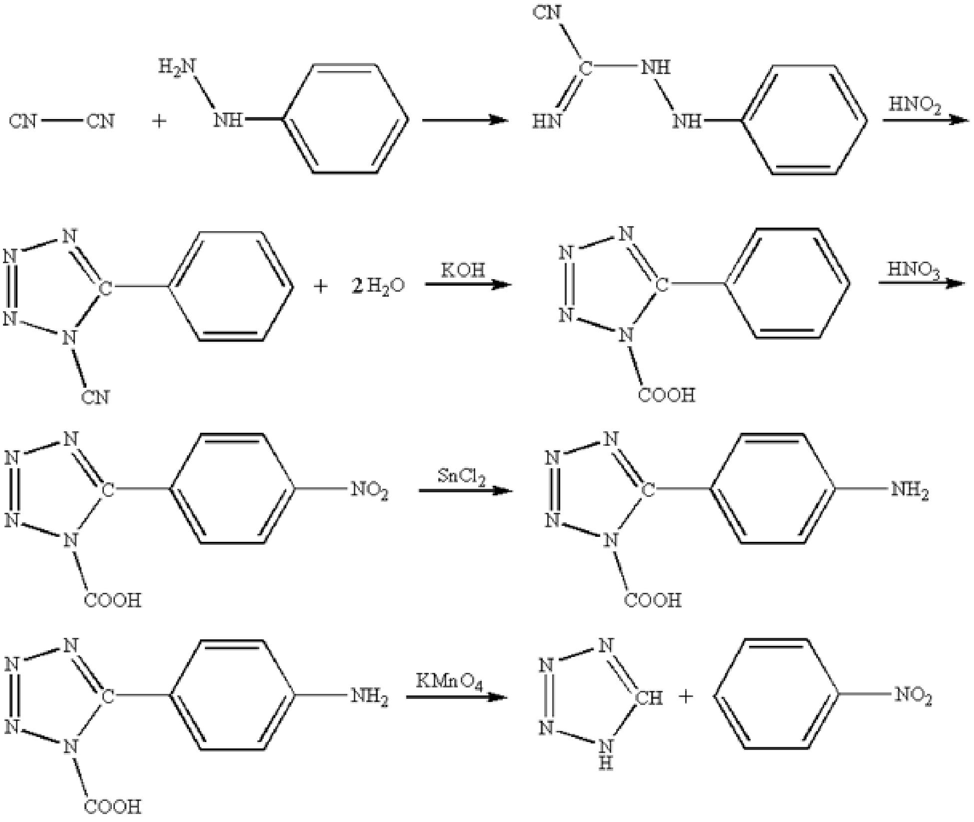
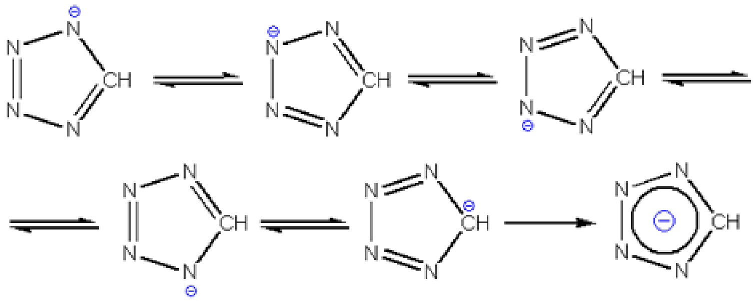
Introduction

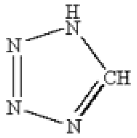
Recently in publications devoted to high-energy substances, considerable interest in tetrazole derivatives has arisen, this is partially the result of them being able to be tailored to be primary explosives with unique properties. The tetrazole heterocycle was first discovered in 1885 by Bladin in Upsal University upon formation of dycyandimethylhydrazine - a product of reaction dicyan with phenylhydrazine [1]. Treatment of dicyanphenylhydrazine with nitrous acid, has led to a substance, which was leter shown to be 5-cyano-2-phenyltetrazole (dicyanphenylhydrazine and its nitrosation product have been prepared before by E.Fisher who however has not undertaken attempts to identify it). Explaination of this reaction have only become possible after establishment of the structure of dicyanphenylhydrazine. Bladin has convincingly proved presence of the tetrazole ring by transformation of cyanophenyltetrazole back into the initial substance:

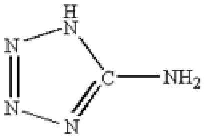


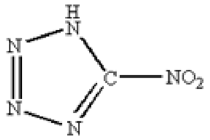
During the preparation of free tetrazole from its derivatives, the heterocyclic ring containing 4 atoms of nitrogen and one of carbon displayed remarkable stability in the presence of acid, alkalis, oxidizing agents and reducing agents, as these were used in this process of forming free tetrazole. The tetrazole ring is thermodynamically stable, as it is recovered unchanged after long periods of boiling and heating. Upon elimination of a proton from the NH group of tetrazole, highly aromatic (A=98) tetrazolate anion is formed. The tetrazolate ion is isoelectronic with the familiar cyclopentadienyl anion.



As a result of the flat structure of the tetrazole ring, along with its high nitrogen content, tetrazole compounds can be of high density releasing plenty of energy and gasses upon decomposition/explosion. This leads to the superior explosive properties in many tetrazole derivatives. Physical and explosive properties of tetrazole derivatives are rather easily modified by replacement of substituents on the tetrazole ring with various functional groups. The combination of interesting energetic properties and unusual chemical structure and draws numerous researchers to this unique class of compounds.


1H-Tetrazole


5-Aminotetrazole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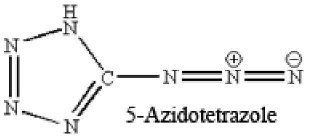
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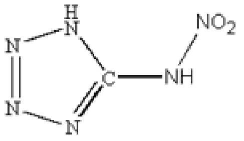
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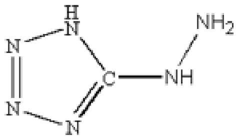
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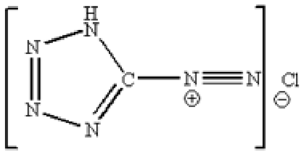
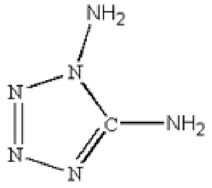

Tetrazolediazonium chloride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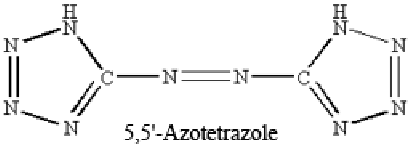
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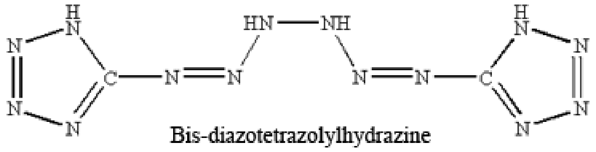
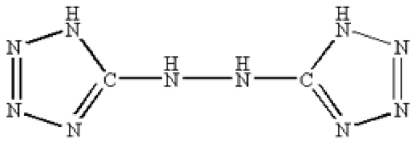
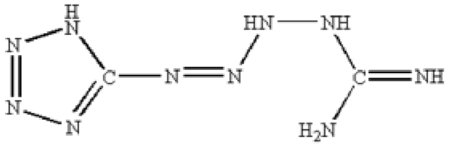
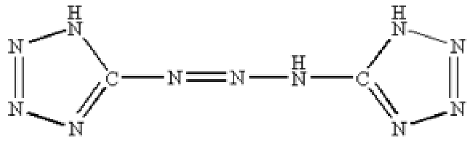

Bis-diazotetrazolylhydrazine


5,5'-Bis-tetrazolylhydrazine


Tetrazene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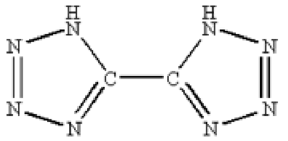
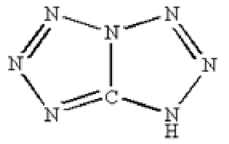

