

Energetic Derivatives of Nitroguanidine – Synthesis and Properties

Mateusz Gratzke^{*[a]} and Stanisław Cudziło^[a]

Abstract: Nitroguanidine is an individual explosive with an established reputation. It is widely used as a component of gunpowder, rocket propellants, and high explosives. Less known and appreciated, however, is its importance as a substrate in the synthesis of other explosive compounds with even better properties. In this work available information on synthetic methods, structure, and properties of compounds containing the nitroguanidine moiety was collected and analyzed. The most attention was paid to

compounds that have already found practical applications and those with unique properties (high-performance, low-sensitivity), as well as compounds that can be further functionalized with energetic functional groups. The results of our literature search indicate that the nitroguanidine moiety should be treated as a particularly interesting building block from the point of view of the synthesis of new high-energy compounds.

Keywords: Nitroguanidine • Derivatives • Synthesis • Explosive • Properties

1 Introduction

In the search for new high-energetic chemical compounds, a couple of major trends can be noticed. The most important of them are increasing the nitrogen content in molecules and designing their structure in such a way that it is possible to create stable intra- and intermolecular hydrogen bonds. Extensive networks of such bonds tend to stabilize the crystal structure and thus reduce the sensitivity to mechanical and thermal stimuli. In both cases, one of the possible ways to obtain the desired result is to introduce a fragment containing a guanidine moiety into the compound structure.

The use of guanidine and its amino derivatives as a cation in high-energy materials of ionic nature is common practice [1–3]. Numerous examples of compounds of this type can be found in the literature [4–9]. Guanidine, mono-, di- and triaminoguanidine cations impart positive enthalpy of compound formation, increase the amount of gaseous decomposition products and exhibit low toxicity [1,2]. The synthesis of these types of compounds is usually simple and proceeds via metathesis reaction between guanidinium salts (commercially available) and an energetic anion-containing salt. The disadvantage of explosive compounds containing guanidine and aminoguanidine cations is primarily lowering of the oxygen balance resulting from the introduction of additional atoms of carbon and hydrogen. Moreover, due to the limited possibilities of further functionalization, it is difficult to use them in more specialized applications, such as obtaining ionic liquids [3].

An approach that is less common, although very perspective, is to use of the nitroguanidine as a building block. Nitroguanidine (NQ) is a high explosive known for its ex-

tremely low sensitivity to mechanical stimuli and shock waves. Despite relatively high detonation parameters, nitroguanidine was used almost exclusively for the production of triple base gunpowders for a long time. This was a result of the fact that nitroguanidine crystallizes in the form of long needles, which makes it difficult to obtain homogeneous explosive compositions [10]. Only after the development of efficient recrystallization methods providing a product with the required morphology and granulometric distribution, nitroguanidine became an important ingredient of many insensitive explosive compositions formed into charges both by pressing and casting [11].

Some properties of nitroguanidine can also be “tailored” by transforming it into a derivative which, while retaining most of the advantages of this compound, would be devoid of its disadvantages, such as inconvenient crystalline form, negative enthalpy of formation, or high melting point. Due to the presence of the strongly electron-accepting nitroimine moiety, the functionalization of nitroguanidine is possible by exchanging the amino groups, substituting the hydrogen atoms of these groups, or by linking a low molecular weight compound with the nitrogen of the amino group/groups. Of course, this approach requires the development of an appropriate synthesis strategy for the target compound, but the presence of a nitroguanyl moiety in its structure has many advantages. This building block contains groups that are both good donors and acceptors of

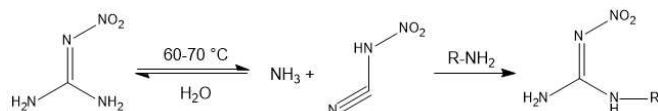
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the electron pair, and this enables the creation of extensive networks of hydrogen bonds and, consequently, contributes to lowering the sensitivity to all types of initiating stimuli. It also has a favorable oxygen balance and contains a large amount of nitrogen, which in turn favors high detonation parameters.

This paper presents a review of the current state of knowledge about the methods of synthesis and reactivity as well as the physicochemical and explosive properties of nitroguanidine derivatives. Special attention was paid to compounds that have already found practical applications and those with unique properties (i.e. characterized by high energetic parameters or low sensitivity), as well as compounds that can be further functionalized. In order to systematize the review, the said derivatives were divided into groups, ordered by the method of their synthesis. Synthesis reactions and characteristics of these compounds in terms of physicochemical and explosive properties and potential use as explosives are presented in the following chapters.

2 Reaction between Nitroguanidine and Aliphatic Amines

In 1926 and 1927 Davis published two papers [12,13], in which he described the reaction of nitroguanidine with aliphatic amines in an aqueous medium. He obtained a total of eleven different N-alkyl-N'-nitroguanidines, and also proposed the mechanism of this reaction (Scheme 1). According to him, when heated to 60–70 °C, nitroguanidine decomposes reversibly into nitrocyanamide, with the release of ammonia molecules. If an aliphatic amine is introduced into the reaction mixture, it reacts with the nitrocyanamide to form an alkyl-substituted nitroguanidine. Davis claimed, that this reaction is irreversible, causing the equilibrium to



Scheme 1. Scheme of the synthesis of alkyl nitroguanidines by transamination, proposed by Davis.

rapidly shift towards the end product. However, this hypothesis was made indirectly, solely on the basis of observations of the reactivity of nitroguanidine in aqueous and H₂SO₄ solutions. Up to this day, no work has been published that would examine in detail the mechanism of this reaction using modern analytical techniques.

Davis also noted that this reaction occurs readily with primary aliphatic amines and more difficult with secondary amines, but aromatic amines do not undergo this reaction at all.

Although the aim of the mentioned works was not to develop new high-energy compounds, their results were particularly interesting due to the low melting points of the obtained derivatives. The attachment of the alkyl chain to the nitroguanidine molecule introduces steric hindrance, partially disrupting the interactions between the atoms involved in the formation of hydrogen bonds. This leads to a reduction of the crystal lattice energy and, consequently, to a lower melting point. Moreover, saturated alkyl chains tends to intensify vibrations of the molecule under the influence of temperature increase, which additionally promotes the formation of a liquid phase at a low temperature [14].

In practice, the presence of an unbranched carbon chain of 3–5 carbon atoms lowers the melting point of the compound below 100 °C without significantly lowering the decomposition temperature relative to pure nitroguanidine. The lowest melting point range was recorded for the n-butyl derivative (84–85 °C), however, n-propyl-nitroguanidine (M_p = 98 °C) has a better oxygen balance and thus higher detonation parameters.

Due to the above properties, the n-propyl derivative (PrNQ) is currently considered as an ingredient of melt-cast explosive compositions that could replace Composition B (RDX/TNT). Intensive work in this area was carried out mainly in the USA, in the research laboratories of the US Army Research Laboratory (ARL) and the US Army Research, Development and Engineering Center (ARDEC). The full results of these studies remain classified, but the published reports [15,16] show that several HMX/PrNQ/Al/wax compositions were successfully obtained, the detonation velocity and pressure of which are similar to the currently used PBXN-109 and Composition B (Table 1).

Table 1. Comparison of the parameters of two prospective compositions based on PrNQ.

Parameter	Composition PAX-PrNQ	DGX-6	Comp. B	PBXN-109
D [m/s]	7760	7280 ^[b]	7900	7600
P [GPa]	~25 ^[c]	23.3 ^[b]	29.7	23.7
IS ^[a] [cm]	> 100	> 100	33.9	80.3
FS [N]	> 360	282	300	> 360
ESD [J]	0.063	0.250	0.250	0.250

^[a] ERL method; ^[b] Recalculated from % or PBXN-109 according to Ref. [15]; ^[c] 25.2 GPa is the P value for IMX-104, that according to Ref. [16] has detonation pressure „Equivalent to PAX-PrNQ“.

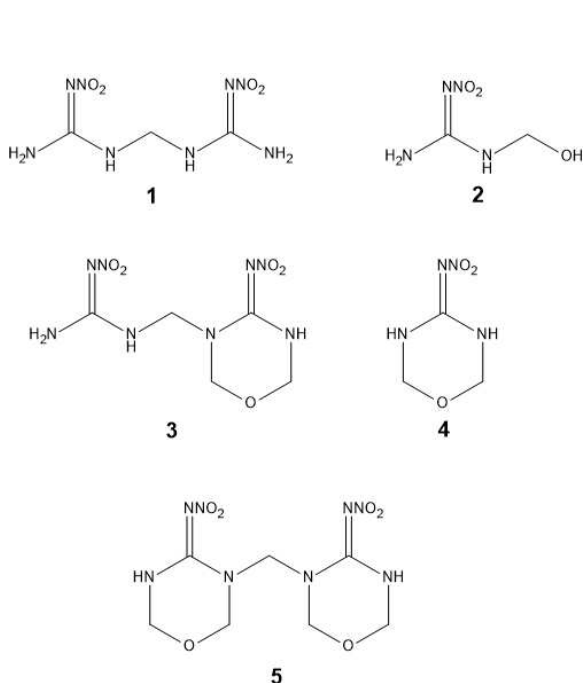
3 Reaction of NQ with Formaldehyde

Reactions of NQ with formaldehyde generate a number of derivatives, the structure of which depends mainly on the molar ratio of the substrates and the pH of the environment (sometimes also temperature and reaction time) [17,18].

