself is only N-nitrated. But in the form of its activated 3-hydroxy derivative it is easily nitrated and affords 5-nitro-1,2,4-triazol-3-one (NTO).

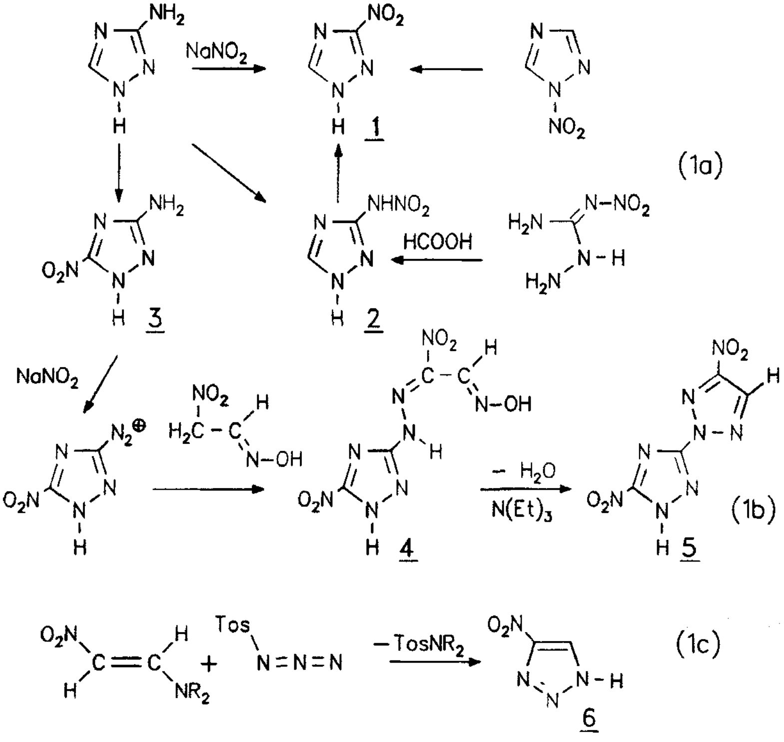
TRIAZOLES

From 3-amino-1,2,4-triazole two nitro compounds can be prepared: By a SANDMEYER reaction without Cu-catalysis 3-nitro-1,2,4-triazole 1 is formed [1]; by direct nitration we obtained the 3-nitramino-1,2,4-triazole 2. The latter one is prepared in a purer form from aminonitroguanidine (ANQ) according to a method given by HENRY [2].

PEVZNER et al. [3] got the 3-amino-5-nitro-1,2,4-triazole (ANTA) 3 by nitrating the aminotriazole (in its acetylated form) in a reaction which we were unable to reproduce. It is better prepared by selective reduction [4] of 3,5-dinitrotriazole which is obtained in the above mentioned one-step diazotization reaction of BAGAL [1] (Scheme 1a).

We also obtained nitrotriazole 1 by oxidizing the nitroaminotriazole 2 with peracetic acid. Since 3-aminotriazole could not be converted to 1 at these reaction conditions we suppose that corresponding to an analogous observation with perfluoracetic acid [5], denitration of the nitramino group is immediately followed by oxidation of the amino group.

Just as the non-nitrated aminotriazole [7], ANTA can be diazotized. After subsequent coupling with methazonic acid ring closure could be brought about by dehydration of the intermediate product 4, yielding the bitriazolyl compound 5. After the 5,5'-dinitro-4,4'-bi-1,2,3-triazolyl, recently described by BARYSHNIKOV [8], and the 3,3'-dinitro-5,5'-bi-1,2,4-triazolyl which seems to have been obtained as a hydrate in the U.S. [9], the missing "mixed" compound from 3-nitro-1,2,4-triazole and 4-nitro-1,2,3-triazole is presented here (Scheme 1b). The 4-nitro-1,2,3-triazole 6 itself is formed in a 1,3-dipolar cycloaddition of the azide ion to nitroethene [6] (Scheme 1c).