Bis-tetrazole

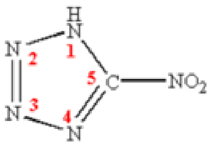

1H-Tetrazolo[1,5-d]tetrazole

Many tetrazole based explosives can employed as primary explosives, sensitizers or components of electric igniters. The most widespread derivative in use is 5-aminotetrazole which is more easy to produce than unsubstituted tetrazole, and is often used as a starting material for the synthesis of other tetrazole derivatives. Oxidation of amino groups in 5-aminotetrazole leads to 5,5 '-azotetrazoles which can be applied as primary explosives or as components of electric igniter mixtures. Condensation of 5-aminotetrazole ring with aminoguanidine results in the known sensitizer tetracene, widely used in initiating mixtures. Diazotization of the amino group in 5-aminotetrazole results in the formation of highly reactive(and explosive) tetrazole-diazonium salts, which are the starting product for many interesting tetrazole derivatives. Condensation of the diazonium salt of tetrazole with 5-aminotetrazole results in salts of diazoaminotetrazole; some have been suggested for use in primary explosive mixtures and compositions for electric igniters. Substitution of the diazo group to the nitro group by the Sandmeyer Reaction results in 5-nitrotetrazole; the basis of the newest class of highly effective primary explosives. Some tetrazole derivatives maintain record values of nitrogen content, for example action of hydrazine chloride on diazotetrazole leads to formation of 5,5'-bis-diazotetrazolehydrazide, containing about 90 mass % of nitrogen, and the action of nitrous acid on 5-tetrazylhydrazine leads to the formation of 5-tetrazylazide, which is one of the richest on nitrogen from all known compounds. Tetrazylazide forms numerous salts, many possessing powerful initiating abilities, and incredible brisance, but are extremely sensitive to external influences. Some researchers have reported that the sensitivity of the tetrazylazides can be reduced in organic derivatives.

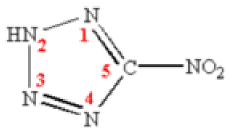
In the subsequent sections these substances and their derivatives will be considered in more detail. At once it would be desirable to note that despite of significant theoretical and practical interest many of these substances, they are investigated badly enough and frequently the trustworthy information about them has only the general character. It is necessary to remember that the highly energetic derivatives of tetrazole always represent some extent of danger, and to work with them demands extensive care and accuracy, as well as knowledge in the field of organic chemistry and experience in working with sensitive explosive materials. The purpose of the given manual is only to supply the beginner researcher with the known facts and to combine the accessible information. Working with these substances you always have to go inside an area of organic chemistry and of explosives which to some extent is novel and has not been completely thoroughly studied. Your actions should be guided by your logic combined with knowledge and experience in similar areas. The authors reserve the rights to not carry the responsibility for any possible negative consequences of practical use of the given materials.

General properties of tetrazoles [2]

Tetrazoles are characterized by five atom ring with two unsaturated bonds, consisting of 4 atoms of nitrogen and 1 atom of carbon. Numbering of the atoms starts from the nitrogen next to the carbon, it has first number, next nitrogen is second, and so on. Tetrazole cycle exists in two tautomeric forms, differing by position of hydrogen atom, to identify one of the isomers isomers, the name of the tetrazole derivative is supplied with acid hydrogen atom position.



5-Nitro-1-H-tetrazole



5-Nitro-2-H-tetrazole

On the basis of the tautomeric formulae shown for 5-monosubstituted tetrazoles (where R is any substituent) there are three classes of monosubstituted and two classes of disubstituted deriva¬tives (where the H is replaced). Also, there are fused ring tetrazoles of the 1,5-disubstituted class. In addition, there are salts and substituted derivatives which have 2,3-, 1,4- and 1,2-substituents. However, compounds of ordinary interest are usually 1,5-, 2,5-or 1,3-substituted. Bis explosive compounds may be connected at the 5,5'-positions. Bis explosive salts may be connected at either the 1,1'- or the 5,5'-position with the metallic anion.

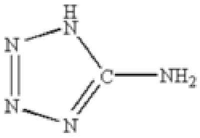
The majority of tetrazoles are crystaline solids. There is considerable variation in thermal stabil¬ity, viz, derivatives which melt above 150°C do so with decomposition, while 5-guanylaminotetrazole does not melt at 300°C. In general, most of the tetrazoles are acids and often yield explosive salts. Tetrazoles are generally soluble in polar solvents, and insoluble in non polar solvents, 1-H tetrazole has good solubility in water. Unsubstituted tetrazole and C-substituted 1-H tetrazoles show amphoteric properties, they are weak NH-acids (for 1-H tetrazole pKa = 2,68) and readily form salts with alkaline and alkali-earth metals, being a weak organic bases tetrazoles form salts with strong mineral acids. With ions of transition metals tetrazoles often form coordination complex compounds through N-2 atom, generally acting as monodentante ligands. Tetrazole and it’s derivatives enter electophilic and nucleophilic substitution reactions generaly on the 5 ring position. Salts of C-substituted 1-H tetrazoles upon alkylation by alkylhalogenides, esters of sulphuric acid or organic acids, or diazomethane, produce mixtures of 1,5- and 2,5- substituted products, because of ambidentate nature of tetrazolate anion. Disubstituted tetrazoles on further alkylation form tertiary salts on N-4 atoms. Thermal destruction of tetrazole cycle usually take place at 150-200°C. The tetrazole ring can also be broken by action of strong acid while heating to 160°C, or by the action of strong aqueous solutions of bases, C-subtituted 1-H tetrazoles are generaly stable at this conditions. It is stable to strong oxidizers, but powerful reducers such as lithium-aluminium hydride (LiAlH4) upon reaction with 1,5-disubsitituted 1-H tetrazoles, causes the ring to rupture forming secondary amines with release of hydrogen azide. The tetrazoles, in general, can be looked upon as gas generators, useful where instantaneous or progressive pres¬sure effects are required. They possess moderate brisance. However, their salts, which may de¬tonate with extreme brisance, can be used as primary explosives, as can 1- and 2-Methyl-5-nitro tetrazoles or other 5-nitrotetrazole derivatives, or tetrazylazide derivatives.

Systematization of data on about twelve 5-substituted tetrazoles allowed Bates and Jenking to make the conclusion that explosive properties of tetrazole are closely related to their structure. Bates and Jenkins have suggested that the ranking in explosive behavior of 5-substituted tetrazoles could be related to the substituent's electron withdrawing power: the more electron withdrawing, the more explosive is corresponding compound. The ranking observed for the substituent in the 5 position ranged from mild ignitions for 5-methyl tetrazole to instability in the following order: CH3 = C6H5 (mild ignitions) < NH2 < H< NHNO2 (componds exploded) < bistetrazole < 5,5'-azoditetrazole (do not detonate RDX), < Cl < NO2 (very powerful expls) < N3 (very sensitive) < N2+ (unstable). The salts of 5-substituted tetrazoles could also be ranked according to their sensitiveness. The salts of Ag, Hg, and Pb gave more sensitive compounds and greater initiating power than the alkali metal salts. The same salts of 5-chlorotetrazole were too sensitive and corrosive, and those of 5-azidotetrazole were too sensitive for handling.

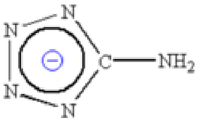
References:

1. R.C. Elderfield “Heterocyclic Compounds” Volume 8, New York, 1961, pp 8-11
2. Basil T. Fedoroff & Oliver E. Sheffield “Encyclopedia of explosives and related items” Volume 9, T111-T112 .