Reaction in dilute hydrochloric acid with a NQ/CH₂O ratio of 2:1 generates as the main product bis (nitroguanidine) methane (1). At a pH close to neutral and an equimolar ratio of the reactants, it is possible to obtain the hydroxymethyl derivative (2). With an excess of formaldehyde and acidification of the medium with concentrated hydrochloric acid, the ring closes and 1-oxa-3,5-diazacyclohexane derivatives are obtained (3–5) (Scheme 2). Compounds (3), (4), and (5) containing secondary nitrogen atoms in the ring can be nitrated with a mixture of nitric acid and acetic anhydride to obtain the corresponding nitroamines. However, the authors do not provide information on the energetic properties and stability of these derivatives.

As reagents for further syntheses, bis(nitroguanidine) methane (1) and hydroxymethyl-nitroguanidine (HMNQ, 2) are particularly interesting. For example, HMNQ can be condensed with nitroform to obtain (2,2,2-trinitroethyl) nitroguanidine [19]. This compound is an interesting energetic material, mainly due to close to zero oxygen balance (−2.99%).

Furthermore, it is possible to remove one of the nitro groups in reaction with potassium iodide and obtain the potassium salt of (2,2-dinitroethyl)nitroguanidine, which, af-



Scheme 2. Compounds obtained in the reaction of NQ with formaldehyde.

ter acidification, can be used as a substrate for the synthesis of further derivatives (Scheme 3) [20].

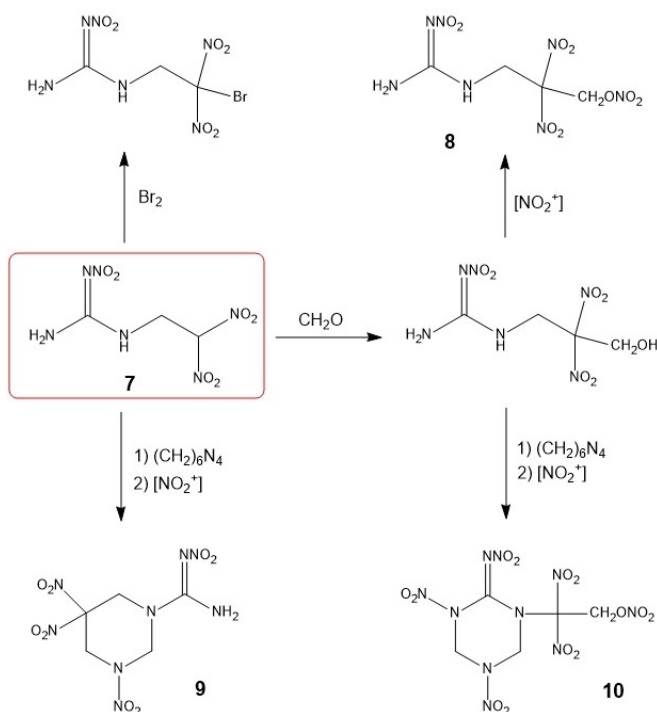
On the other hand, bis(nitroguanidine)methane is a substrate for the synthesis of a number of 1,3,5-triazacyclohexane derivatives substituted with the nitroimine group (Scheme 4, Table 2) [17].

The highest nitrate compound (1,5-dinitro-2,4-nitroimino-1,3,5-triazacyclohexane, 12) is characterized by a slightly positive oxygen balance (+2.73%) and has excellent detonation parameters ($D = 9250$ m/s for $\rho = 1.88$ g/cm³, 96% TMD). Unfortunately, it is hydrolytically and thermally unstable (decomposition at 114 °C) and therefore cannot be used as a high explosive.

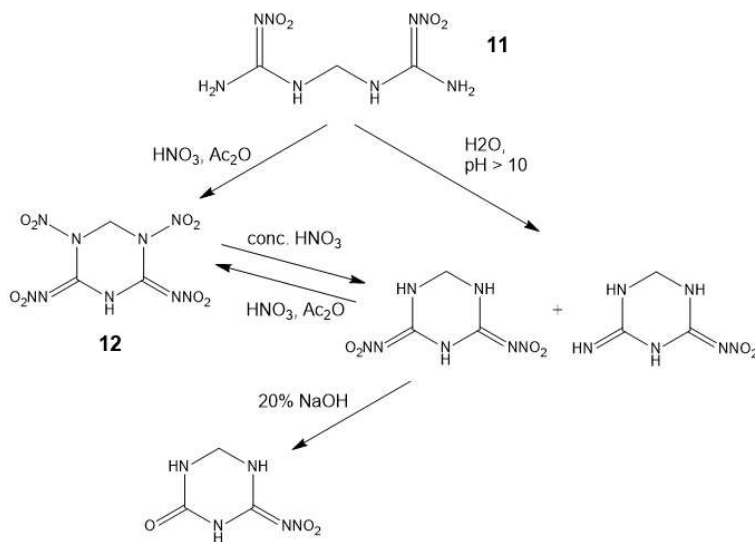
4 Reaction of NQ with Hexamethylene-Tetramine (Hexamine, HMTA)

Nitroguanidine reacts with hexamethylenetetramine in hydrochloric acid. The result of this reaction depends on the concentration of the acid – when it is diluted (up to 18%) 2-nitroiminohexahydro-1,3,5-triazine is obtained, while in concentrated acid, the product is the monohydrochloride of this compound [18]. These compounds can be nitrated, firstly by using a mixture of HNO₃/H₂SO₄ (a nitro group is introduced in position 5) and then HNO₃/Ac₂O, yielding 1,3,5-trinitro-2-nitroiminohexahydro-1,3,5-triazine (Scheme 5).

The oxygen balance of this compound is zero, so that it could be an interesting high explosive, unfortunately, it is



Scheme 3. (2,2-dinitroethyl) nitroguanidine reactions.



Scheme 4. Derivatives of bis(nitroguanidine)methane.

Table 2. Basic information about compounds 6–12.

Parameter	Compound 6	7	8	9	10	11	12
Acronym	TNENQ	DNENQ	–	–	–	BNGM	–
Formula	C ₃ H ₅ N ₇ O ₈	C ₃ H ₆ N ₆ O ₆	C ₄ H ₇ N ₇ O ₉	C ₅ H ₈ N ₈ O ₈	C ₅ H ₈ N ₈ O ₁₁	C ₃ H ₈ N ₈ O ₄	C ₃ H ₃ N ₉ O ₄
M [g/mol]	267.11	222.12	297.14	308.17	356.16	220.15	293.11
OB [%]	–2.99	–21.61	–13.46	–31.15	–13.48	–43.61	+2.73
%N	36.7	37.8	33.0	36.4	31.5	50.9	43.0
M _p [°C]	165–167 (dec)	96	94–95	174	154	n/a	114 (dec)

OB – oxygen balance {1600*(O-2 C-1/2H)/M}; n/a – data not available; dec – decomposes.

unstable above 50 °C. It is also prone to hydrolysis, both in the presence of strong acids and bases, which results in ring opening and formation of alkylnitramines (Scheme 6) [17]. On the other hand, 5-nitro-2-nitroiminohexahydro-1,3,5-triazine (NNHT, 13) has been extensively studied and has been patented as a prospective insensitive explosive, an additive for rocket or gun propellants, or a component of the compositions for gas generators in airbags [21–24].

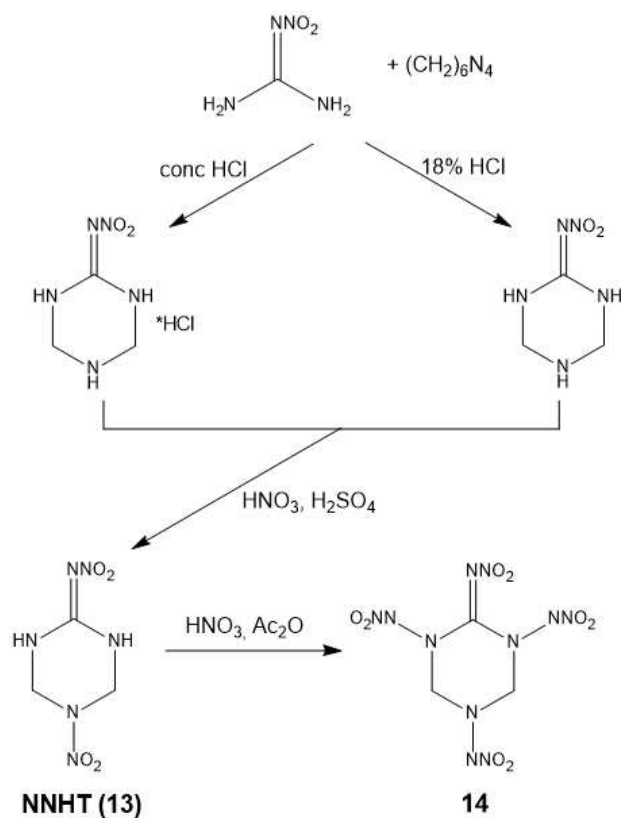
During these studies, an alternative synthesis route was proposed - nitroguanidine was condensed with formaldehyde and tert-butylamine, and the resulting 2-nitroimino-4-tertbutylhexahydro-1,3,5-triazine (NBHT) was nitrated with HNO₃ in the presence of catalytic amounts of NH₄Cl [23, 25]. This method turned out to be much safer when conducting the process on a large scale, because it does not exhibit such strong exothermic effects as in the case of direct nitration of the hydrochloride [23].

