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Synthesis, Structure, and Properties of *N,N′*-Dinitrourea

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Abstract: Information on synthesis methods and properties of *N,N′*-dinitrourea and its salts, which were reported virtually simultaneously by different authors in different publications, is summarized and systematized. Merits and drawbacks of various approaches for the synthesis of the target products are discussed. The reactivity of *N,N′*-dinitrourea and its salts in the reactions of nucleophilic substitution and condensation is discussed.

Keywords: *N,N′*-Dinitrourea · Nitramides · Nitramines · Nitration · Reactivity

1 Introduction

Information on the synthesis and properties of 1,3-dinitrourea, despite the simplicity of its structural formula, emerged virtually simultaneously in diverse literature sources at the turn of the 20th [1] to the 21st century [2]. Studies on the urea nitration with different nitrating agents to produce nitro compounds were previously reported in sufficient detail [3]. The $O_2NNCONNO_2$ moiety has been known for a long time as a structural constituent of such compounds as *N,N′*-dinitro ethyleneurea [4], tetranitro glycoluril [5], etc.
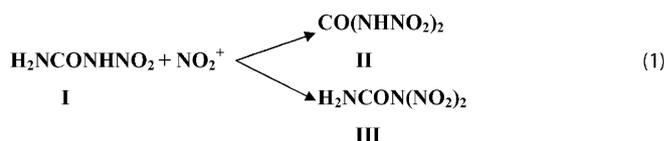
N,N′-dinitrourea is of interest as a source for the preparation of nitramide [6] that is a primary "brick" for building known compounds of the nitramine class, for instance dinitramide [7], and for synthesizing new high-energy substances [8].

Details on synthesis methods, physicochemical, and chemical properties of *N,N′*-dinitrourea reviewed herein may spark the interest of experts working in the field of synthesis and technology development of high-energy compounds.

2 Synthesis Methods

The first synthesis of *N,N′*-dinitrourea is described as direct nitration of urea with equal portions of mixed 98% nitric acid and 20% oleum at −15 to −10 °C while holding for 30 min at −5 °C. The resultant dinitrourea then precipitates and all that is left to do is to filter it off. At room temperature, in the presence of trace amounts of water and acids, dinitrourea undergoes degradation. Therefore, the synthesized compound was identified via its stable diammonium salt by elemental analysis and the IR spectrum [1]. Thermograms for the diammonium, dipotassium, and hexamethyleneamine salts are also given.

The nitration of urea may be accompanied by the formation of two types of nitro compounds:

$$H_2NCONHNO_2 + NO_2^+ \begin{array}{c} \nearrow CO(NHNO_2)_2 \quad \textbf{II} \\ \searrow H_2NCON(NO_2)_2 \quad \textbf{III} \end{array} \qquad (1)$$

$$\textbf{I}$$

The synthesis of dinitroureas (**II**) and (**III**) depends on the reaction conditions. For example, the nitration of nitrourea (**I**) with nitronium salts (tetrafluoroborate and hexafluorosilicate) in organic solvents (ethyl acetate, butyl acetate, and acetonitrile) at −10 to −20 °C leads to *N,N′*-dinitrourea (**II**) [2], while at −30 to −40 °C it leads to gem-*N,N*-dinitrourea (**III**) [9] presented as an intermediate, from which ammonium dinitramide is produced. As an individual compound, urea **III** was not identified.
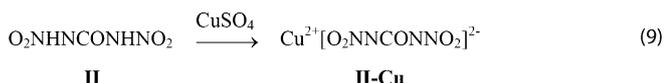
While nitrating nitrourea **I** to dinitrourea **II**, the best results were achieved using nitronium tetrafluoroborate in ethyl acetate. The yield was 55% when equimolar amounts of nitrourea and the nitrating agent were used. In diethyl ether, the nitration of nitrourea **I** was not practically observed [2].

The urea nitration with nitronium tetrafluoroborate in ethyl acetate resulted in dinitrourea **II** in a 15% yield.
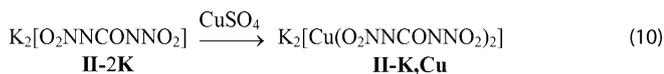
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The studies of the urea nitration with concentrated (98%) nitric acid showed that, depending on conditions, either nitrourea I or dinitrourea II could be formed. The yield of dinitrourea II at a nitrating agent/urea mass ratio of 100 was 28% (determined spectrophotometrically) [2], while the use of freshly distilled nitric acid with 100% concentration and nitric acid containing N_2O_5 (calculated as HNO_3 102.5%) increased the yield of dinitrourea up to 50% at a nitrating agent/urea mass ratio of 18 [2].

The study of the dinitrourea II formation laws depending on the mixed acid composition showed that the target product yield increased to 100% with increasing sulfuric acid concentration in the mixed acid [2]. The quantitative yield of dinitrourea II could be attained within 10 min when oleum/nitric acid mixtures (anhydrous, with free SO_3) containing 50% of sulfuric acid were employed.

For the dinitrourea synthesis, Goede et al. [10] used 95% sulfuric acid and 100% nitric acid. In all other respects, the urea nitration stage did not differ from the methods described above [1,2].