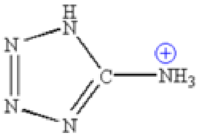
5-Aminotetrazole and derivatives



5-Aminotetrazole



5-Aminotetrazolate anion



5-Aminotetrazolate cation

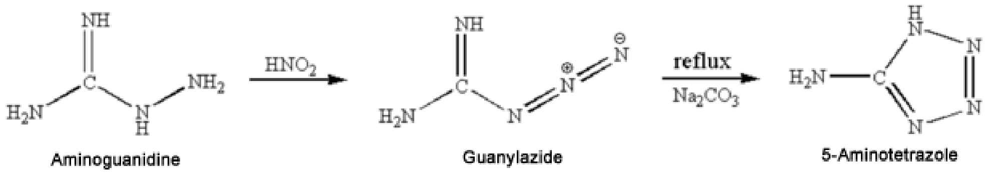
5-Aminotetrazole was first prepared by Thiele, by diazotation of aminoguanidine with sodium nitrite in hydrochloric acid environment. 5-Aminotetrazole crystallizes from water solution in the form of the monohydrate, which are colorless prisms or leaflets, losing water above 100°C and melting with decomposition at 200-203°C. 5-Aminotetrazole is badly soluble in alcohol and more readily in ether. It is also soluble in water solutions of bases and strong acids, and has good solubility in hot and poor solubility in cold water. 5-aminotetrazole's heat of combustion is 246.2 kcal/mol, standard enthalpy of formation is -49.7 kcal/mol. 5-Aminotetrazole shows weak acid properties, and in the anhydrous state is extremely hygroscopic. It is stable to heat, and its dissociation constant is about 1*10-4. Besides its acid properties, upon reaction with strong mineral acids 5-aminotetrazole can act as base, as can many organic amines. In general 5-aminotetrazole acts as an amphoteric substance, with behavior similar to that of amino acids. [3,4]

5-Aminotetrazole draws itself attention as high nitrogen substance for its use as components of rocket propellants, explosive mixtures and as starting material for synthesis of other tetrazole derivatives. The high chemical stability of the tetrazole ring in addition to fact that substituents on the tetrazole ring are usually entered during ring formation, leaves the amino group as the only reasonable target for chemical manipulations. The amino group of 5-aminotetrazole has all the common properties of that functional group, and can be related in chemical behavior to the amino group of aniline.

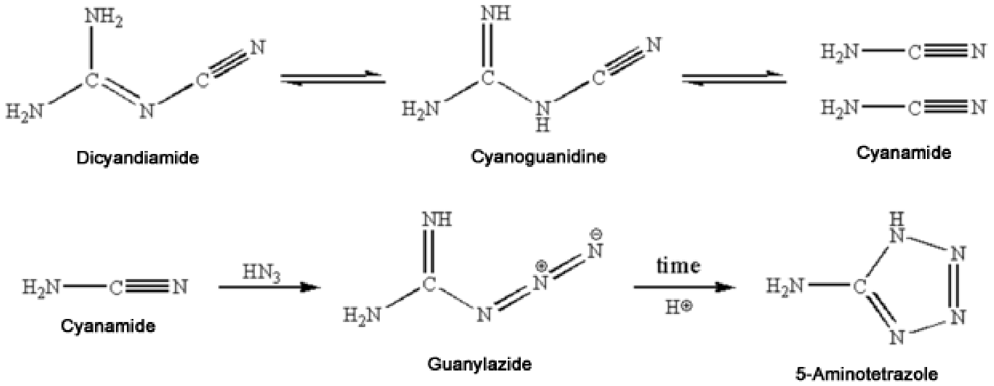
5-Aminotetrazole forms salts with metallic cations, some of them are explosive. The cobalt salt Co(CN5H2)2∗XH2O, exists as pink water soluble crystals which explode upon heating to 228°C. The nickel salt Ni(CN5H2)2∗H2O exists as blue water soluble crystals which explode upon heating at 290°C. The lead salt Pb(CN5H2)2 , exists as colorless crystals which deflagrate upon heating to 303°C. The mercury salt Hg(CN5H2)2 exists as white water insoluble crystals, they explode when dropped on a hot plate heated to 256°C. The Hg salt's shock sensitivity in the lead weight test is 50% explosions using a 2.5 kg weight and 38 cm drop height. The copper salt Cu(CN5H2)2∗H2O exists as green very slightly water soluble crystals. A 2.5 kg weight with an drop height of 68 cm gives 50% of explosions when the copper salt is tested and it deflagrates when heated to 164°C. Aminotetrazole in the presence of copper sulfate and sodium acetate produces a green amorphous precipitate, which can be used as a diagnostic test for aminotetrazole. This precipitate is insoluble in acetic acid, and is soluble in hydrochloric acid. [3,4]

Treatment of 5-aminotetrazole with sodium nitrite in hydrochloric acid was attempted by Thiele. It resulted in formation of compound which was not identified because it exploded in solution at 0°C. Later it was shown, than this reaction results in formation of extremely unstable and sensitive diazotetrazole, which can spontaneously detonate in solution as weak as 1%.[1,2] However the formation of the diazonium compound is very useful in the synthesis of other 5-substituted tetrazoles, such as the nitro, bu the Sandmeyer Reaction. 5-aminotetrazole is not explosive by itself, its use is as a starting product for synthesis of many explosive derivatives such as 5,5’-azotetrazole, 5-nitrotetrazole, bis-diazotetrazylhydrazine, 5-nitraminotetrazole, 5-chlorotetrazole, and others. The high safety and stability of 5-aminotetrazole allows its preparation on any desired quantity; in the lab or mass industrial production. When not being used for the synthesis of other tetrazoles, this high nitrogen compound fins use as cooling agent in rocket propellants, where it produces almost smokeless burning without any impairment of ballistic potential.

There are many different ways to produce 5-aminotetrazole, although among them there are only two methods of practical interest. By the Thiele method 5-aminotetrazole is produced by the action of nitrous acid on aminoguanidine nitrate. Later Ganch showed doubt of Thiele's views and proved that the product of this reaction is guanylazide, which on boiling in presence of a base cyclizes to 5-aminotetrazole[2]:



The cyclization of guanylazide is also catalyzed by acid. Ganch and Fort showed that boiling of guanylazide nitrate in water for 2 hours also results in formation of 5-aminotetrazole, without release of hydrogen azide. Later Shtolle and Shick are succeeded in the synthesis of 5-aminotetrazole by action of hydrogen azide on dicyandiamide (cyanoguanidine). A detailed look at the reaction mechanism has revealed that dicyandiamide first forms 2 molecules of cyanamide, which react with hydrogen azide forming guanylazide, which is later cyclized to 5-aminotetrazole. Reaction with free cyanamide proceeds in the same way[2]:



Both methods give good results, but also have advantages against each other. Advantage of Thiele method is speed and safety – whole process takes time about several hours, but yield is 75%(I got 82% yield, and microtek has cited 99% yield). Shtolle method has the advantage of higher overall yield and slightly better product quality, but is very time consuming (process takes time about several weeks) and forces working with dangerous, highly toxic, and explosive hydrogen azide. Both methods yield 5-aminotetrazole pure enough for any potential use. Synthesis with both methods are shown bellow:

Thiele method[1]. 34g (0.25 mol) of aminoguanidine bicarbonate is added to 217 ml of 15% nitric acid (0.561 mol), and mixed until evolution of carbon dioxide is stopped and resulted aminoguanidine nitrate is fully dissolved in solution. Yellow transparent solution is diazotized by slow addition of 17.2g sodium nitrite (0.25 mol) in 35 ml of water. Addition is accompanied by stirring, and temperature buring all addition period is kept between 20-25°C by using water bath if needed (note #1). After completion of reaction the diazotation mixture is allowed to sit for 20 minutes at room temperature, and 29g of sodium carbonate is added (or 46g of sodium bicarbonate). Mixture is then heated on a waterbath and refluxed for 4 hours. The solution is then neutralized by 30% sulphuric acid to pH=4, cooled to room temperature and allowed to sit over night (note#2). The precipitated crystals of 5-aminotetrazole monohydrate are filtered, washed with cold water and dried. Yield is about 70-74% based on aminoguanidine.

Notes:

1. Diazotation proceeds smoothly with little exotherm. If reaction mixtures begins to foam (this is the result of decomposition of nitrous acid), mixture must be stirred until form is settled before adding new a portion of nitrite solution. If reaction is carried put in the right way, it takes time about 10-15 minutes and proceeds with negligible evolution of nitrogen oxides.

2. 5-Aminotetrazole has an affinity to form supersaturated solutions. Often it does not begin crystallization even after full cooling, in that case crystallization should be assisted by introduction of a seed crystal, or by rigorous friction of a glass rod on side wall of reaction vessel (below liquid). Crystallization is generally fully complete after 12 hours from start.