Energetic properties of NNHT, as well as a couple of other heterocyclic nitroguanidine derivatives are listed in the Table 3.

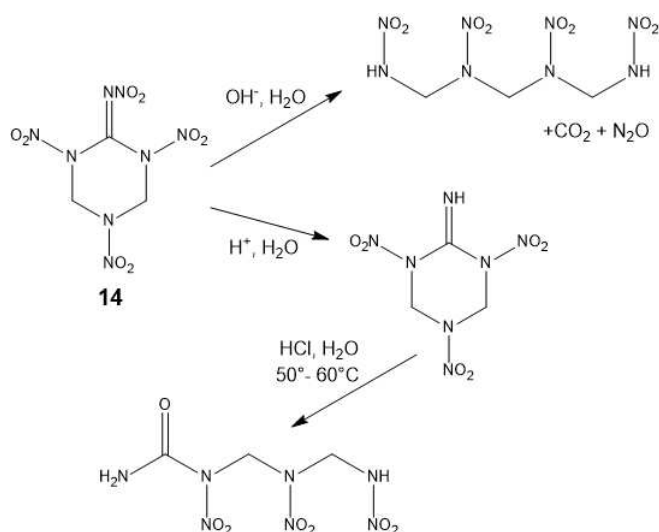
5 Glyoxal-Based NQ Derivatives

Nitroguanidine reacts with glyoxal at a pH value of about 8, resulting in the closure of the five-membered ring. The 3,4-dihydroxy-1-nitroimino-2,5-diazacyclopentane formed can then be reacted with guanidine hydrochloride to form the hydrochloride 2-imino-5-nitroiminotetrahydroimidazo [4,–5d] imidazole (INI-Cl) (Scheme 7) [26]. The INI cation is proposed as a component of high-energy salts characterized by positive enthalpies of formation and high nitrogen content in the molecule. The work [27] presents the results of studies on nine salts of this type, both with simple anions (e.g. nitrate, dinitramine) and heterocyclic anions based on tetrazole or furazan rings. In all cases, despite the extremely negative oxygen balance, these compounds were equal to or exceed TNT in terms of detonation parameters, and the best of them had parameters similar to RDX (Table 4).

In Ref. [28] the synthesis of symmetrical 3,7-bis-(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane (15) is presented. It consists in the condensation of an excess of guanidine nitrate with glyoxal in an alkaline medium, resulting in the formation of 3,7-bis-imino-2,4,6,8-tetraazabicyclo[3.3.0]octane dinitrate, which is then nitrated with 100% nitric



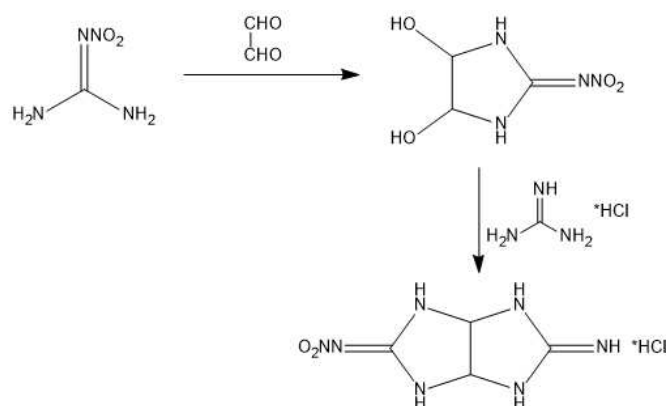
Scheme 5. Reactions between NQ and HMTA.



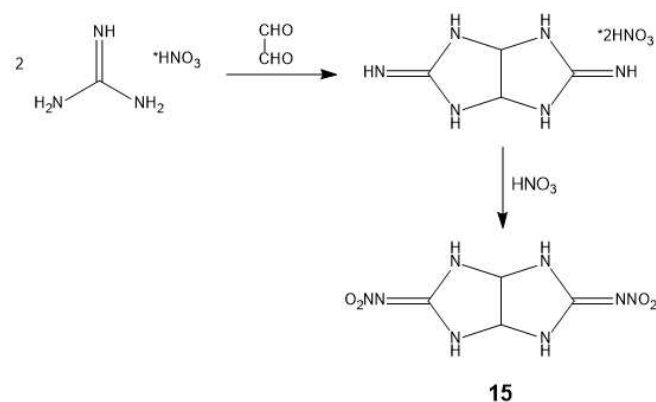
Scheme 6. Hydrolysis of 1,3,5-trinitro-2-nitroimino-1,3,5-triazine.

acid (Scheme 8). Alternatively, this compound can also be synthesized by nitration of INI-Cl [26,29].

Despite a highly negative oxygen balance, the calculated detonation parameters of the dinitrimine derivative



Scheme 7. Scheme of INI-Cl synthesis.



Scheme 8. Synthesis of 3,7-bis-(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane.

are slightly better than those of RDX [28]. This is likely the result of the high density of compound 15.

In the paper [29], molecular calculations were also performed to determine the possibility of further nitration of the compound 15. The authors predict that subsequent nitro groups could be attached to nitrogen atoms in positions 1 and 4. The hypothetical tetranitro compound has excellent predicted energy parameters ($\rho = 1.91 \text{ g/cm}^3$, $D = 9.2 \text{ km/s}$, $P = 44 \text{ GPa}$), however, it has not been synthesized so far.

Heterocyclic derivatives of nitroguanidine can also be obtained from 2,3,5,6-tetrahydroxypiperazine-1,4-dicarbaldehyde (THDFP) – which is prepared by condensing glyoxal with formamide in the presence of a base (as a catalyst). THDFP undergoes a condensation reaction with guanidine hydrochloride in hydrochloric acid, and the result of this reaction depends on the concentration of hydrogen chloride in the solution, and the molar ratio of the reactants [30]. When the ratio of THDFP to Gu^*HCl is 1: 2 and ~35% hydrochloric acid is used, 4,5-diamino-2-iminoimidazolidine is obtained. The compound is then condensed with formaldehyde in a basic medium, and the resulting bicyclic product is gradually ni-

Table 3. Summary of properties of cyclic nitroamines and nitroimines derived from NQ.

Parameter	Compound NNHT (13)	15	16	17	RDX	NQ
Formula	C ₃ H ₆ N ₆ O ₄	C ₄ H ₆ N ₈ O ₄	C ₄ H ₆ N ₈ O ₆	C ₆ H ₈ N ₁₂ O ₈	C ₃ H ₆ N ₆ O ₆	CH ₄ N ₄ O ₂
M [g/mol]	190.12	230.14	262.14	376.20	222.12	104.07
OB [%]	−42.1	−48.7	−30.5	−34.0	−21.6	−30.7
%N	44.2	48.7	42.7	44.7	37.8	53.8
T _{dec} [°C]	207	326	207	299	205	254
ΔH _f ° [kJ/mol]	+ 68.2	+ 221.7	+ 215.1	+ 407.5	+ 61.5	−92.5
ρ [g/cm ³]	1.75	1.87	1.85	1.83	1.80	1.77
D [m/s]	8280	8890	n/a	n/a	8754	8344
P [GPa]	28.6	35.8	33.8	32.3	34.7	27.0
IS [J]	n/a	10	n/a	n/a	7.4	> 50
FS [N]	> 360	> 360	> 360	24	108	> 360

n/a – data not available.

Table 4. Energetic parameters of exemplary INI⁺ salts presented in Ref. [27].