(1a)

(1b)

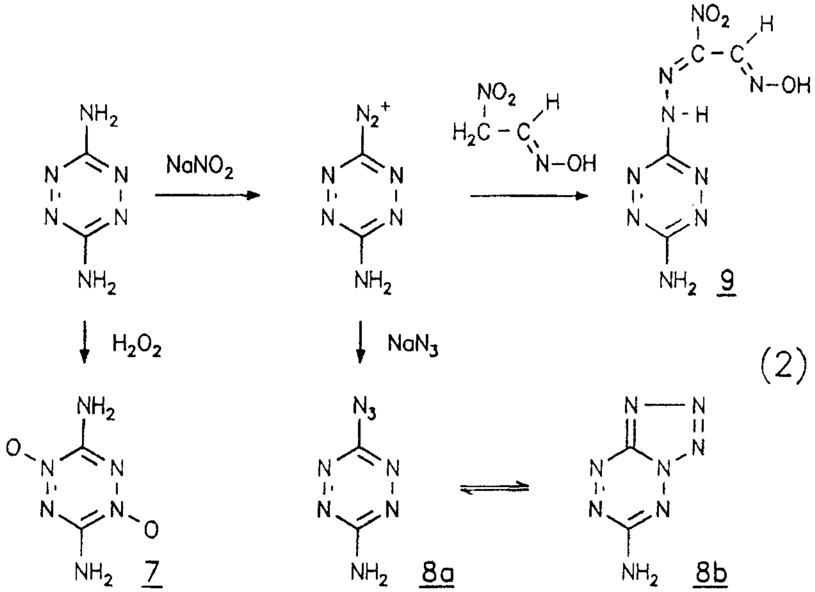
(1c)

TETRAZINES

The probably most accessible tetrazine compound is 3,6-diamino-1,2,4,5-tetrazine [10] which can be prepared without any problems - with small yields (10 %), however - from thiosemicarbazide. In analogy to the oxidation of other heteroaromatics (aminonitropyridines e.g. [11]) with peracids we obtained from diaminotetrazine an "explosive without nitro groups", the 3,6-diamino-1,2,4,5-tetrazine 1,4-dioxide 7. This compound - slightly soluble in standard solvents and difficult to purify - has been prepared in the U.S., too [12]. By nitration of diaminotetrazine, Chinese scientists [13] had obtained the 3,6-dinitramino-1,2,4,5-tetrazine, a brisant and rather unstable explosive.

One of the two amino groups of diaminotetrazine could be diazotized in our experiments. The diazonium salt underwent SANDMEYER reaction with azide ions to give 3-amino-6-azido-1,2,4,5-tetrazine 8a; it shows a solvent dependent azido-tetrazole tautomerism, known from other heteroaromatic azido compounds [14]: In the solid state the absence of azido absorption bands in the IR-spectrum indicates the existence of the tetrazole form 8b, also predominating in polar solvents like ethanol, whereas apolar solvents favour the azido form 8a, as can be concluded from distinctly differing UV-VIS absorption spectra of 8 in several solvents.

While we were unable to convert the diazonium salt into a aminonitrotetrazine - analogously to the synthesis of nitro- and dinitrotriazole -, a coupling reaction could be realized with methazonic acid. The coupling product 9 was destructed when we tried its cyclization by dehydration. (Scheme 2).

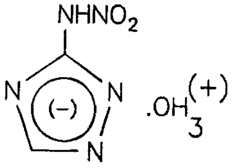


(2)

CHEMICAL AND SPECTROSCOPIC PROPERTIES

We found for many nitrotriazoles a distinct tendency to form solvates with polar solvents in the solid state. Bitriazolyl 5 seems to represent a special case. A chelate like structure of its solvates - similar to bipyridyl - might be responsible for the pronounced stability of these solvates, which often cannot be liberated from the solvent without destruction of the compound. Therefore, only apolar solvents (toluene, xylene) should be used for a recrystallization.

Some hydrates among the solvates were confirmed by microanalysis. We suggest the existence of stable ion pairs like 10 due to the high acidity of the nitrotriazoles. ^1H NMR spectroscopy excludes the formation of covalent hydrates observed in the pyrimidine chemistry [15].



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Another effect of the acidity was found in ^1H NMR spectroscopy. The proton exchange in nitrotriazoles - even in d_6-DMSO as solvent - occurs so quickly that a discrete NH-signal is not always recorded. Whilst for example the coupling product 9 of methazonic acid with the diazotized diaminotetrazine gave the expected three signals for NH_2, NH, and OH (integral 4H), one NH-signal of bitriazolyl 5 and of the coupling product 4 from ANTA was missing. In the hydrate of the bitriazolyl (5 * H_2O) the NH-signal was recorded, this time coinciding with the signal of the water traces in d_6-DMSO.

PHYSICAL AND EXPLOSIVE PROPERTIES

We measured the following physical data of the compounds discussed here (tab. 1).