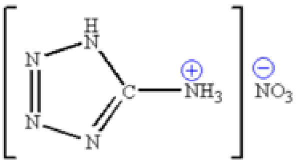
Schtolle method[2]: 84g (1 mol) of dicyandiamide and 130g (2 mol) of sodium azide are dissolved in 1 liter of water at 50°C, then 172 ml of 36% hydrochloric acid is added slowly with shaking in small portions (note #1). Mixture is allowed to sit for 4-5 days, precipitated 5-aminotetrazole monohydrate is filtered off, washed with cold water and dried. Yield can be up to 97% (note №2).

Notes:

1. Reaction proceeds with release of highly volatile and highly toxic hydrogen azide, which causes severe headaches and decomposition erythrocytes in the bloodstreamI inhalation of fumes in high concentration can cause death because of paralysis of breath center. Work should be carried out in an efficient hood or outdoors. Drying wet product must also be done with efficient ventilation as a result of residual hydrogen azide.

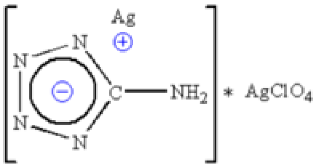
2. After noted time crystallization may not start (see note#2 in Thiele method). Product yield strongly depends on sitting time, literature sources show that it can reach 97% of theory upon very long standing, however after 5 days the yield is only about 65% of theoretical. Yield is also dependant on minimizing evaporation of hydrogen azide, so for maximum yields it is beneficial to carry out the reaction in a sealed vessel to minimize evaporation.

Additional information



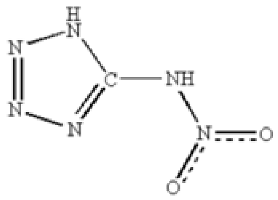
5-Aminotetrazole nitrate

1. 5-Aminotetrazole nitrate[3]. Compound is a simple salt of 5-aminotetrazole, which forms a cation through the aminogroup, in analogous manner to ammonia forming ammonium salts. It is a colorless crystalline substance which melts with explosion at 174°C. Heat of combustion is measured at 224.1 kCal/mol. Solutions of 5-aminotetrazole nitrate show acidic pH as a result of hydrolysis and the compound decomposes in base environment. It can be simply made by crystallization of a hot solution of 10g anhydrous 5-aminotetrazole in 16 ml concentrated niric acid and 15 ml of water[5]. Prolonged heating leads to decomposition. The crude product, wet with nitric acid is recrystallized from water, filtered and dried. Yield is about 15g of pure product (97%).

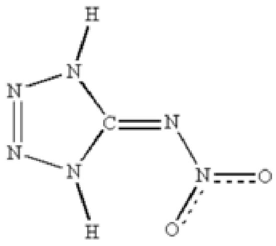


Silver 5-Aminotetrazoltato-perchlorate

2. Double salt of 5-aminotetrazole with silver perchlorate Ag(N4C)NH2*AgClO4. This compound has been proposed for use as thermally stable primary explosive[6]. Salt is powerfull enough to initiate TNT and hexanitrostilbene, and was shown to be thermally stable during heating for 50 hours at 260°C. It is easily ignited by an electic wire and it's preparation is given in patent US3663553: A solution of 8.2g 5-aminotetrazole in 184 ml of 70% perchloric acid is added with stirring to solution of 16.6g of silver perchlorate in 32 ml of water. Mixture is stirred for 30 minutes, 380 ml of water is added and stirring is continued for another 30 minutes. Precipitate is filtered off, washed with water, then isopropyl alcohol and dried at 150°C for 5 hours.



5-Nitraminotetrazole



5-Nitriminotetrazole

3. 5-Nitraminotetrazole H(CN4)NHNO2. Exists as colorless crystals, exploding with an orange flash when heated to 140°C. Heat of decomposition is 2.63 MJ/kg, and its standard heat of formation is -944 kJ/mol, calculated density and detonation velocity are 2.06 g/cm3 and 9130 m/sec respectively, however these values are probably overestimated[7]. It is extremely sensitive to shock and friction and has good solubility in water, ether and dioxane, poor solubility in benzene. Forms hydrates. Exists as a double basic acid, strong by first stage, dissociation constants pKa = 2.5 and 6.1 respectively. Initially it was thought that the acidic hydrogen atom was situated in the nitramine group, but now it is proved that acidic protons are situated on the tetrazole ring, and one of them forms an intramolecular hydrogen bond, so substance can be more correctly called 5-nitriminotetrazole. 5-Nitraminotetrazole forms stable salts, many of which are explosive. Potassium salt KCHN6O2 exists as almost colorless plates, exploding with aviolet flash when dropped on a hotplate heated to 220°C. The diammonium salt (NH4)2CN6O2 exists as short colorless needles with a melting point of 220°C. The silver salt AgCHN6O2 is an amorphous white powder, insoluble in water, deflagrates on heating.

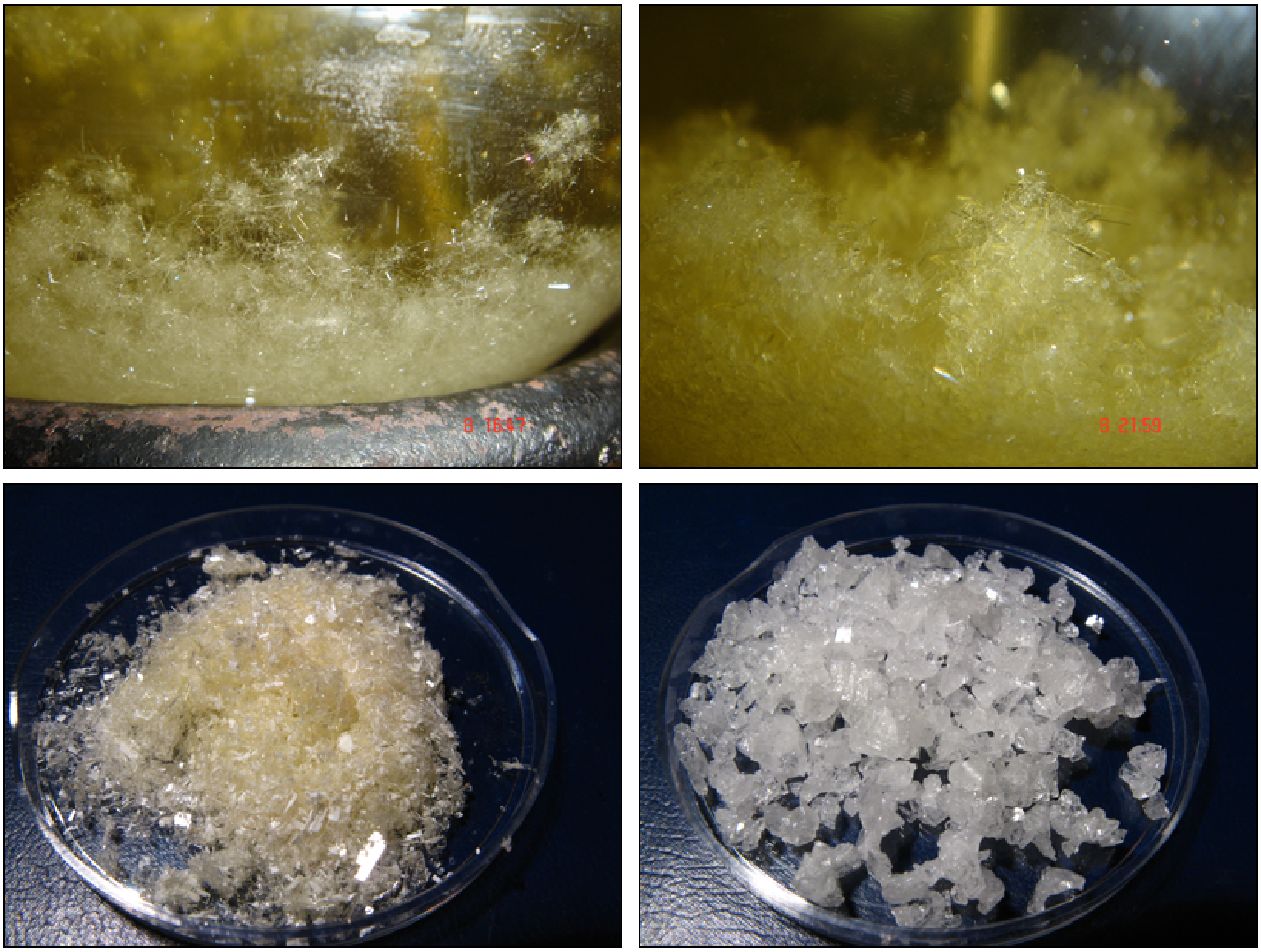
5-Nitraminotetrazole synthesis[5]: 14.8g of 5-aminotetrazole nitrate is with stirring and cooling, added to 20 ml of concentrated sulphuric acid. Mixture is allowed to sit at room temperature until it becomes homogeneous then 250 ml of ice and water is added and the whole mixture is then neutralized with barium carbonate. The mixture is heated on a water bath until carbon dioxide evolution stops and it is filtered to remove the insoluble barium sulphate precipitate. The precipitate is then washed with few portions of water, and combined filtrate is evaporated under reduced pressure to volume of about 100 ml. Product is extracted with 5 portions of 100 ml of ether and extract is evaporated almost to dryness and then 250 ml benzene is added. 5-Nitraminotetrazole precipitates as colorless plates, yield is about 57%.