The indirect synthetic route to dinitrourea involves hydrolysis of dinitroguanidine in water [11]:

$$O_2NN{=}C(NH_2)NHNO_2 + H_2O \longrightarrow \underset{\textbf{II}}{CO(NHNO_2)_2} \qquad (2)$$

3 Isolation Methods

The most important aspect in the synthesis of dinitrourea II is its preparative isolation.

When the urea nitration mixture comprising of nitric acid mixed with sulfuric acid or oleum is cooled to −15°C, the dinitrourea II precipitates from the mixture and may be collected [1,2,6]. The resultant dinitrourea II comprises up to 40% of sulfuric acid. When additionally washed with dichloromethane, dinitrourea II increases its content in the precipitate up to 80% [2,6]. To wash out mineral acids, trifluoroacetic acid allows obtaining high-quality dinitrourea II devoid of mineral acid impurities [10].

When nitronium salt is used as a nitrating agent, dinitrourea II is synthesized after bubbling hydrogen chloride through an ether suspension of its salts, both II-K and II-2K [2]. In this case, the dinitrourea II sample has no impurities.

For X-ray structural characterization, a sample of dinitrourea II was obtained by recrystallization from mixed diethyl ether/hexane [12].

$$\underset{\textbf{II-K}}{K^+[O_2NNCONHNO_2]^-} \xrightarrow{HCl} \underset{\textbf{II}}{CO(NHNO_2)_2}$$

$$\underset{\textbf{II-2K}}{K^+_2[O_2NNCONNO_2]^{2-}} \qquad\qquad (3)$$

4 Chemical Properties

4.1 Reaction with Alkalis and Bases

Dinitrourea II is quite a strong dibasic acid capable of detaching protons in a stepwise manner to form acid salts and normal salts [13].

$$\underset{\textbf{II}}{CO(NHNO_2)_2} \xrightarrow{MOH} \underset{\textbf{II-K, II-Na, II-Cs, II-NH}_4}{M^+[O_2NNCONHNO_2]^-} \xrightarrow{MOH} \underset{\substack{\textbf{II-2K, II-2Na, II-2Cs,}\\ \textbf{II-2NH}_4}}{M^+_2[O_2NNCONNO_2]^{2-}} \qquad (4)$$

$M = $ K (II-K, II-2K), Na (II-Na, II-2Na), Cs (II-Cs, II-2Cs), NH_4 (II-NH$_4$, II-2NH$_4$ [1]).

The sustained heating of an aqueous solution of acid salt II-K results in normal salt II-2K. Excess alkali completely decomposes the resulting salt.

Studies of the reaction between the dinitrourea II acid salts and alkali led to salts containing different cations: ammonium potassium salt of dinitrourea (II-NH$_4$,K) and potassium silver salt of dinitrourea (II-Ag,K) [13].

$$\underset{\textbf{II-NH}_4}{NH^+_4[O_2NNCONHNO_2]^-} \xrightarrow{KOH} \underset{\textbf{II-NH}_4\textbf{, K}}{NH^+_4[O_2NNCONNO_2]^{2-}K^+} \qquad (5)$$

$$\underset{\textbf{II-K}}{K^+[O_2NNCONHNO_2]^-} \xrightarrow{AgNO_3} \underset{\textbf{II-Ag, K}}{Ag^+[O_2NNCONNO_2]^{2-}K^+} \text{ (100%)} \qquad (6)$$

The salt II-Ag,K was also obtained from dipotassium salt II-2K by metal exchange reaction.

When dinitrourea II itself is used, the reaction affords the disilver salt (II-2Ag).

$$\underset{\textbf{II}}{O_2NHNCONHNO_2} \xrightarrow{AgNO_3} \underset{\textbf{II-2Ag}}{Ag^+[O_2NNCONNO_2]^{2-}Ag^+} \text{ (100%)} \qquad (7)$$

Treating dinitrourea II and its salts either with bases or with the corresponding bivalent metal salts results in a possible synthesis of salts containing both identical and variable cations, depending on the reaction conditions [13].

$$\underset{\textbf{II}}{O_2NHNCONHNO_2} \xrightarrow{M(OH)_2} \underset{\textbf{II-Mg, II-Ca, II-Ba}}{M^{2+}[O_2NNCONNO_2]^{2-}} \qquad (8)$$

$M = $ Mg (II-Mg); Ca (II-Ca); Ba (II-Ba)

In the case where the copper cation is used, a complexation reaction proceeds, wherein the dinitrourea anion acts as a ligand.

$$O_2NHNCONHNO_2 \xrightarrow{CuSO_4} Cu^{2+}[O_2NNCONNO_2]^{2-} \quad (9)$$
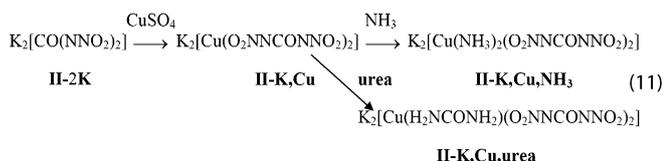$$\textbf{II} \qquad\qquad\qquad \textbf{II-Cu}$$