TABLE 1

Physical and explosive properties

Compound	1	2	5	6	7	8
Crystal density ϱ (g/cm^3)	1.72	1.83	1.90	1.73	1.85	
Deflagration T_{ex} (°C)	218	226	247-264	218	266	200 expl.
Heat of formation $\Delta H_f°$ (kcal/mol)	23.39	22.43	45.37	39.90	48.02	
(kJ/mol)	97.91	93.89	189.90	167.02	201.02	

ϱ by gas pycnometry

T_{ex} decomposition peak from DTA (heating rate 6°/min)

All compounds are proved to be thermally stable. The heats of formation (+ : endothermal) from combustion measurements enabled us to estimate the performance by an equation of KAMLET [16] - in addition to an empirical one of ROTHSTEIN [17].

The tetrazolotetrazine **8b** should be regarded as a primary explosive because of its distinct shock and friction sensitivity and strongly exothermal decomposition in the thermal analysis. The other explosives can be handled without restrictions. Their sensitivity is between that of RDX and of an IHE (Table 2).

TABLE 2

Mechanical sensitivity

Compound	1	2	5	6	7	8
Friction sensitivity (1.reaction)	> 36	19	> 36	29	> 36	0.5 kp
Shock sensitivity (1.reaction)	> 25	6.5	15*)	4.5	12.5	1.5 N·m

BAM friction and drop weight apparatus resp.

Reference data: RDX: 12 kp / 6.5 N·m

TNT: > 36 kp / 15 N·m

*)decomposition in the drop weight test

PERFORMANCE

The calculations [16,17] result in rather differing predictions (table 3) for the here investigated materials. In contrast to common explosives, for which the calculations are tailor-made and where excellent conformity is found, these compounds exhibit a special elemental composition, characterized by a high nitrogen content. So, a conclusive assessment is not possible.

TABLE 3

Prediction of detonation velocity D and GURNEY constant $\sqrt{2E_G}$

Compound		1	2	5	6	7	
D [a]	(d=ϱ)	7589	7876	7985	7854	8235	m/s
	(d=0.95·ϱ)	7315	7603	7701	7571	7952	
$\sqrt{2E_G}$ [a]	(d=ϱ)	2.56	2.61	2.61	2.64	2.72	mm/μs
	(d=0.95·ϱ)	2.50	2.56	2.56	2.59	2.66	
D_{max} [b]		8830	8806	9248	8830	8786	m/s

a) calculated acc. to KAMLET [16]

b) calculated acc. to ROTHSTEIN [17] for "aromatic structure"

d charge density

Although measured results are not yet available - measurement of detonation velocity and GURNEY constant are envisaged by us after preparing the needed quantities - we suppose the results according to [17] to be overestimated, also for the assumption of a non-aromatic structure. It seems probable that energetic materials of such a high nitrogen content primarily exhibit the properties of gas generators rather than of high explosives.

EXPERIMENTAL

Poor agreement of theory and result in elemental analysis may be explained by the well known intrinsic problems of microanalysis with high N-content and explosive compounds.

3-Nitro-1,2,4-triazole 1 (from nitraminotriazole):

3-Nitramino-1,2,4-triazole 2 [2] (26 g) in acetic acid (300 mL) is refluxed with 84.5 % H_2O_2 (60 mL) for 6 hours. After several hours at room temperature crystals separate which are filtered. The filtrate is concentrated and the main crop is isolated. Yield : 15.5 g (68 %) 3-nitro-1,2,4-triazole 1, m.p. 212°C (lit. 215-16 [7]).

3-Nitramino-1,2,4-triazole 2 :

To a solution of 3-amino-1,2,4-triazole (8.4 g, 0.1 mol) in 98% sulfuric acid (50 mL) is added 100% HNO_3 (8 ml, 0.2 mol) at 50°C. The solution is stirred for 5 hours and poured onto ice. 3-Nitramino-1,2,4-triazole 2 * H_2O (11 g, 75%) is obtained as a white solid. After recrystallization from water it has to be dried at 60°C for several hours to get a water-free product. The IR spectrum is identical with that described in [3]; m.p. 208°C (lit. 212°C [2] and 210°C [3], resp.).