Diammonium salt synthesis: 127.5g of 5-aminotetrazole monohydrate is added with stirring to 300 ml of concentrated sulphuric acid heated to 40°C, mixture is stirred until 5-aminotetrazole dissolves, and then cooled to 20°C. 120 ml of 90% nitric acid is added drop by drop with good stirring, keeping temperature in the 20-25C range by means of ice bath. When addition is finished the mixture is then taken out of the ice bath and allowed to sit for 15 minutes at room temperature after which it is and poured onto 3 kg of crushed ice, and neutralized by 25% ammonia solution to pH=5. Reaction mixture is allowed to sit for a night at 0-5°C during which time crystals of the diammonium salt precipitate. The 5-nitraminotetrazole is filtered and dried.

References:

1. P.F. Bubnov “Primary Explosives and Initiation Devices” part 1, Moscow, 1940, pp 309-311.
2. L.I. Bagal “Chemistry And Technology of Primary Explosives”, Moscow, 1975, pp 394-395.
3. Basil T. Fedoroff & Oliver E. Sheffield “Encyclopedia of explosives and related items” Volume 1, A258-A259.
4. Basil T. Fedoroff & Oliver E. Sheffield “Encyclopedia of explosives and related items” Volume 9, T116-T117.
5. Journal of Organic Chemistry, 18-8, pp 941 – 945 ; R.M.Herbst, J.A.Garrison “The Nitration Of 5-Aminotetrazole”.
6. US Patent №3663553, Disilver aminotetrazole perchlorate, patented 16 may 1972.
7. T.M.Klapotke “High Energy Density Materials”, Springer, pp 99-113.

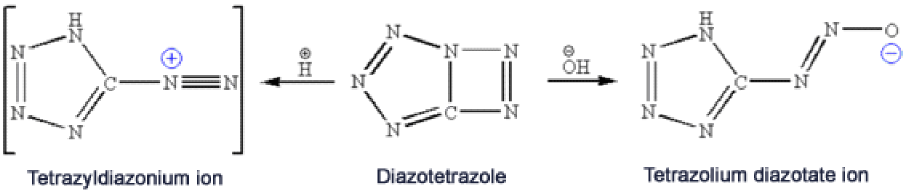
Some photos for this chapter



Description: Two photos at the top show, 5-aminotetrazole crystalls floating in mother liquer obtained by Thiele method, at lower left crystalls are dried on the air, lower right photo shows 5-ATZ obtained by Schtolle method.

Description: This two photos are small lustrous needle like crystalls of ammonium 5-nitraminotetrazole, made by nitration of 5-aminotetrazole with sulphuric/nitric acid mixture and allowing solution to sit for a night.

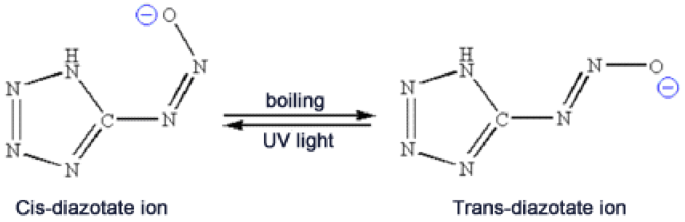
5-Diazotetrazole and derivatives



Diazotetrazole was first prepared by Thiele during the diazotation of 5-aminotetrazole with sodium nitrite in hydrochloric acid, but he failed to indentify reaction product, because at 0°C it exploded in solution. Later it was shown that the product of this reaction is the extremely unstable diazotetrazole. Diazotetrazole is an extremely sensitive and unstable explosive, 6-7% solutions can explode spontaneously even at 0°C, breaking the glassware used for the diazotation. In acidic environment diazotetrazole forms ions of tetrazolediazonum, which are combined with acid anion to form the diazonium salt. Tetrazole diazonium salt is also very unstable and its behavior resembles that of free diazotetrazole. In a basic environment diazotetrazole forms anions of tetrozoliumdiazotate, which are combined with base cations to form stable salts, readily soluble in water, and explosive in the dry state[1].

The extremely unstable nature if diazotetrazole and it's diazonium salts is almost unprecedented for known chemical compounds, it can explode even in 1% solutions. The most likely reason for this instability is the strong electron withdrawing effect of the diazogroup, which lowers the stability of tetrazole ring and lowers the activation energy for decomposition to a neglible level. Stability of tetrazoliumdiazotate salts can be explained by the electron saturation of diazogroup by hydroxide ions, oxygen atom on the end of a diazogroup lowers its electron withdrawing ability and stabilizes the tetrazole ring. Tetrazolediazotate salts are so stable, what they can be simply prepared in free state.

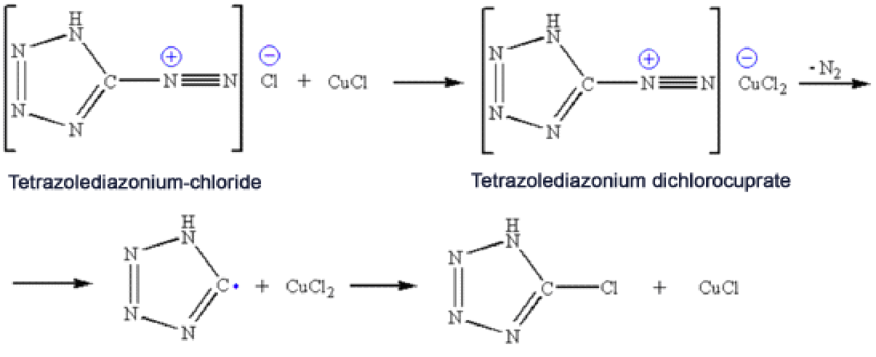
Tetrazoliumdiazotate can exist in two isomeric forms; cis and trans form. Usualy the unstable cis form is formed first, and transforms to stable trans form by long boiling, reverse transformation takes place only by action of ultraviolet radiation:



The difference in stability of two forms is so great, that they can be practically be termed as different substances, because of the large difference in physical properties. For example the pale yellow or colorless trans diazotate salts are quite stable in the dry state, but the cis diazotate salts are unstable and explosive in dry state even with stabilizing aromatic rings. During acidification the bifunctional trans-diazotate anions transform to trans-diazotetrazole hydroxide or to N-nitrosoamine, which are further transformed to the cation of tetrazolediazonium. Formation of nitrosoamine can be easily noted by green coloration of solution, usual for nitrosoamines. Freshly prepared diazotetrazole solutions are always slightly green colored.