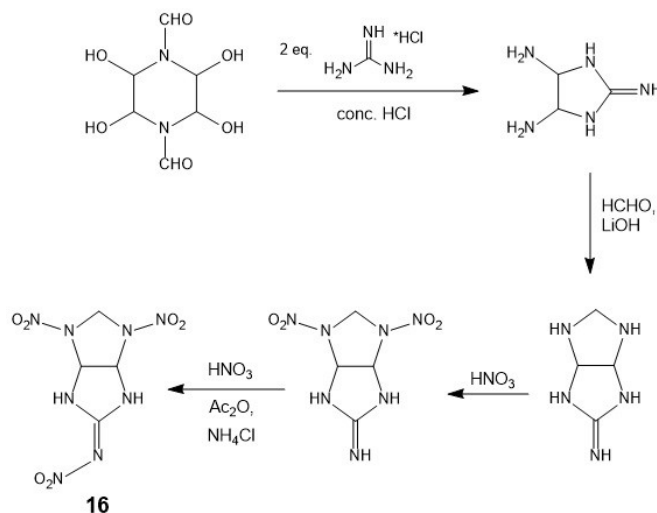
Parameter	Anion N(NO ₂) ₂ [−]	C(NO ₂) ₃ [−]	NIT ^{−[a]}	BTA ^{2−[b]}
Salt formula	C ₄ H ₈ N ₁₀ O ₄	C ₅ H ₈ N ₁₀ O ₈	C ₅ H ₉ N ₁₃ O ₄	C ₁₀ H ₁₆ N ₂₂ O ₄
M [g/mol]	292.17	336.18	315.21	508.38
T _{dec} [°C] ^[c]	193	104	224	282
ρ [g/cm ³]	1.84	1.77	1.74	1.67
%N	47.9	41.7	57.8	60.6
OB [%]	−32.9	−28.6	−53.3	−75.5
ΔH _f (salt) ^[d]	+ 174.5	+ 64.9	+ 352.9	+ 1127.1
D [m/s]	8916	8409	8619	8177
P [GPa]	34.4	29.9	28.3	24.1
I _{sp} [s] ^[e]	240	244	209	217

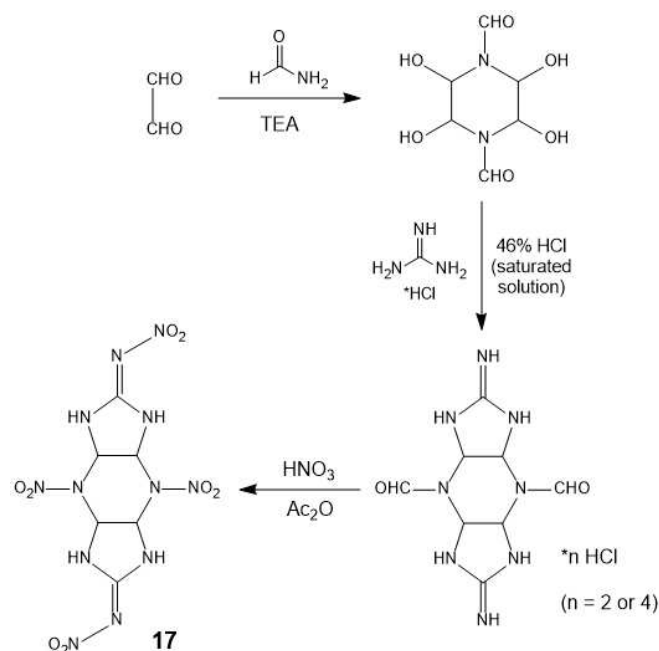
[a] (5-Nitroimino)tetrazolate; [b] Bistetrazolate; [c] decomposition temperature; [d] enthalpy of salt formation; [e] Specific impulse.

trated to obtain 1,3-dinitro-5-(nitroimino)octahydroimidazo[4,5-d]imidazole (16) (Scheme 9).

On the other hand, when THDFP is condensed with Gu*HCl in a saturated solution of hydrogen chloride, and the molar ratio of reagents is 1:5, the main product of the reaction is tricyclic 2,6-diiminododecahydrodiimidazo[4,5-b:4',5'-e]pyrazine, isolated as a tetrahydrochloride salt. This intermediate is then purified by dissolving it in water and reprecipitated by pouring it into THF. Purified compound (in form of dihydrochloride) can be then nitrated, to obtain 4,8-dinitro-2,6-bis(nitroimino)dodecahydrodiimidazo[4,5-b:4',5'-e]pyrazine (17) (Scheme 10).

The results of initial tests of derivatives 15–17, as well as NNHT are presented in the work [21]. The authors performed the basic physicochemical characterization of 4 said heterocyclic NQ derivatives, investigated the thermal and hydrolytic stability, determined the sensitivity to mechanical stimuli, and calculated the theoretical values of the detonation pressure using the Kamlet method. They found that fused-ring compounds 15–17 have a single crystal density slightly higher than RDX (1.83–1.87 vs 1.81 g/cm³), and for this reason, their explosive parameters are quite similar to this compound, despite a worse oxygen balance.

**Scheme 9.** Scheme of 1,3-dinitro-5-(nitroimino)-octahydroimidazo[4,5-d]imidazole synthesis.



Scheme 10. Scheme of 4,8-dinitro-2,6-bis(nitroimino)-dodecahydrodiimidazo[4,5-b:4',5'-e]pyrazine synthesis.

All tested compounds were characterized by excellent hydrolytic and thermal stability. They also show decent insensitivity to friction, with the exception of compound 17 which is highly sensitive (24 N).

The comparison of the parameters of heterocyclic NQ derivatives (NNHT and 15–17) is presented in Table 3.

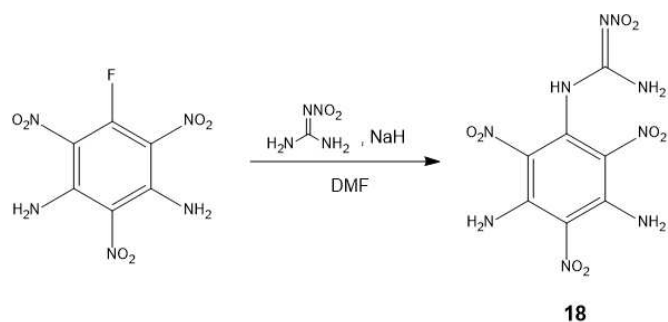
6 Reactions of the Alkali Salts of Nitroguanidine

Nitroguanidine in the presence of strong bases, such as alkali metal amides, hydrides, or alkoxides is deprotonated and forms corresponding salts that can be isolated from the reaction mixture [31]. These salts are relatively thermally stable (e.g. the potassium salt melts at about 155 °C), but decomposes back into nitroguanidine under the influence of moisture.

The alkali metal nitroguanidine salts act as strong nucleophiles, which allows to use them in nucleophilic substitution reactions. For example, Chaykovski and Adolph [32] described the reaction of the NQ sodium salt with 5-fluoro-1,3-diamino-2,4,6-trinitrobenzene (F-DATB), in which 5-(nitroguanidine)-1,3-diamino-2,4,6-trinitrobenzene (18) was obtained in 52.2% yield (Scheme 11).

Another publication [33] describes the reactions of nitroguanidine sodium salt with 3,6-bis-(3,5-dimethylpyrazole-1-yl)-1,2,4,5-tetrazine (DMPT).

The product was obtained in the form of the sodium salt ($\text{Na}_2\text{NQ}_2\text{Tz}$) which can be converted into 3,6-bis-(nitro-



Scheme 11. Synthesis of 5-(nitroguanidine)-1,3-diamino-2,4,6-trinitrobenzene.

guanidine)-1,2,4,5-tetrazine (NQ_2Tz) by acidification with hydrochloric acid, or it can be used for the synthesis of other high-energetic salts in the double exchange reaction (Scheme 12). The sodium salt is also proposed as a source of ligands for obtaining energetic metal-organic framework (MOF) compounds [34].

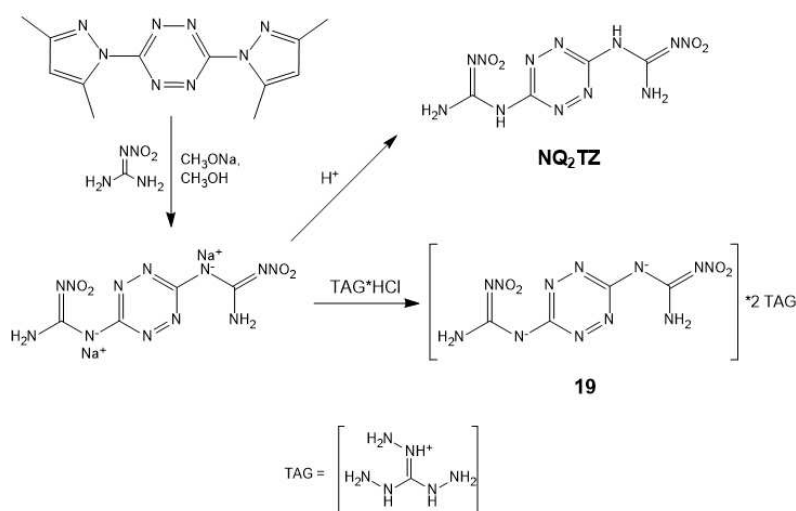
The subsequent work [35] describes the results of detailed studies on the energetic characteristics of NQ_2Tz and its triaminoguanidine salt. The results of research on the characteristics of the combustion process turned out to be particularly interesting. Both compounds show a very low pressure dependence of combustion rate, which makes them suitable for applications in rocket propulsion and gas generating mixtures. According to the authors, NQ_2Tz has the lowest value of burn rate pressure exponent among all monopropellants known in the literature (Table 5).