1-Hydroximino-2-nitroglyoxal-(5-nitro-1,2,4-triazol-3-yl)-hydrazone 4 :

A suspension of ANTA - diazotized in water at 0°C with HNO_3/ $NaNO_2$ [7]- is reacted with an aqueous solution of one equivalent of sodium methazonate. The coupling product precipitates immediately, is filtered, and washed with water. The hydrazone 4 is obtained as a hydrate in a 60% yield. Recrystallization from ethanol gives a pale yellow substance melting at 113°C. ^1H NMR (d_6-DMSO) : 8.48 (s, 1H), 13.0 (br s, 2H)

$C_4H_6N_8O_6$ (262.14)

needs 18.33 % C, 2.31 % H, 42.75 % N, 36.62 % O;

found 18.37 % C, 2.37 % H, 41.58 % N, 36.18 % O.

4-Nitro-2(5-nitro-1,2,4-triazol-3-yl)-1,2,3-triazole 5 : "bitriazolyl"

Hydrazone 4 (5 g, 19 mmol) is dissolved in a mixture of triethylamine (TEA) (30 mL) and water (70 mL) to give a deep red solution. After addition of glacial acetic acid (7 mL) one adds simultaneously acetic anhydride (7 mL) and sufficient TEA to maintain the solution just alkaline. Stirring for 30 minutes at room temperature and subsequent acidification with glacial acetic acid affords crystals of the TEA salt of the bitriazolyl 5. The salt is suspended in 10% HCl (40 mL) to give the bitriazolyl 5 as a hydrate which becomes water-free after recrystallization from toluene. Nearly colourless powder melting at 178°C, yield : 50 %.

MS : m/z = 226 (M^+). ^{1}H **NMR** (d_6-DMSO) : 8.9 (s, 1H)

$C_4H_2N_8O_4$ (226.11)

needs 21.25 % C, 0.89 % H, 49.56 % N, 28.30 % O;

found 21.86 % C, 0.91 % H, 49.94 % N, 28.04 % O.

3,6-Diamino-1,2,4,5-tetrazine 1,4-dioxide 7 :

3,6-Diamino-1,2,4,5-tetrazine (1 g, 9 mmol) is suspended in glacial acetic acid (10 mL). 84 % H_2O_2 (10 mL) is added and the suspension heated for 6 hours to 60°C. The oxidation of the originally purple starting material is perceived by the bright red colour of the new product. The tetrazine dioxide 7 is filtered and dried to give a 50% yield. Recrystallized from DMF/ethanol it decomposes without melting at 266°C. ^{1}H **NMR** (d_6-DMSO) : 7.16 (br s)

$C_2H_4N_6O_2$ (144.09)

needs 16.67 % C, 2.80 % H, 58.32 % N, 22.21 % O;

found 17.30 % C, 2.94 % H, 57.05 % N, 22.30 % O.

6-Amino-tetrazolo[1,5-b]-1,2,4,5-tetrazine, 8b :

3,6-Diamino-1,2,4,5-tetrazine is dissolved in concentrated H_2SO_4, diazotized with $NaNO_2$ in H_2O, and added slowly to a threefold excess of an aqueous solution of NaN_3 (gas evolution). After standing at room temperature for several hours a solid separates from the orange solution; it was filtered (37 % yield) and recrystallized from ethanol to give a yellow solid decomposing without melting at 200°C. **IR:** 3320 (NH_2); 1637 (C=N); 1549 (NO_2); 1250 (NO_2).

$C_2H_2N_8$ (138.09)

needs 17.40 % C, 1.46 % H, 81.14 % N;

found 18.05 % C, 1.54 % H, 79.62 % N.

1-Hydroximino-2-nitroglyoxal-(6-amino-1,2,4,5-tetrazin-3-yl)-hydrazone 9 :

3,6-Diamino-1,2,4,5-tetrazine is dissolved in concentrated H_2SO_4, diazotized with $NaNO_2$ in H_2O, and reacted with an aqueous solution (50 vol.%) of one equivalent of sodium methazonate at pH = 4. The reddish-brown coupling product precipitates immediately; it is filtered, washed with water and dried to give 9 in a 55% yield. After recrystallization from acetonitrile it decomposes without melting at 196°C. **^{1}H NMR** (d_6-DMSO) : 7.98 (br s, 2H), 8.58 (s, 1H), 12.7 (br s, 1H), 12.9 (br s, 1H).

$C_6H_6N_{12}O_6$ (342.19)

needs 21.15 % C, 2.22 % H, 55.50 % N, 21.13 % O;

found 21.07 % C, 2.35 % H, 54.06 % N, 22.02 % O.

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