The complexation of copper(II) sulfate with salt **II-2K** in water was studied spectrophotometrically by the molar ratio method. The copper(II) ion was shown to react in a stepwise manner with the dinitrourea anion to afford anion complexes in solution at mole ratios from 1:1 to 1:6 [13]. Only two compounds were identified: the copper(II) salt of dinitrourea (**II-Cu**) and the potassium bis(N,N'-dinitroureato) cuprate(II) (**II-K,Cu**).

$$K_2[O_2NNCONNO_2] \xrightarrow{CuSO_4} K_2[Cu(O_2NNCONNO_2)_2] \quad (10)$$
$$\textbf{II-2K} \qquad\qquad\qquad \textbf{II-K,Cu}$$

The synthesis of potassium bis(N,N'-dinitroureato)diammine cuprate(II) (**II-K,Cu,NH₃**) and potassium bis(N,N'-dinitroureato)urea cuprate(II) (**II-K,Cu,urea**) indicates manifold possibilities of utilizing the dinitrourea anion in the chemistry of metal complexation compounds.

$$K_2[CO(NNO_2)_2] \xrightarrow{CuSO_4} K_2[Cu(O_2NNCONNO_2)_2] \xrightarrow{NH_3} K_2[Cu(NH_3)_2(O_2NNCONNO_2)_2]$$
$$\textbf{II-2K} \qquad\qquad \textbf{II-K,Cu} \searrow \text{urea} \qquad \textbf{II-K,Cu,NH}_3 \quad (11)$$
$$K_2[Cu(H_2NCONH_2)(O_2NNCONNO_2)_2]$$
$$\textbf{II-K,Cu,urea}$$

Dinitrourea **II** affords the respective salts [12,14], when treated with amines, imines, and amides under mild conditions.

$$CO(NHNO_2)_2 \xrightarrow{A} A^+[O_2NNCONHNO_2]^- \quad (12)$$
$$\textbf{II} \qquad\qquad \textbf{II-NH}_4[2], \textbf{IIa-m,urea} [6]$$
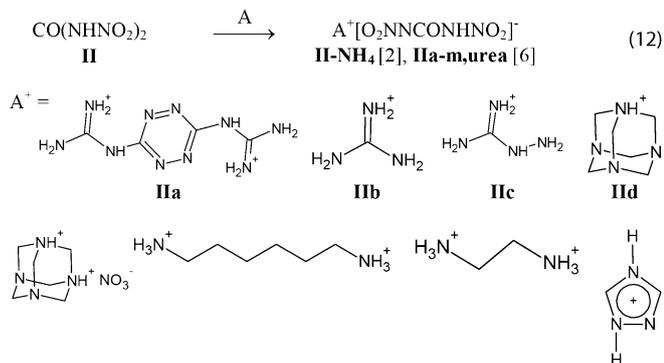
Excessive amounts of ammonia and amines decompose dinitrourea salts to form onium salts of nitrourea and N-alkyl-N'-nitroureas [13].

Dinitrourea dipotassium salt **II-2K** reacts readily with NH₃, CH₃NH₂, and CH₃(CH₂)₃NH₂ in water to furnish the respective potassium salts of nitrourea and N-alkyl-N'-nitroureas.

The amine basicity is essential in the nitramidation of amines with dinitrourea salts; however, one cannot neglect steric factors. In the case of the secondary amines, for in-

$$(H_3NR)^+{}_2[O_2NNCONNO_2]^{2-} \xrightarrow{H_2NR} (H_3NR)^+[O_2NNCONHR]^- \quad (14)$$
$$\textbf{II-2H}_3\textbf{NR} \qquad\qquad \textbf{1-H}_3\textbf{NR, IV-H}_3\textbf{NR}$$
$$R = H\ (\textbf{1}),\ Me\ (\textbf{IV}),\ Bu\ (\textbf{IV})$$
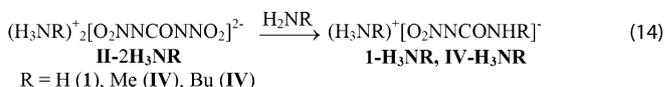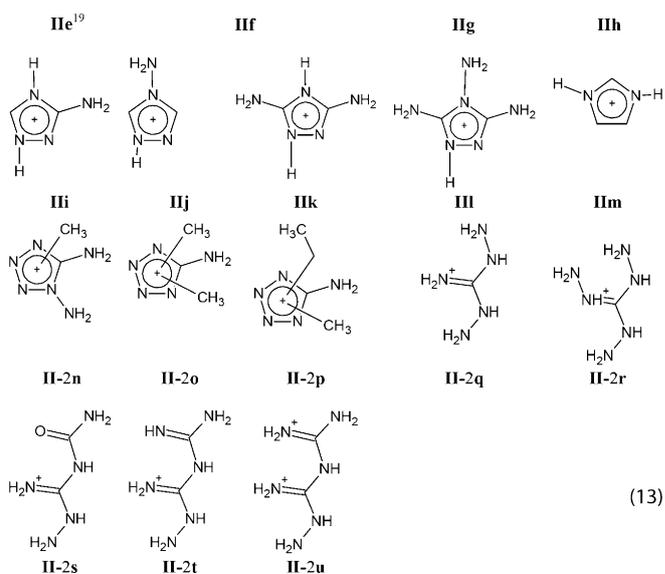
stance, the addition product resulting in N,N-dialkyl-N'-nitroureas was not observed [13].