Despite the instability of tetrazolediazonium cations, they have sugnificant practical importance in the chemical reactions of the aminogroup in 5-aminotetrazole. The tetrazolediazonium cation is very reactive and readily loses nitrogen, that allows for replacement of the diazo group with many other funtional groups. This replacement takes place during Sandmeyer reaction – replacement of diazogroup by halogen or pseudohalogen in presence of cupric salts, this reaction was first discovered in 1884 by T. Sandmeer and now it is very important in many fields of organic synthesis. The reaction scheme and mechanism are shown on picture below:

X = Cl, Br, CN, NO2, SO3H, SCN, SH, N3

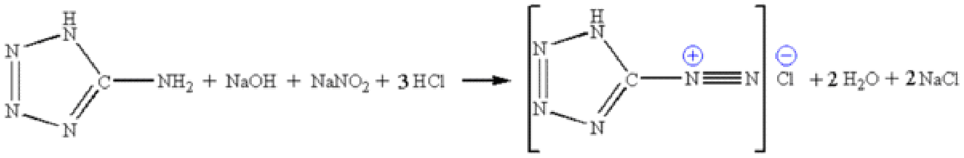


The reaction also takes place in the presence of cooper (II) salts or in the presence of copper powder (Gatterman reaction). Because of the extreme instability of diazotetrazole, diazotation and replacement of diazogroup are usually made simultaneously, in conditions optimized for maximally fast transformation of tetrazolediazonium cation to final product. This can be achieved by an excess of cupric salt catalyst and usage of reverse diazotation, conditions by slow addition of an acidified solution of 5-amino tetrazole to copper salt/nitrite mixture. The reaction is carried out with strict temperature control, which is essential for the stability of the diazonium salt, while allowing for a maximum rate of diazo group replacement (15-18°C Resultant copper salt of the desired 5-substituted tetrazoles are usually insoluble in cold water and precipitate from the reaction mixture. Side reactions also take place, resulting in the formation of 5,5'-azotetrazole, 5,5'-bistetrazole and 5-hydroxytetrazole, as impurities in reaction product.

Another important reaction of diazotetrazole is additon to electron donating moieties. For example the action of a slightly acidic solution of sodium nitrite on 5-aminotetrazole results in formation of tetrazolediazonium salt, which is further condensed with unreacted 5-aminotetrazole, forming 5,5'-diazoaminotetrazole. Salts of tetrazolium diazotate in fairly concentrated solultion on prolonged boiling or action of a stream of carbon dioxide, are transformed into extremely explosive salts of hydroxyazotetrazole; the mechanism of this reaction is unknown.

The Sodium salt of trans-tetrazolium diazotate Na(N4C)-N=N-ONa, exists as white needle-like crystals, is very soluble in water, and weakly soluble in ethanol[1]. On heating the salt deflagrates without melting, solutions of the salt is acidic due to the hydrolysis. In a neutral or weakly acidic environment sodium salt solution reacts with lead salts, forming the lead salt of oxyazotetrazole, insoluble in water, alcohol and either, but soluble in hydrochloric acid, sodium hydroxide and ammonia. Salt deflagrates at 360°C. Barium salt of tetrazoliumdiazotate BaCON6 – yellow crystalls, readily soluble in water[1].

Diazotetrazole synthesis[2]: 5g of aminotetrazole is dissolved in 30 ml of water, then 6 ml of 25% sodium hydroxide and 3.4g of sodium nitrite are added. After the nitrite is completely dissolved the mixture is cooled in an ice bath, placed in dropping funnel and is added slowly in 10-12 minutes with efficient stirring and cooling by ice cold water to mixture of 16 ml of 30% HCl with 170g of ice. Temperature of the reaction mixture should be below or at 0°C all times (Note №1). In the end of reaction mixture has slightly green color, because of presence of equlibrium quantities of nitrosoamine. Diazotetrazole solution is best used imidately, if that is imposible, it should be imidately transformed to tetrazolium diazotate by treatment with solution of sodium hyroxide (Note №2). Reaction scheme is shown below:

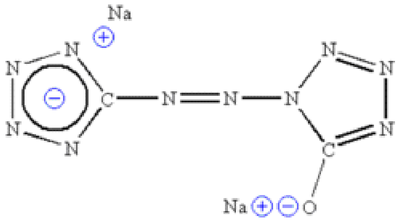


Hazard notes:

1. Diazotetrazole is an extremely sensitive explosive, it's water solutions at concentrations about 6-7% explode spontaneously even at 0°C, breaking up glassware used for diazotation. According to some sources at 0°C even 2% solutions can explode.

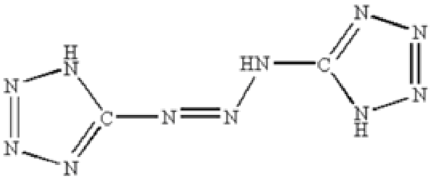
2. Because of the extreme unstable nature of diazotetrazole, it's usually produced in the form of 2-3% solutions with use of appropriate safety procedures (use of shields), and if it is not needed for further synthesis, diazotetrazole must be imidately transformed into tetrazolium diazotate salt by action of 25 ml of 25% sodium hydroxide (until basic reaction). If diazotetrazole is needed for further synthesis, the solution of tetrazolium diazotate salt is cooled to 0°C and is activated by addition of corresponding amount of hydrochloric acid.

Additional information



Sodium oxyazotetrazolate

1. Sodium salt of oxyazotetrazole $Na_2C_2N_{10}O*5H_2O$. Then sodium tetrazolium diazotate solution in fairly concentrated solution is boiled for long time, or it's warm solution is treated with stream of CO_2, sodium salt of diazotetrazole transforms to sodium salt of oxyazotetrazole, precipitated from solution because of moderate solubility in water[1]. Salt can be easily differed from diazotate by its characteristic dark-yellow color. Mechanism of this reaction is unknown, but it is most possible it is the same as formation of oxyazobenzene from benzolediazonium-nitrate and barium carbonate. The sodium salt of oxyazotetrazole exists as yellow crystaline plates, relatively insensitive to friction or impact, but exploding with terrible violence on heating. The barium salt of oxyazotetrazole is also known, it is a yellow compound crystallizing into a needle shape with 4 molecules of water. On prolonged boiling the salt slowly decomposes with formation of gaseous products, attempts to isolate free acid by action by action of strong acid solution on sodium salt resulted in formation of a solution, containing an unidentified substance which readily decomposed in solution. Structure of substance was not discovered because of very small amounts were available for analysis.

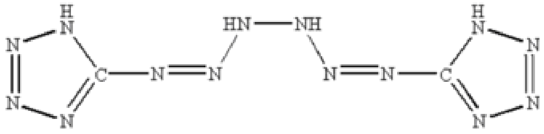


5,5'-Diazoaminotetrazole

2. 5,5'-Diazoaminotetrazole H(N4C)-N=N-NH-(CN4)H*H2O. This substance is the product of condensation of diazotetrazole with 5-aminotetrazole. In its pure form it is almost colorless, lustrous plates with double raytrayce, and crystallizes with one molecule of water[4]. The substances contain three acidic hydrogen atoms, which can be replaced by metal ions. There are some patents, proposing salts of diazoaminotetrazole as components of electro-igniter mixtures, and as sensitizers for conventional primary explosives. Monosodium salt of diazoaminotetrazole $NaC_2N_{11}H_2$ exists as yellow needles, readily soluble in water [2,3,4]. Copper salt $Cu_3(C_2N_{11})_2$ – amorphous precipitate with an olive-green color, almost insoluble in water, insoluble in organic solvents. Sensitive to impact and friction, on strong grinding in mortar, only part of product is exploded (whitch was directly below the pestle), explodes from fire, flash point 195-220°C [2,3,4]. Copper-ammonium salt $Cu_3(C_2N_{11})_2 * 2NH_3$ – dark green plates, expoding from friction, impact or heating, more sensitive then simple copper salt, flash point 220-230°C, mixture with potasium chlorate, has more initiation power then same mixture with mercury fulminate [2,3,4]. Silver salt $Ag_2C_2HN_{11}*H_2O$ – white amorphous powder, exploding on heating or strong friction. Barium salt $Ba_3(C_2N_{11})_2*8H_2O$ - yellow plates, explodes on moderate heating [2,3,4].

Monosodium salt synthesis[2]: 25g of aminoguanidine nitrate is dissloved in 125 ml of warm 12-13% acetic acid, 12.5g of sodium acetate is added and the mixture is cooled to 8-10°C and a solution of 17.5g sodium nitrite in 75 ml H2O is added with stirring over 30-40 minutes. Temperature of reaction mixture must be kept below 12-15°C all times, perfectly around 5-7°C. After addition of sodium nitrite, the solution is taken out from the cooling bath and is allowed to sit at room temperature, soon after that evolution of nitrogen is started, sometimes accompanied by heating up to 25°C. Aproximately after 12 hours, gas evolution stops and precipitation of product is starts, and is completed after 24 hours. Precipitated crystals are filtered off, washed with ice cold water acidified with acetic acid and is dried at room temperature.