7 Nitroguanylation

One of the oldest known methods for the synthesis of substituted guanidines is the reaction of amines with so-called guanylating reagents, i.e. compounds containing a combination of a carboxyiminoamine moiety with a good leaving

Table 5. Properties of compounds synthesized with NQ salts.

Parameter	Compound 18	NQ_2Tz	$\text{NQ}_2\text{Tz} \cdot 2\text{TAG}$
Formula	$\text{C}_7\text{H}_7\text{N}_9\text{O}_8$	$\text{C}_4\text{H}_6\text{N}_{12}\text{O}_4$	$\text{C}_6\text{H}_{22}\text{N}_{24}\text{O}_4$
M [g/mol]	345.19	286.17	494.40
%N	36.5	58.7	68.0
OB [%]	–44.0	–39.1	–61.5
M_p [°C]	184	228 (dec)	166 (dec)
ρ [g/cm ³]	1.65	1.76	1.61
D [m/s]	–	7840	7620
P [GPa]	–	26.0	21.9
I_{sp} [s]	–	219	236.5
IS [cm]	46.6	65	114
FS [N]	–	> 353	> 353
ESD [J]	–	> 0.36	> 0.36

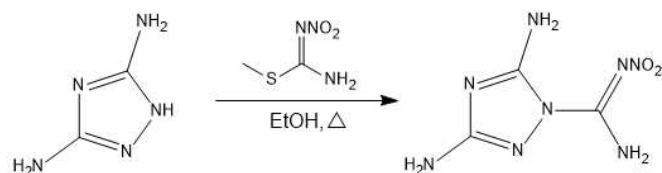


Scheme 12. Synthesis of NQ₂Tz and NQ₂Tz*2TAG.

group. This approach was first described in 1881 by Bernhard Rathke [36], and for this reason, it is sometimes called Rathke's guanidine synthesis. Historically, the first guanylating reagents were the salts of the alkylisothioureas. A number of alternative substances have been described over time, including those in which the amino or imino groups have been protected to prevent side reactions. One of the proposed methods of protecting an imino group was its conversion into the nitroimino group. The nitro group was usually removed after condensation by catalytic hydrogen transfer reaction [37,38].

Reagents of this type turned out to be equally useful in the synthesis of energetic nitroguanidine derivatives. At least several nitroguanylating reagents are known today, the most popular are S-methyl-N-nitrosoisothiourea [39], N-methyl-N-nitroso-N'-nitroguanidine (MNNG) [40], and 3,5-dimethyl-N-nitro-1-H-pyrazole-1-carboximidamide (DMNPC) [41].

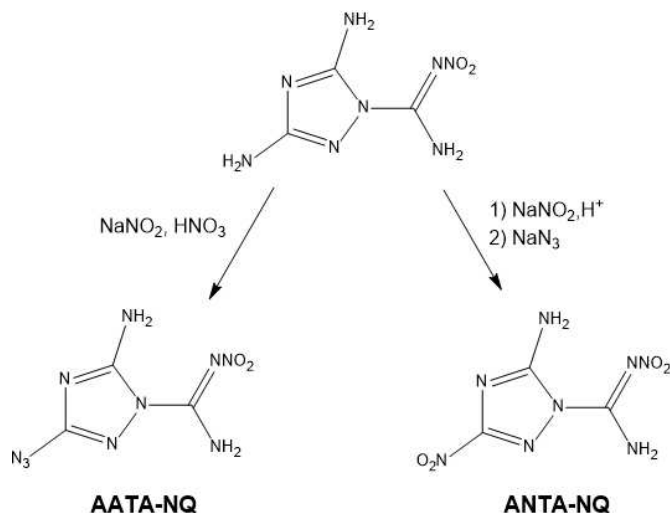
In Ref. [42], a Russian team described the reaction of S-methyl-N-nitrosoisothiourea with 3,5-diamino-1,2,4-triazole. They discovered, that in this reaction position 1 in the ring is selectively substituted, which results in 3,5-diamino-1-nitroguanyl-1,2,4-triazole formation (Scheme 13). The yield varied in a range of 58–91% depending on the reaction time. The authors also presented a method of converting the product into nitrate and perchlorate salt. However, the



Scheme 13. Synthesis of 3,5-diamino-1-nitroguanyl-1,2,4-triazole.

energetic properties of any of the compounds have not been described.

3,5-diamino-1-nitroguanyl-1,2,4-triazole, obtained by the method mentioned above, was used as a starting material in the synthesis described in [43]. The authors used the reactivity of the amino groups in positions 3 and 5 to replace one of them with the nitro (ANTA-NQ) or azide (AATA-NQ) group (Scheme 14). Both obtained derivatives are characterized by quite high detonation parameters - detonation velocities calculated using the Cheetah thermochemical code are respectively 8.3 km/s for the nitro derivative and 8.2 km/s for the azide derivative at a density of 1.79 g/cm³ and 1.73 g/cm³, respectively. Moreover, ANTA-NQ meets the criteria of a low-sensitivity explosive - the value of impact sensitivity h_{50} is 46 J, while in the friction sensitivity test, it



Scheme 14. Synthesis of ANTA-NQ and AATA-NQ.

shows no reaction even at the maximum load of 360 N (Table 6).

Another example of using S-methyl-N-nitrosothiourea is the conversion of 5-amino-1H-tetrazole into 5-nitroguanidine tetrazole (HNGT) (Scheme 15), first described in the patent [44]. The reaction is carried out in an alkaline aqueous medium. The yield of the reaction varied in a range of 38–52 % depending on the conditions.

The cited patent also describes the synthesis of guanidine salt (GuNGT). Both compounds have been proposed as components of multi-base gunpowders with a low combustion temperature, but characterized by a higher combustion rate than nitroguanidine-containing propellants.

The topic of HNGT salt synthesis was significantly expanded in [45]. The authors obtained salts with 10 different high-nitrogen cations and characterized their basic physicochemical properties. Using the Cheetah thermochemical code, their energetic parameters were also calculated. Some of these compounds have impressive detonation velocity values – the highest value (9469 m/s) was obtained for the triaminoguanidinium salt. Despite the high detonation rates, the calculated detonation pressures of all the compounds described were lower than RDX.

Another example of a nitroguanidylating reagent is N-methyl-N-nitroso-N'-nitroguanidine (MNNQ). The discovery of this compound was inspired by previous studies on the reactivity of nitrosoguanidine, which forms alkylguanidines in reaction with alkylamines [40,46].

MNNQ was used in Ref. [47] for the synthesis of nitrogen-rich, high-energy materials containing sym-triazine, sym-tetrazine, and carbazide moiety. The authors observed

that under the proposed conditions, in the case of amine derivatives of triazoles and tetrazoles, there was no substitution with a nitroguanidyl fragment, while hydrazine derivatives reacted even below room temperature. Six novels, nitrogen-rich compounds were described, all of them characterized by high resistance to mechanical stimuli, and detonation parameters only slightly lower than RDX. With one exception, the compounds decomposed at about 200 °C.

8 Reactions with Aminonitroguanidine

Aminonitroguanidine (ANQ), first obtained by Phillips and Williams in 1928 [48] in the reaction of nitroguanidine with hydrazine, is a high-energetic material with detonation parameters similar to NQ, but unlike it has a positive enthalpy of formation. ANQ is more sensitive to mechanical stimuli – the sensitivity to impact is 20 J, and to friction is 144 N [49]. Due to the relatively high cost of synthesis (mainly due to the necessity of very strict control of conditions and only moderate yield) has not found wider application as a high explosive. However, it has been used as a substrate in the synthesis of other compounds.

Similar to other aminoguanidines, the amino group of the ANQ exhibits a hydrazine-like character. The only difference is that due to the presence of a highly electron-accepting nitro group in the molecule, its basic character is weakened, and as a result, it is stable as a free compound. However, many ANQ salts are known with strong oxidizing acids, as well as with high-energy anions, e.g. derivatives of triazoles, tetrazoles, or with the dinitramide anion [45,50–52]. Aminonitroguanidine is also used as a ligand in complex compounds [53].

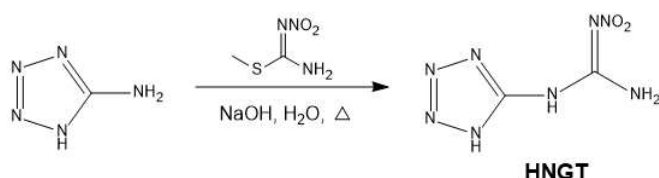
The presence of the highly reactive amino group in the ANQ molecule allows it to carry out similar reactions as in the case of hydrazine derivatives. It is possible to create analogs of hydrazones by reaction with aldehydes or ketones, conduct nucleophilic substitution, and even obtain an azide group by diazotization. The last of the mentioned reactions was used in 1951 by Lieber as an intermediate step in obtaining 5-nitroiminotetrazole [54].