The obtained mononitro alkylureas were nitrated with mixed sulfuric-nitric acids to the respective monoalkyl dinitroureas [15].

$$O_2NHNCONHR \xrightarrow[H_2SO_4]{HNO_3} O_2NHNCONRNO_2 \quad (15)$$
$$\textbf{IV}, \qquad\qquad\qquad \textbf{V}$$
$$R = Me\ (\textbf{IV, V}),\ Bu\ (\textbf{IV, V})$$

When dinitrourea was treated with hydrazine at a mole ratio of 1:(1–2), 4-nitrosemicarbazide (**VI**) was isolated and identified. Excess hydrazine afforded the hydrazinium salt of nitrosemicarbazide.

$$O_2NHNCONHNO_2 \xrightarrow{H_2NNH_2} O_2NHNCONHNH_2 \quad (16)$$
$$\textbf{II} \qquad\qquad\qquad \textbf{VI}$$

This synthesis method for nitrosemicarbazide and its salts [13] is nowadays unique because the direct nitration of semicarbazide with mixed acids gives carbamic azide.

The chemistry of 4-nitrosemicarbazide starting from dinitrourea **II** is currently progressing [16,17].

The synthesis method for nitramino hydroxamic acid (**VII**) by reaction of dinitrourea **II** with hydroxylamine is nowadays as unique as that for 4-nitrosemicarbazide **VI** [13].

$$CO(NHNO_2)_2 \xrightarrow{H_2NOH} (H_3NOH)^+[O_2NNCONHOH]^- \quad (17)$$
$$\textbf{II} \qquad\qquad\qquad \textbf{VII-(H}_3\textbf{NOH)}^+$$

$$\xrightarrow{H_2SO_4} O_2NNCONHOH$$
$$\textbf{VII}$$

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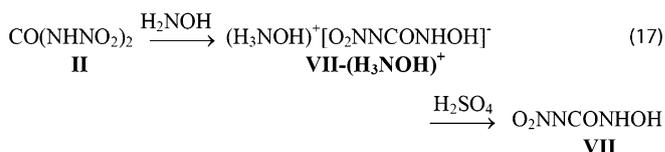
This compound may be attractive for the synthesis of novel energy-rich compounds and medicinal substances.

When acetonitrile is employed as a solvent, the reaction takes place between dinitrourea **II** and 2-amino-1,3-diazido-2-(azidomethyl)propane at a mole ratio of 1:1 to afford 1-[1,3-diazido-2-(azidomethyl)-2-propyl]-3-nitrourea (**VIII**) at room temperature [18]:
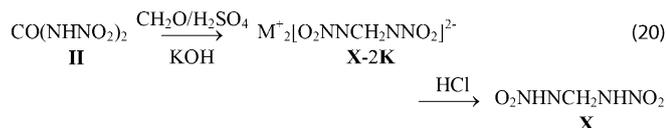
$$\tag{18}$$

II　　　　　　　　**VIII**
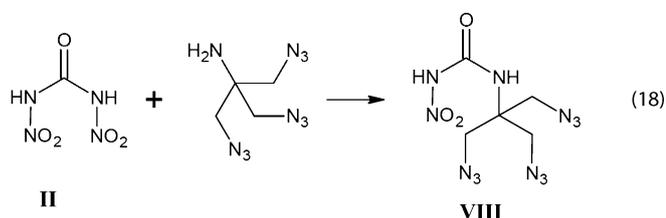
4.2 Reaction with Alcohols

Even at low temperatures, when dinitrourea **II** is allowed to react with alkyl alcohols, the corresponding alkyl nitrocarbamates (**IXa–c**) are formed [13].

$$O_2NHNCONHNO_2 \xrightarrow{ROH} O_2NHNCOOR \tag{19}$$
$$\textbf{II} \qquad\qquad \textbf{IXa-c}$$
$$R = Me(a),\ Et(b),\ Pr(c)$$

This devised process of producing nitrourethanes is very handy and straightforward to run.

4.3 Reaction with Formaldehyde and Glyoxal

The reaction of dinitrourea with formaldehyde at a mole ratio of 1:1 in water in the presence of sulfuric acid at 20–80 °C followed by treatment with potassium hydroxide resulted in the corresponding methylenedinitramine salt (45%) [19].

$$CO(NHNO_2)_2 \xrightarrow[\text{KOH}]{CH_2O/H_2SO_4} M^+_2[O_2NNCH_2NNO_2]^{2-} \tag{20}$$
$$\textbf{II} \qquad\qquad\qquad \textbf{X-2K}$$
$$\xrightarrow{HCl} O_2NHNCH_2NHNO_2$$
$$\textbf{X}$$

An increase in the formaldehyde mole fraction up to 2 relative to dinitrourea **II** leads to a series of compounds, depending on the conditions.

For instance, the extraction from an aqueous medium at 0 °C gave mixed hydroxymethyl derivatives of nitramide-hydroxymethylnitramine and dihydroxymethylnitramine (**XI**) [19]. These products are likely formed during hydrolysis of unstable *N*-hydroxymethyl-*N,N'*-dinitrourea and *N,N'*-dihydroxymethyl-*N,N'*-dinitrourea.

Besides the hydroxymethyl derivatives of nitramide, 3,7-dinitro-1,5-dioxa-3,7-diazacyclooctane (**XII**) (dioxyoctogen) and polymethylene polynitramine (**XIII**) were isolated [19]. Nitramine **XIII** corresponds to the previously reported

$$\tag{21}$$
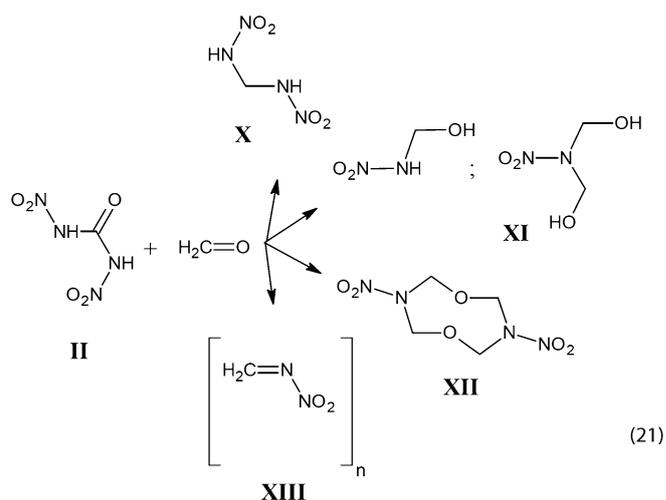
methylenenitrimine, $CH_2=NNO_2$ [20], and is also similar to the pentamer [21].

$$H{-}\left[\,\underset{NO_2}{N}{-}CH_2\,\right]_5{-}OH \tag{22}$$

Dinitrourea **II** in water in the presence of excess formaldehyde (over 4 mol) decomposes to form dihydroxymethylnitramine (**XI**) [19]. On the basis of this reaction a technique was developed for producing the diol **XI** directly from urea in 56–60% yield [19].

Either in nitric acid or in its mixture with sulfuric acid, dinitrourea enters into reaction with the moieties of the urotropine nitrolysis to afford 1,3,5-trinitro-1,3,5-triazacyclohexane-2-one (**XIV**) [19].

$$\tag{23}$$

IIe　　　　　　　　**XIV** (93%)
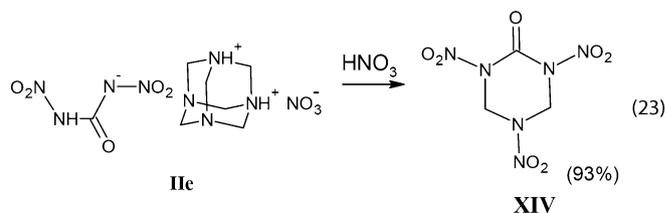
Compound **XIV** [22–24], a powerful explosive, is stable under normal conditions but decomposes to 1,3,5-trinitro-1,3,5-triazapentane (**XV**) in dioxane [8] and to methylene dinitramine salts in an aqueous medium [25–26] upon contact with moisture, amines, bases, alkalis, metals, etc. Thermolysis of **XIV** in DMF leads to polymethylene polynitramine (**XIII**) [26].

Compound **XV** can be obtained by nitrolysis of dinitropentamethylene tetramine (**XVI**) with mixed sulfuric-nitric acids in the presence of dinitrourea **II** [19].

The synthesis of diol **XI** from compound **II** made it possible to develop an accessible method to prepare **XVI** [19, 27, 28].

NaOMe
MeOH
Dioxane

XV

KOH

X-2K (24)

XIV
(K-6)

XIII

II **XVI** HNO$_3$/H$_2$SO$_4$ **XV** (60%) (25)

II + H$_2$C=O NH$_3$ **XVI** (60%) (26)

H$_2$SO$_4$/HNO$_3$ **II** CH$_2$O **XI** (27)