The reaction of ANQ with formaldehyde produces 1-hydroxymethylamino-2-nitroguanidine [55]. This compound reacts with nitroform in a similar manner as HMNQ. As a result 1-(2,2,2-trinitroethylamino)-2-nitroguanidine (TNEANG) can be obtained, and then derivatization to 1-(2,2-dinitroethylamino)-2-nitroguanidine (DNEANG) (or its potassium salt) is also possible (Scheme 16) [56]. Both the dinitro and trinitro derivatives melt at low temperatures (93–94 °C and 95–96 °C, respectively), so they are perspective melt cast explosives [49]. However, the energetic parameters of these compounds have not been fully described so far.

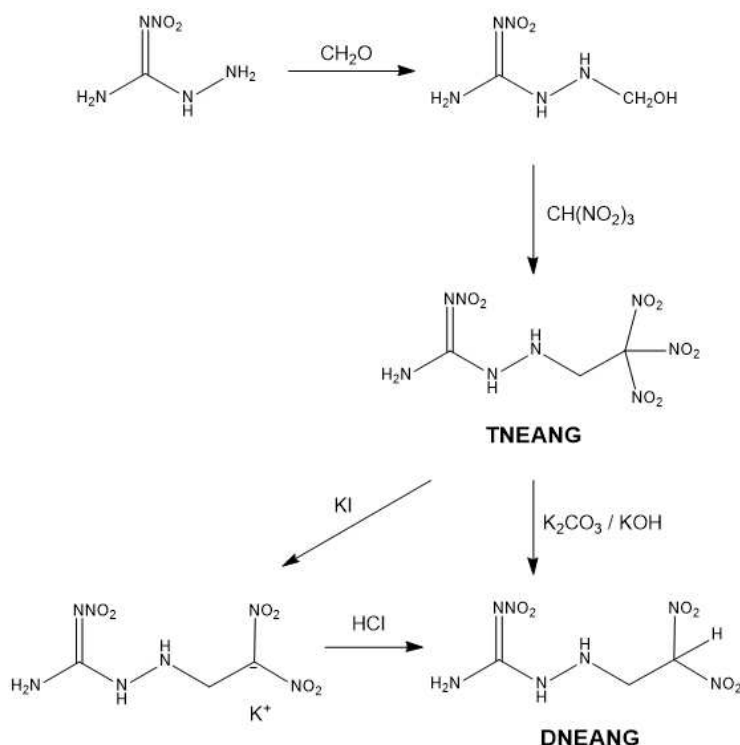
Reactions of aminonitroguanidine with glyoxal may lead to a number of compounds, depending on the pH of the environment and the molar ratio of the reactants [57,58].

Table 6. Properties of ANTA-NQ and AATA-NQ.

Parameter	Compound ANTA-NQ	AATA-NQz	TATB
Formula	C ₃ H ₄ N ₈ O ₄	C ₃ H ₄ N ₁₀ O ₂	C ₆ H ₆ N ₆ O ₆
M [g/mol]	216.12	212.13	258.15
%N	51.8	66.0	32.55
OB [%]	–29.6	–45.2	–55.8
M _p [°C]	200 (dec.)	200(dec.)	350
ρ [g/cm ³]	1.79	1.73	1.88
D [km/s]	8.3	8.2	7.76
P [GPa]	29.0	25.7	29.0
IS [J]	46	9.1	> 78.4
FS [N]	> 360	249	> 360
ESD [J]	0.125	0.125	0.125



Scheme 15. Synthesis of HNGT.



Scheme 16. Synthesis of TNEANG and DNEANG.

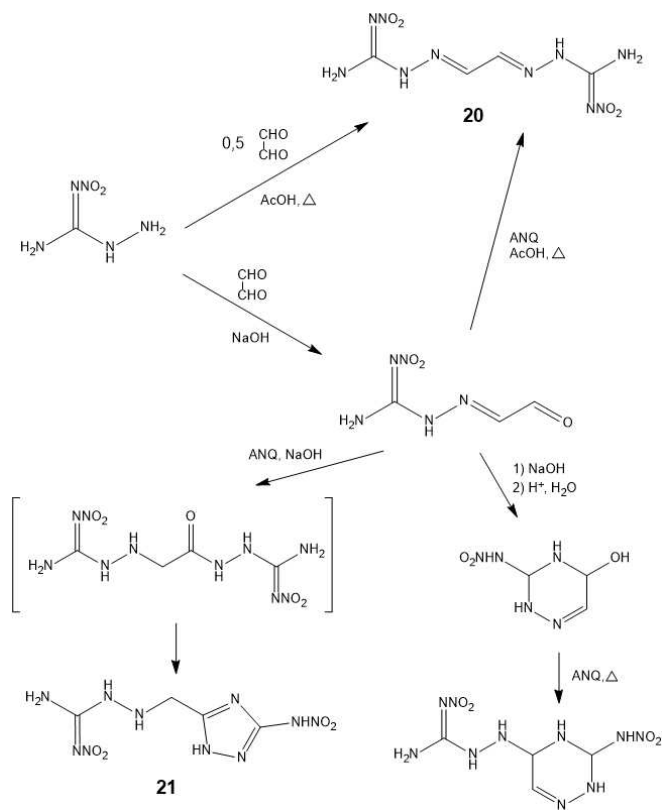
By heating an excess of ANQ with glyoxal in the presence of acetic acid, asymmetrically substituted glyoxal dihydrazone is obtained. By reacting with an equimolar amount of glyoxal in an alkaline medium, it is possible to obtain monohydrazone as the major product. This compound, after adding another molar equivalent of ANQ, undergoes a second substitution followed by the closure of the triazole ring.

The reaction also produces some 3-nitroamino-4,5-dihydro-1,2,4-triazin-5-ol as by-product, which can be isolated by concentrating the reaction solution. This side product can be reacted with another ANQ molecule to substitute the hydroxyl group (Scheme 17, Table 7).

Aminonitroguanidine also forms hydrazones with aromatic aldehydes. Examples of such compounds are presented in [59]. 2,4,6-Trinitrobenzaldehyde and 3-methyl-4-furoxanecarboxaldehyde were used as precursors (Scheme 18). The basic energetic properties of the obtained compounds are presented in Table 8.

In reaction with oxalic acid, ANQ forms oxalyl hydrazides substituted on terminal nitrogen atoms with a nitroguanyl moiety. These compounds when heated with potassium hydroxide or carbonate undergo cyclization with the formation of triazole rings [60] (Scheme 19).

Alternatively, they can also be obtained starting from N-methyl-N-nitroso-N'-nitroguanidine and oxalic acid hydrazides [61].



Scheme 17. Reactions of ANQ with glyoxal.

Table 7. Basic properties of derivatives obtained from ANQ.

Parameter	Compound TNEANG	DNEANG	20	21
Formula	C ₃ H ₆ N ₈ O ₈	C ₃ H ₇ N ₇ O ₆	C ₄ H ₈ N ₁₀ O ₄	C ₃ H ₆ N ₁₀ O ₄
M [g/mol]	282.13	237.13	260.17	246.14
OB [%]	−5.7	−23.6	−49.2	−32.5
%N	39.7	41.3	56.9	56.9
M _p [°C]	95–96	93–94	dec > 300	192 (dec)

Table 8. Comparison of energetic properties of compounds 22 and 23.

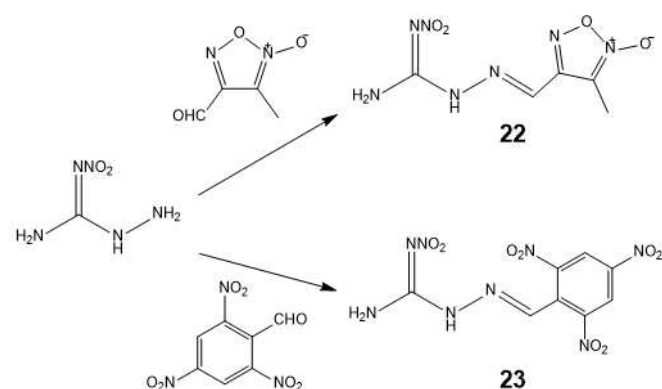
Parameter	Compound 22	23	RDX
T _{dec} [°C]	218	204	205
Δ _f H _m [kJ/mol]	+421.6	+306.2	+61.5
ρ [g/cm ³]	1.65	1.79	1.80
D [m/s]	7670	7965	8754
P [GPa]	24.8	28.1	34.7
IS [J]	19	24	7.4
FS [N]	128	168	120

Table 9. Comparison of energy parameters of selected bis [3-(5-nitroimino-1,2,4-triazole)] salts presented in Ref. [62].