SOCl$_2$ Ac$_2$O

XIX NaN$_3$ **XVIII** HCl AcO **XVII**
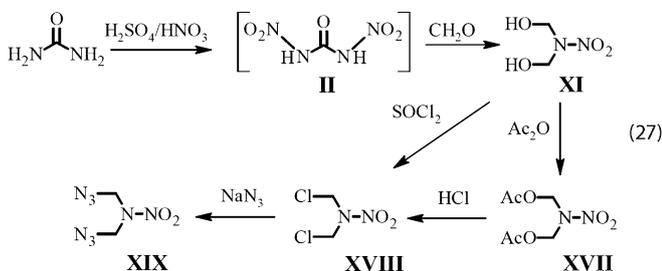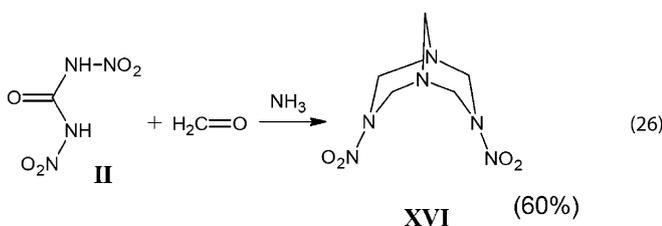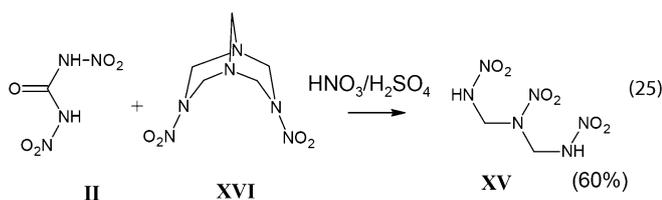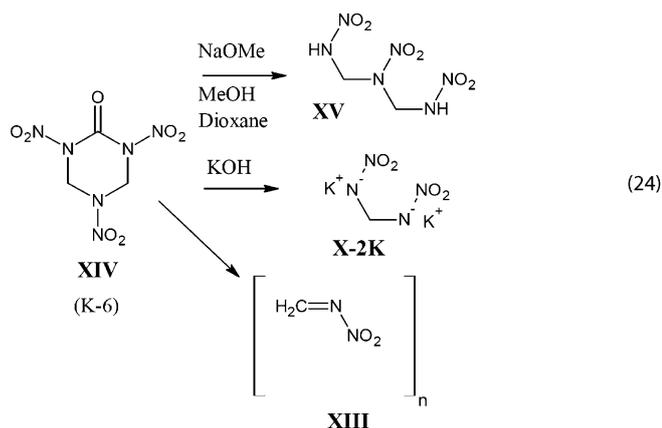
Diol **XI** also plays an important role in the synthesis of other high-energy compounds, for example, DANP (**XIX**) [29].

As a consequence of the studies, a selective method has been developed to synthesize 1,3-diazido-2-nitro-2-azapropane from urea by nitration of urea to N,N′-dinitrourea that is subsequently transformed into the desired product. The preparation of 1,3-dichloro-2-nitro-2-azapropane was shown to be possible via two methods: acylation of 1,3-di-hydroxy-2-nitro-2-azapropane and further treatment either with hydrogen chloride or with thionyl chloride. The total yields of the products were 11 and 20 %, respectively.

Dinitrourea **II** dissolution in aqueous glyoxal at a temperature below 40 °C leads to 1,3-dinitro-1,3-diaza-4,5-dihydrox-ycyclopentane-2-one (**XX**) [30]. The use of trifluoroacetic acid as the medium for this reaction contributed to an increase in the yield of compound **XX** up to 96 % [31].

II + **XX** (28)
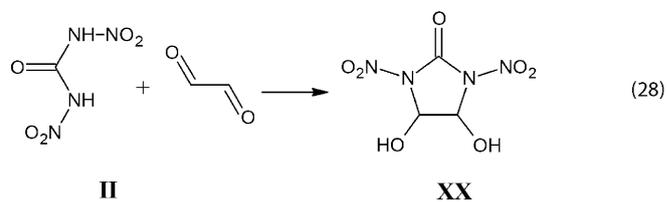
The given reaction can be regarded as promising for the synthesis of polycyclic nitramines.

4.4 Hydrolysis

A stoichiometric amount of water decomposes dinitrourea to nitramide (**XXI**) in almost quantitative yield [6].

$$O_2NHNCONHNO_2 \xrightarrow{H_2O} 2NH_2NO_2 \quad 100\% \quad (29)$$
II $\qquad\qquad$ **XXI**

This reaction is of importance since nitramide is a "building material" in the synthesis of other high-energy compounds [32]. An excess of water makes the isolation of ni-tramide (**XXI**) impossible.

Under laboratory conditions nitramide (**XXI**) is produced from dinitrourea **II** and its salts by hydrolysis in organic solvents of low dielectric permeability [6].

5 Spectral Characterizations

5.1 UV and IR Spectroscopy

According to the UV spectra of dinitrourea **II** and its salts **II-K** and **II-2K** in an aqueous solution, the dinitrourea anion exhibits absorption at 272–275 nm [2,33,34]. In low-polar organic solvents (dichloromethane, 1,2-dichloroethane, di-oxane, etc.), the dinitrourea **II** anion is not detected [33].

The functional groups present in dinitrourea **II** were shown by IR spectroscopy to be associated [33,34]. The IR spectrum of an acetone solution of dinitrourea **II** shows high-frequency stretching vibrations both for the C=O group (1780 cm^{-1}) and for the NO$_2$ group (1620–1610 cm^{-1}).

The recording of IR spectra of the dinitrourea **II** sample in low-polar organic solvents (dichloromethane, 1,2-di-chloroethane) revealed that the N–H group proton is associated (3300 cm^{-1}) with the C=O group because a displacement is observed of the carbonyl vibrational band to 1760 cm^{-1} [33].