Parameter	Cation(s) 2 NH ₃ OH ⁺	2TAG ⁺	CHZ ²⁺	Gu ₂ Tz ²⁺
Formula	C ₄ H ₁₀ N ₁₂ O ₆	C ₆ H ₂₀ N ₂₂ O ₄	C ₅ H ₁₀ N ₁₄ O ₅	C ₈ H ₁₂ N ₂₀ O ₄
M [g/mol]	322.20	464.37	346.22	452.31
%N	52.2	66.4	56.6	61.9
OB [%]	−34.8	−62.0	−46.2	−63.7
T _{dec} [°C]	218	244	222	290
ρ [g/cm ³]	1.78	1.64	1.95	1.80
D [km/s]	8856	8705	9399	8267
P [GPa]	32.4	27.0	36.0	24.3
I _{sp} [s]	240	221.9	194.7	182.8
IS [J]	n/a	23	38	32

CHZ²⁺ – carbonylhydrazide cation; Gu₂Tz²⁺ – 3,6-bis(guanidino)-1,2,4,5-tetrazine cation.

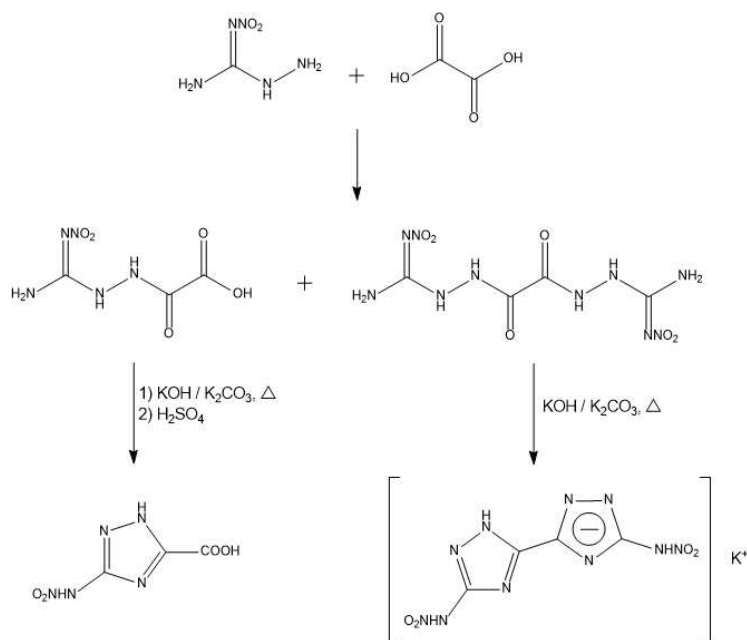
A particularly interesting derivative is the bicyclic bis [3-(5-nitroimino-1,2,4-triazole)], as its molecule contains two



Scheme 18. Examples of preparations of ANQ hydrazones.

protons of an acidic nature, and therefore it can form monovalent or divalent salts. The synthesis and properties of high-energy materials based on these anions are described in paper [62] (Table 9). The authors obtained 11 salts with nitrogen-rich cations, which were characterized by high positive enthalpies of formation, high density, good thermal stability, and low impact sensitivity. Particularly noteworthy are the very high values of the calculated detonation parameters (e.g. for the carbazide salt D = 9399 m/s, P = 36.0 GPa).

Another interesting nitroguanidine derivative is hydrazobis(nitroformamidine) (1,6-dinitrobiguanidine). This compound can be synthesized in several ways: by reducing azobis(nitroformamidine) with hydrogen sulfide, by reacting N-methyl-N-nitroso-N'-nitroguanidine with amino-nitroguanidine, or by condensation of nitroguanidine with hydrazine hydrate in a carefully selected molar ratio, and



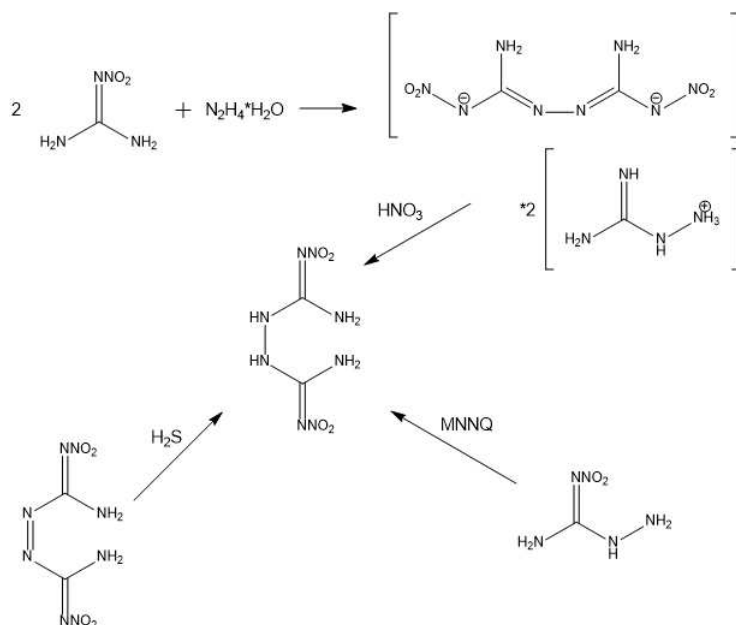
Scheme 19. Reactions of ANQ with oxalic acid.

subsequent acidification of the resulting aminoguanidine salt (Scheme 20) [63,64].

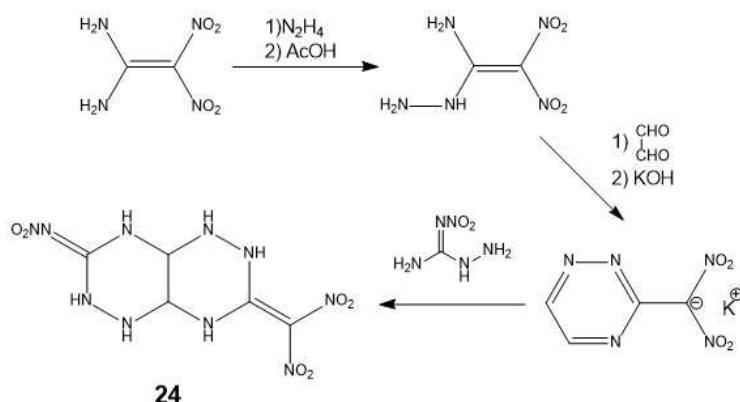
All the above-mentioned methods are complicated and have serious drawbacks: the first one is based on a precursor that is difficult to obtain, the second one requires very long reaction times (weeks or even months), while the last one requires very strict control of temperature and reaction time. In all cases, the synthesis yield does not exceed

45% (although usually is much lower, at 10–20%). For this reason, 1,6-dinitrobiquanidine is not used as an individual high explosive. However, the literature proposes its use as a substrate for further syntheses [64,65].

Aminonitroguanidine was also used in [66] as a precursor of 3-nitroimino-7-dinitromethyleneoctahydro-[1,2,4] triazino-[6,5-e][1,2,4]triazine (24). This compound is formed in a three-step reaction path, starting from another en-



Scheme 20. Methods of preparation of 1,6-dinitrobiquanidine.



Scheme 21. Synthesis of 3-nitroimino-7-dinitromethylene-octahydro-[1,2,4]triazino-[6,5-e][1,2,4]triazine.

ergetic compound – 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7) (Scheme 21).

3-nitroimino-7-dinitromethyleneoctahydro-[1,2,4]triazino-[6,5-e][1,2,4]triazine has a positive enthalpy of formation (+304.2 kJ/mol). The calculated values of the detonation parameters are slightly lower than RDX ($D=8492$ m/s, $p_C=29.4$ GPa). It is also characterized by a moderate sensitivity to mechanical stimuli (8 J, >360 N), however, due to the low decomposition temperature (123.5 °C), the practical applications of this compound are rather limited.

The heating of the ANQ mixture with sodium azide and triethyl orthoformate in acetic acid leads to 1-nitroguanidine tetrazole (Scheme 22). After recrystallization from ethanol, the product decomposes at 221 °C [67]. The authors of the cited paper did not determine the sensitivity to mechanical stimuli nor detonation parameters.

9 Further Nitration of Nitroguanidine

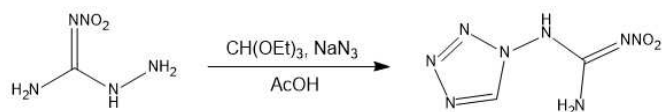
Nitration of guanidine salts with nitric acid, or its mixtures with sulfuric acid, yields nitroguanidine in a high yield. For a long time, nitroguanidine was considered the final product of this reaction. However, in 2003 Russian researchers published a paper [68] in which they presented the results of research on the reaction of further nitration of nitroguanidine with more active nitrating mixtures. They found that when mixtures of anhydrous nitric acid with N_2O_5 or 98% HNO_3 with oleum are used, it is possible to obtain 1,2-dinitroguanidine (DNQ) with a yield of 59–80%. They also found that it was possible to obtain DNQ directly from gua-

nidine nitrate or sulfate by introducing a solution of the corresponding salt in 98% HNO_3 into the aforementioned nitration mixtures. After pouring the reaction mixture onto the ice, DNQ is isolated by extraction from the aqueous phase with ethyl acetate.