The IR spectra of dinitrourea **II** [2,33] recorded in KBr are characterized by a low-frequency stretching vibration (3200, 3180 cm^{-1}) of the N—H bond participating in hydrogen bonding with the nitro and carbonyl groups (marked decrease in vibrational frequencies of the carbonyl and nitro group by 25–30 cm^{-1} and 10 cm^{-1}, respectively). The stretching vibrational frequency is 1760 cm^{-1} for C=O and 1620–1600 cm^{-1} for the nitro group.

According to data from reference [10] the vibrational frequency for C=O is 1684 cm^{-1} and that for the nitro group are 1544, 1419, and 1224 cm^{-1}, which does not correspond to the reported IR spectrum [2]. It can be attributed to the possibility that the isolated compound is another compound or a mistake made by the experimenter, who recorded the IR spectrum; more specifically, it may be attributed to the making of a KBr tablet. For spectroscopists, this is a well-known fact: the cation exchange reaction with KBr. In our case, it is quite possible that dinitrourea, as a stronger acid, formed HBr from KBr, forming a mixture with salts **II-K** and **II-2K**.

The IR spectrum of the crystalline potassium salt **II-K** (in KBr) [33] indicates that the nitramine group, which is not involved in salification, has the true structure of nitramine (doublet: 1620, 1600 cm^{-1}), and the proton participates in either intermolecular or intramolecular hydrogen bonding with oxygen atoms of the nitro and carbonyl groups as the proton's vibrational frequency decreases to 3180, 3220 cm^{-1}. A strong band (doublet) is observed at 1418, 1422 cm^{-1} known in the literature as N=N→O(OK) for primary nitramines [35,36]. The C=O group's vibrational frequency decreasing from 1760–1730 cm^{-1} to 1700 cm^{-1} is evidently attributed to the interaction of the carbonyl oxygen atom with both the proton and the potassium ion of the neighboring molecule.

The IR spectrum of the dipotassium salt of dinitrourea **II-2K** (in KBr) [13] differs from both the IR spectrum of dinitrourea and that of the dinitrourea monopotasium salt. The difference lies, first, in lacking any band within the region of 3600–3000 cm^{-1} (N—H group and hydroxonium ion) and within the region of 1530–1620 cm^{-1} (asymmetric vibrational frequencies of the nitro group) and, second, in the observed vibrational frequencies for both nitro groups in the aci-form N=N→O(OK) (1390, 1380, and 1210 cm^{-1}).

In addition, the substitution of potassium for the proton on the amine nitrogen atom decreases the C=O group vibrational frequency from 1700 to 1660 cm^{-1}, which indicates an interaction between the carbonyl oxygen atom and potassium ions.

The IR spectrum of the diammonium salt **II-2NH$_4$** as well as that of the dipotassium salt **II-2K** is marked by decreased vibrational frequencies for C=O, 1640 cm^{-1}, and for NO$_2$ (v_s, v_{as}), 1400 and 1208 cm^{-1} [1].

5.2 NMR Spectroscopy

Chemical shifts (δ) in the ^{1}H, ^{13}C, and ^{14}N NMR spectra of dinitrourea **II** and its salts are given in references [10,12,14,33]:

^{1}H NMR (DMSO-d_6): $\delta = 8.05$ (s, 2H). ^{13}C NMR (DMSO-d_6): $\delta = 149.2$ [10];

^{1}H NMR (CD$_3$CN): $\delta = 11.48$ (br. s, 2H). ^{13}C NMR (CD$_3$CN): $\delta = 142.3$ [12];

^{1}H NMR (CD$_3$CN): $\delta = 11.48$ (br. s, 2H). ^{13}C NMR (CD$_3$CN): $\delta = 142.3$ [14];

^{14}N NMR (DMSO-d_6): $\delta = 223.0$ (N—NO$_2$); $\delta = 352.4$ (N—NO$_2$) [33].

5.3 Mass Spectrometry

The mass spectrum (MS-EI) of dinitrourea **II** contains a molecular ion peak 150 [M$^+$, 0.1] and constituent moieties such as 107 (0.2), 89 (0.4), 62 (3.2), 46 (100) [12]; *m/z*: 18, 28, 30, 32, 42, 43, 44, 46 and 62 [10].

5.4 X-ray Structure Analysis

With X-ray structure analysis, molecular structures of dinitrourea **II** [12] and its salts were determined: **II-K** [33,34], **II-2K** [33,34], **IIh** [12], and **II-2t** [14].

As ascertained by XSA, single crystal diffraction for dinitrourea **II**: prismatic; space group *Fdd2*, $a = 1.20015(9)$, $b = 1.76425(13)$, $c = 0.45555(4)$ nm, $V = 0.964565(4)$ nm^3, $\beta = 1341.44(4)°$, [CH$_2$N$_4$O$_5$] $M = 150.07$, $Z = 8$, $T = 90(2)$ K; $\rho_{calc} = 2.067$ g cm^{-3}, $\mu = 0.210$ mm^{-1}.

Crystallographic data for compound **II-K**: monoclinic crystal system, space group *Cc*, $a = 1.3839(1)$, $b = 0.60882(4)$, $c = 0.97264(8)$ nm, $\beta = 1341.44(4)°$, $V = 0.58806(8)$ nm^3, [CHN$_4$O$_5$]$^-$K$^+$, $M = 188.16$, $Z = 4$, $\rho_{calc} = 2.125$ g cm^{-3}, $\mu = 0.886$ mm^{-1}.