1,2-Dinitroguanidine is a colorless solid with a melting point of 169 °C. It is moderately soluble in water, ethyl acetate, ethanol, acetone, and acetonitrile. Unlike nitroguanidine, it is quite a strong acid (pK_a is 1.11 and 11.5 respectively, versus 13.6 for nitroguanidine). For this reason, it forms stable, monovalent salts. The authors described the methods of synthesizing alkali metal salts, as well as ammonium, monomethyl- and dimethylammonium, hydrazine, and guanidine. However, the energy characteristics of any of the compounds were not given.

Further investigation of the properties of DNQ are presented in [69]. The authors optimized the conditions of DNQ synthesis and purification, as well as obtained several alkyl derivatives and salts of this compound. Moreover, they tested the thermal stability of DNQ and its selected prospective derivatives using the DSC technique and STANAG4582 long-term stability test. Free DNQ was the only compound that met the stability criterion of STANAG4582, however, the authors concluded that its acidity was too high to allow wider practical application of the compound.

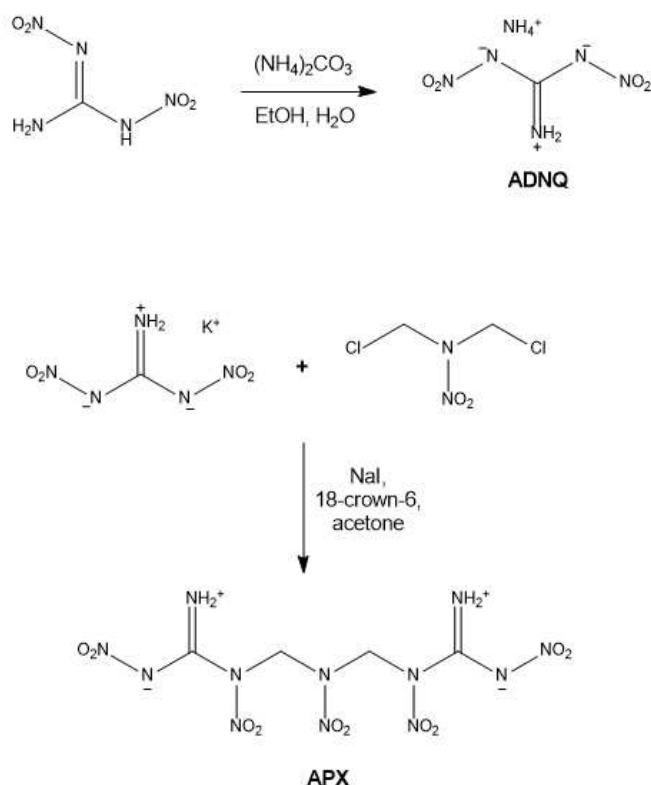
The explosive properties of two 1,2-dinitroguanidine derivatives: ammonium salt (ADNQ) and 1,7-diamino-1,7-dinitroimino-2,4,6-trinitro-2,4,6-triazaheptane (APX) have been extensively described in work [70]. The authors synthesized both derivatives with high yield (85–90%) (Scheme 23), determined the crystallographic structure, examined the thermal stability, and calculated the explosive parameters. In addition, the sensitivity to mechanical stimuli of both derivatives was determined, and for APX, the measurement of the detonation velocity and the Koenen test was also performed. Both ADNQ and APX are characterized by impressive values of detonation velocity and pressure, unfortunately, they decompose below the temperature of 200 °C, and their sensitivity to mechanical stimuli is high



Scheme 22. Synthesis of 1-nitroguanidine tetrazole.

(especially in the case of APX). The basic explosive properties of both compounds are summarized in Table 10.

On the other hand, the topic of 1,2-dinitroguanidine salts was also explored in Ref. [71]. The authors presented the synthesis of six new compounds with mono-, di- and triaminoguanidine cations and three high-nitrogen heterocyclic cations. The individual salts were obtained by reacting DNQ silver salt with the appropriate hydrochloride, or DNQ with the free base. Predicted detonation velocities of the compounds range from 7665 to 8422 m/s, and detonation pressures change from 25.3 to 30.3 GPa. Most of the described salts decompose at relatively low temperatures. Only two of them (INI and 3,4,5-triaminotriazole cations) are thermally stable up to 200 °C.



Scheme 23. Scheme of ADNQ and APX synthesis.

Table 10. Comparison of energetic properties of ADNQ and APX.

Parameter	Compound ADNQ	APX
T_{dec} [°C]	197	174
ρ [g/cm ³]	1.735	1.911
D [m/s]	9066	9540
P [GPa]	32.7	39.8
IS [J]	10	3
FS [N]	252	80
ESD [J]	0.4	0.1

10 Conclusion

The nitroguanidine moiety is a building block of particular interest for the synthesis of new high-energy compounds. Its introduction into the molecule usually leads to the formation of an extensive network of hydrogen bonds, which provides additional stabilization of the structure. Compounds that contain them usually show high resistance to mechanical stimuli and shock waves. Many energetic nitroguanidine derivatives are characterized by high nitrogen content in the molecule, which makes them suitable for use as components of modern gunpowders, rocket fuels, or gas generating mixtures, and is also important from the point of view of “green chemistry”.

Particularly noteworthy is the possibility of derivatization of some of the already known high-energy compounds, especially in the reaction of nitroguanidylating reagents with amino groups, which commonly appear in modern explosives. Due to the presence of oxygen in the nitro group, the addition of the nitroguanidine fragment hardly influences the oxygen balance of the functionalized compounds, allowing to “tailor” properties of explosive without significantly decreasing its energetic parameters. Similarly interesting are the nucleophilic substitution reactions of a halogen or other good leaving groups by reaction with in situ generated alkaline nitroguanidine salts.

The preparation of new nitroguanidine derivatives requires the development of an appropriate synthesis strategy and experimental selection of reaction conditions in order to obtain the desired product. However, due to their potential benefits, nitroguanidine derivatives remain an interesting and relatively unexplored area in the field of high energy compound chemistry.

Abbreviations

AATA-NQ	1-nitroguanidyl-3-azido-5-amino-1,2,4-triazole
ADNQ	dinitroguanidine ammonium salt
ANQ	aminonitroguanidine
ANTA-NQ	1-nitroguanidyl-3-nitro-5-amino-1,2,4-triazole
APX	1,7-diamino-1,7-dinitroimino-2,4,6-trinitro-2,4,6-triazasheptane
ARDEC	US Army Development and Engineering Center
ARL	US Army Research Laboratory
CHZ ²⁺	Carbohydrazide cation
DADNE	1,1-diamino-2,2-dinitroethene
DGX-6	aluminized melt cast composition based on PrNQ and HMX
DMNPC	3,5-dimethyl-N-nitro-1-H-pyrazole-1-carboximidamide
DMPT	3,6-bis-(3,5-dimethylpyrazole-1-yl)-1,2,4,5-tetrazine
DNEANG	1-(2,2-dinitroethylamino)-2-nitroguanidine
ESD	sensitivity to electrostatic discharge
F-DATB	5-fluoro-1,3-diamino-2,4,6-trinitrobenzene

FOX-7	1,1-diamino-2,2-dinitroethene
FS	friction sensitivity
Gu	guanidinium cation
GuNGT	5-nitroguanidine tetrazole guanidinium salt
Gu ₂ Tz ²⁺	3,6-bis(guanidino)-1,2,4,5-tetrazine cation
HMNQ	hydroxymethylnitroguanidine
HMTA	hexamethylenetetramine, hexamine
HMX	1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane, octogen
HNGT	5-nitroguanidine tetrazole
INI	2-imino-5-nitroiminotetrahydroimidazo [4, -5d] imidazole cation
IS	impact sensitivity
MNNG	N-methyl-N-nitroso-N'-nitroguanidine
MOF	metal-organic framework
NBHT	2-nitroimino-4-tertbutylhexahydro-1,3,5-triazine
NNHT	5-nitro-2-nitroiminohexahydro-1,3,5-triazine
NQ	nitroguanidine
NQ ₂ Tz	3,6-bis-(nitroguanidino)-1,2,4,5-tetrazine
PAX-PrNQ	melt cast composition based on PrNQ and HMX
PBXN-109	polymer-bonded explosive formulation, composed of 64% RDX, 20% Al, and 16% binder
P _{CJ}	detonation pressure in Chapman-Jouguet point
PrNQ	N-propyl-N'-nitroguanidine
RDX	1,3,5-Trinitro-1,3,5-triazinane, hexogen
TAG	triaminoguanidinium cation
T _{dec}	decomposition temperature
THDFP	2,3,5,6-tetrahydropiperazine-1,4-dicarbaldehyde
TMD	theoretical maximum density
TNEANG	1-(2,2,2-trinitroethylamino)-2-nitroguanidine
TNT	2,4,6-trinitrotoluene

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Data Availability Statement

Data openly available in a public repository that issues datasets with DOIs.

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