Crystallographic data for compound **II-2K**: monoclinic crystal system, space group *P2$_1$/n*, $a = 0.68308(4)$, $b = 0.73295(7)$, $c = 1.35064(9)$ nm, $\beta = 99.079(8)°$, $V = 0.66774(9)$ nm^3, [CN$_4$O$_5$]$^{2-}$ 2[K$^+$], $M = 226.25$, $Z = 4$, $\rho_{calc} = 2.251$ g cm^{-3}, $\mu = 1.409$ mm^{-1}.

Crystallographic data for compound **IIh**: monoclinic crystal system, space group *P2$_1$/n*, $a = 0.76156(3)$, $b = 0.49837(2)$, $c = 1.03119(4)$ nm, $\beta = 95.530(1)°$, $V = 0.38955(3)$ nm^3, [CHN$_4$O$_5$]$^-$ [C$_2$H$_4$N$_3$]$^+$, $M = 219.14$, $Z = 2$, $T = 90(2)$ K, $\rho_{calc} = 1.868$ g cm^{-3}, $\mu = 0.173$ mm^{-1}.

Crystallographic data for compound **II-2t**: triclinic crystal system, space group *P$\bar{1}$*, $a = 0.72721(2)$, $b = 0.84244(2)$, $c = 1.18190(2)$ nm, $\beta = 80.918(1)°$, $V = 0.71224(3)$ nm^3, [CHN$_4$O$_5$]$^-$ [C$_2$H$_4$N$_3$]$^+$, $M = 219.14$, $Z = 2$, $T = 90(2)$ K, $\rho_{calc} = 1.615$ g cm^{-3}, $\mu = 1.236$ mm^{-1}.

6 Physicochemical Properties

N,N′-Dinitrourea recrystallized from mixed ethyl acetate/1,2-dichloroethane has melting points with decomposition of 101–104 °C in capillary and 107–110 °C on a Boetius heating plate [2]. DSC and TGA studies (using Mettler Toledo instruments) [10] showed that at a heating rate of 10 °C min^{-1} dinitrourea **II** is thermally stable up to 80 °C, while at a higher heating rate there is observed mass loss (sharp, in the range from 110 to 120 °C). The thermogram showed that an intensive decomposition of sample 2 occurs at 147–149 °C [1].

The density of dinitrourea **II** is 1.98 g cm^{-3} (floatation method) [2], (helium pycnometer) [10], 2.067 g cm^{-3} (X-ray at 90 K) [12], and 2.33 g cm^{-3} (PM3/VSTO-3G computed molecular density) [37].

Dinitrourea **II** is easily dissolved in water [1,2,12], acetonitrile, alcohols, ether, ethyl acetate, cyclohexanone, THF, DMSO, nitric acid, dichloromethane [12], chloroform [12], and is difficulty soluble [2] in dichloroethane and sulfuric acid; it is insoluble in hexane, dichloromethane, chloroform, and carbon tetrachloride [2].

Dinitrourea salts **II-K**, **II-Na**, and **II-Cs** are poorly soluble in water; **II-2K**, **II-2Na**, **II-2Cs**, **II-NH$_4$**, and **II-2NH$_4$** are water-soluble and insoluble in organic solvents [13].

The anionic complex salts of dinitrourea **II-K,Cu**, **II-K,Cu,NH$_3$**, and **II-K,Cu,urea** are poorly soluble in water and organic solvents, except for DMSO and DMF [13].

The dinitrourea salts are more thermally stable [1,12,13] than dinitrourea **II** itself [38].

The acid and normal salts of dinitrourea **II**, depending on the cation, have different detonation velocities and can be classified into very sensitive and low sensitive explosives with respect to mechanical impacts [12,16].

Dinitrourea **II** salts are specifically attractive as ingredients of high-performance gas generating compositions since thermodynamic calculations show that they decompose to low enthalpy compounds releasing large volumes of gas [39]. Moreover, owing to the low sensitivity to mechanical impacts, they represent a potential alternative to expensive dinitramide salts [14].

7 Conclusions

The DNU synthesis and reactivity is an important research area in terms of developing high-energy compounds. The high reactivity of dinitrourea is concurrently its virtue and drawback. The purposeful activation of reaction sites of the dinitrourea molecule has a great effect on the reaction outcome. For instance, conditions that exclude nucleophilic attack allow construction of reaction products with preserved dinitrourea moiety. Conversely, highly polar media dramatically influence the chemical stability of the dinitrourea structure but favorably contribute to nucleophilic substitution reactions. When affected by an equimolar amount of water in an organic solvent, dinitrourea is decomposed into nitramide, which is a key building block for all known nitramines and nitramides. The technique elaborated for producing nitramide from dinitrourea in high yield holds hope for further progress in the synthesis of promising and novel high-energy compounds [7, 8, 27, 29, 40]. Furthermore, the great variety and availability of nitramides and nitramines producible from dinitrourea creates incentives for exploratory research to reveal new fields of their application.

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