Copper salt synthesis[2]: 43g of monosodium salt is dissolved in 350 ml of water, with added 23 ml of 25% sodium hydroxide. After monosodium salt is fully dissolved, 350 ml of 10% copper sulphate solution is added slowly with stirring. Olive-green precipitate is filtered off, washed with water, ethanol, either and dried at room temperature. Copper-ammonium salt can be prepared by threatment of precipitated copper salt with strong ammonia solution, copper salt dissolves, and long green prisms of copper-ammonium salt crystals precipitate short after.



5,5'-Bis-diazotetrazolylhydrazine

3. Bis-diazotetrazolylhydrazine (H(CN4)-N=N-NH-)2 – yellowish crystaline plates, with characteric star like edges. Poorly soluble in water and organic solvents [2,3,4,5]. Due to the high nitrogen content (14 nitrogen atoms and only 2 carbon atoms), the substance is an extremely powerful explosive. Pure product, thoroughly washed by ethanol melts at 120-123°C, where as the crude product explodes with terrible violence when heated to 90°C. Quite stable at room temperature, but very sensitive to friction and impact, violently explodes when rubbed with a glass rod or spatula. The action of alkaline solutions result in fast decomposition to 5-azidotetrazole, 5-aminotetrazole, nitrogen, ammonia and dicyan. Slowly decomposed when stored underwater due to hydrolysis. Can form extremely explosive salts, if water suspension of bis-diazotetrazolylhydrazine at 0°C is treated with a 20% solution of copper sulphate, greenish crystalls of copper salt are formed. Copper salt is extremely sensitive to friction, impact and fire, flash point 185°C. Bis-diazotetrazolylhydrazine is one of the richest on nitrogen from all known organic substances, containing 87.5% nitrogen.

Synthesis of bis-diazotetrazolylhydrazine[2]: 0.75g of hydrazine chloride and 1.5g of sodium acetate are dissolved in 3 ml of water, solution is cooled in a sodium chloride/ice bath and a solution of 1.9g diazotetrazole (Note №1) is slowly added with stirring. The yellow amorphous precipitate is washed with ice cold water, alcohol, and ether and is dried at room temperature. This work requires the greatest caution, due the extremely explosive nature of synthesized substance.

Hazard Notes:

1. Solutions of diazotetrazole are extremely explosive and can explode spontaneously, so appropriate safety measures should be taken into account all the times. It's not recommended to make amounts bigger than those presented in the synthesis procedure due to safety reasons. All works should be carried out by experienced chemist, with the greatest caution.

References:

1. Annalen der Chemie, 273-2,3, pp 144-160, 1893, J.Thiele, J. T. Marais, "Tetrazolderivate aus Diazotetrazotsäure".
2. P.F. Bubnov "Primary Explosives And Initiation Devices" part 1, Moscow, 1940, pp 311-314.
3. L.I. Bagal "Chemistry And Technology of Primary Explosives", Moscow, 1975, pp 399-401.
4. L.I. Khmelnitskij "Handbook Of Explosive Materials" Part 2, Moscow, 1961, pp 89-90,96.
5. Patents DE362433C1, DE400814C1.

Some photos for this chapter

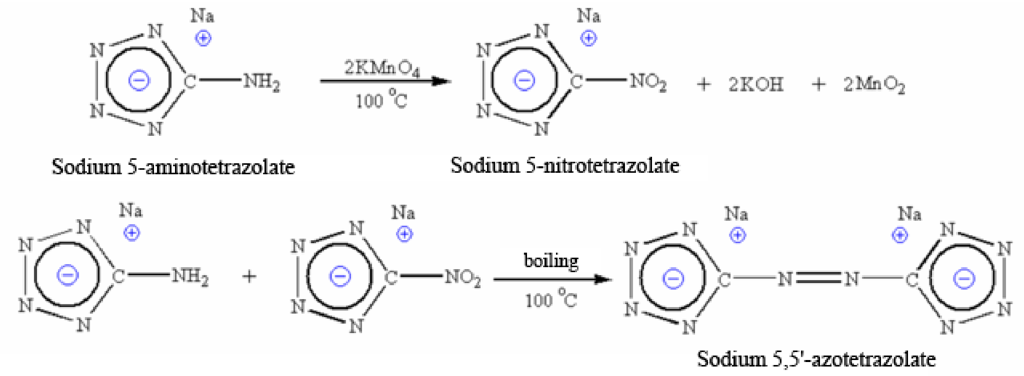
Description: Synthesis of diazoaminotetrazole from aminoguanidine, photos show amorhous grape like agglomerates of monosodium salt of diazoaminotetrazole free floating in mother liquer, on filter and in dry state.

Description: Left photo is solution of diazoaminotetrazole trisodium salt, with characteristic red-yellow color rights photo is amorphous powder of copper diazoaminotetrazolate, obtained by mixing with copper sulphate.

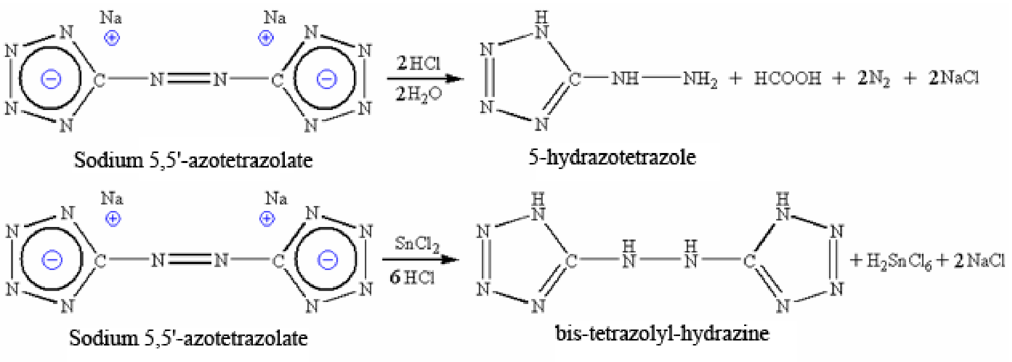
5,5’-Azotetrazole and derivatives

5,5’-Azotetrazole salts were first prepared by Rathsburg by action of permanganate on salt of 5-aminotetrazole in presence of excessive ammount of alkali. Free 5,5’-azotetrazole is unstable and attempts to make it in free state by action of strong acids have failed – free 5,5’-azotetrazole imidately decomposed to tetrazylhydrazine, nitrogen and formic acid. Nitric acid causes deeper decomposition with formation of tetrazylazide. Reaction with warm sulphuric acid goes on usual way, but then cold acid is used reaction results in formation of unindentified brown explosive solid. Azotetrazole is two basic acid and forms stable salts with metallic ions. All salts of 5,5’-azotetrazole are explosive and have characteric yellow color in solution[1].

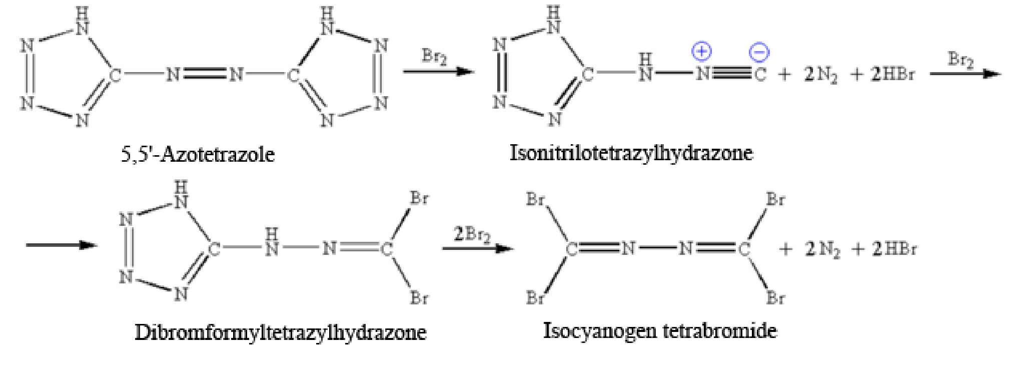
Discovery of 5,5’-azotetrazole is result of first, unsuccessfull attempts to prepare 5-nitrotetrazole. 5-Aminotetrazole contains amino group, whitch can be oxidised, what resulted in idea to make 5-nitrotetrazole by oxidation of 5-amino tetrazole by strong oxidisers, this attempts resulted in formation of yellow solution with yellow collor characteric for azo compounds, evaporation of water resulted in isolation of sodium salt of 5,5’-azotetrazole. More extensive view on reaction mechanism revealed that 5-nitrotetrazole probably forms, but in reaction conditions it imidately reacts with unreacted 5-aminotetrazole, forming 5,5’-azotetrazolates[1]:



From chemical point of view 5,5’-azotetrazole is typical azocompound, having all common properties characteric for azo compounds, tetrazolic ring provide stable aromatic rings and acidic properties. Because of strong acidic properties of tetrazole rings, salts of 5,5’-azotetrazole are stable to hydrolisis, have neutral pH and are stable to prolonged boiling. Reduction of azogroup with strong reducing agents such as tin dichloride or powdered magnessium results in reduction of azo group with formation of 5,5’-bistetrazolylhydrazine. Action of acids such as hydrochloric acid results in quantative destruction of one tetrazole ring with formation of 5-tetrazylhydrazine and release of nitrogen:



Another interesting property of azotetrazole salts is reactions with water solutions of bromine, whitch leads to decomposition of both tetrazole rings with formation of derivatifes of isocyan (unknown in free state). Action of alcohol solution of strong alkalis on this derivatives results in formation of unstable gas, with strong isonitrile odor, probably gas contains some ammount of free isocyan[1]. Up to date this is only known way to produce this interesting exotic compound. Rection scheme is shown on picture below:



5,5’-azotetrazole is important intermediate in synthesis of many other tetrazoles, many of them can be used to make compounds with even more nitrogen and higher energetic properties. Salts of azotetrazole itself are proposed for use in primary explosive mixtures and igniter compositions, for example basic lead salt was widely advertised as component of electro-igniter mixtures; copper, lead and silver salts were proposed as primary explosives; dihydrazinium salt was proposed as new high energetic, high nitrogen material, low sensitive to friction and impact and containing 85.5% of nitrogen.

Generaly salts of 5,5’-azotetrazole are crystalline solids, containing different ammount of crystallization water, colored in solution with yellow collor, characteric for azocompounds. Anhydrous salts are usualy sensitive to impact and friction and easily explode from fire, hydrated salts are less sensitive and can be grinded in mortar safely, on contact with flame they only fizz and crackle, whole mass explodes only after complete dehydration. Salts of alkali metalls are good soluble in water, salts of alkaline-earth metalls are good soluble in hot water, copper, silver, mercury and iron salts are almost insoluble [2,3,4].

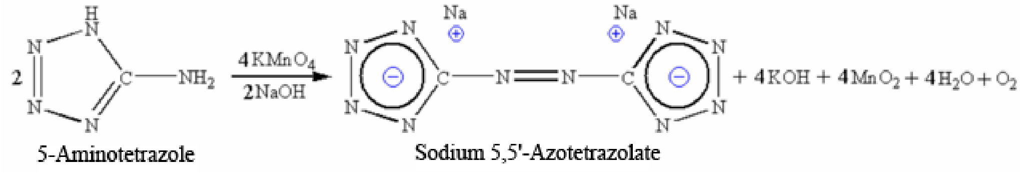
Sodium salt of azotetrazole $Na_2C_2N_{10}$ is yellow crystalline plates good soluble in water. From boiling water salt crystalizes with 5 molecules of water, salt solution has neutral pH. Then heated to 30°C solid salt losses 2 molecules of water, and at 70°C dehydrates completely. Hydrated salt is relatively low sensitive to friction and flame, can be safely grinded in mortar, on action of flame it only crackles and fizz. Anhydrous salt on friction, heating or impact explodes with loud report, explosion of 10g in Trauzl bomb gives expansion 120 ml. Flashpoint is 245-250°C. [2,3,4]

Potassium salt $K_2C_2N_{10}*5H_2O$ – is good crystallizing needles or plates, very soluble in water, quckly dehydrating in air stream. Barium salt $BaC_2N_{10}*5H_2O$ – yellow needle like crystalls, badly soluble in cold water and good soluble in hot water, at 140°C losses only 3 molecules of water. Calcium salt $CaC_2N_{10}*8H_2O$ – small yellow prisms, badly soluble in cold water and good soluble in hot water, at 110C losses only part of crystallization water, further dehydrations proceeds slowly only on prolonged heating at 140°C. [2,3,4]

Iron salt FeC_2N_{10} – black colloidal precipitate, after 3 hours of standing and passing air stream to solution, is filtered out as small dark brown crystalls. Badly soluble in water and alcohol, unsoluble in acetone, soluble in alkali solutions. Not explodes on friction and impact, flashpoint 164-165°C. Lead salt $PbC_2N_{10}*5H_2O$ – orange crystalls insoluble in water and organic solvents, soluble in alkali and acid solutions. Storage at 40C for one month not caused any changes. Puffs on action of flame, explodes on friction or impact, flashpoint 199-202°C. Zinc salt – yellow lustrous rhombic crystalls (after passing air stream to solution), slightly soluble in water, not explodes from friction or impact, flashpoint 176°C, slowly decomposes above 60°C. [2,3,4]

Copper salt CuC_2N_{10} – sky blue crystalline precipitate (after passing the air-stream), almost insoluble in water, very sensitive to impact, stab, friction and flame. Silver and mercury salts $Ag_2C_2N_{10}$ and HgC_2N_{10} – unsoluble in water, in dry state explodes on sligtest stimulus (even on touch), in difference with other salts, these are unsoluble in deluted HNO3, expode more violently then corresponding azides. [2,3,4]

Synthesis of sodium 5,5’-azotetrazolate[2]: 51g of 5-aminotetrazole monohydrate is dissolved in 500 ml of 15% solution of sodium hydroxide, resulted solution is heated to 100C (Note №1) and 70g of pottasium permaganate is added slowly by portions, until coloration of solution no longer dissappear. While permanganate is added liquid can begin to boil because of strong heat evolved by redox reaction. After oxidation is completed excess of potassium permanganate is destroyed by addition of 1-2 ml ethanol, hot solution is filtered from voluminous precipitate of manganesse dioxide and is concentrated to 1/3 of initial volume on steam bath. Product crystalizes as beautiful yellow prysms, yield is 70% (Note №2).



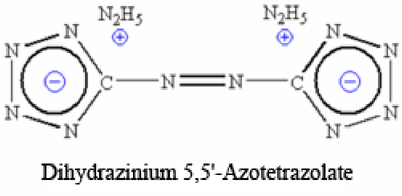
Notes:

1. According to some sources absence of excess alkali in reaction mixture during oxidation, can lead to formation of highly toxic and dangerous hydrogen cyanide. Alkalis transfrom unstable tetrazole rings to highly resonance-stabilized tetrazolate anions, and simplify condensation of reaction intermediates.

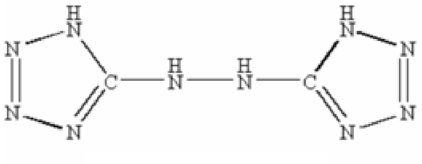
2. Potassium permangantate is strong oxidizer capable to oxidize water. At room temperature this reaction proceeds slowly, but at 100°C this reaction accelerates greatly and part of potassium permanganate is destroed by water, before it have time to react with aminotetrazole. Reaction equation shown above includes this side reaction.

Synthesis of other 5,5'-azotetrazolates[2]: Potassium salt of 5,5'-azotetrazole is synthesised in similar way, but sodium hyrdoxide is replaced with potassium hydroxide. Potassium salt is a lot more soluble then sodium salt, and solution must be concentrated much futher before product become to precipitate. Barium salt can be made by mixing solution of sodium salt with solution of soluble barium salt, barium salt is badly soluble in cold water and precipitate as yellow crystaline material upon cooling. Iron salt can be made by reaction of 30% solution of sodium salt with saturated solution of iron sulphate at 25°C, zinc salt is made in same manner but solution of zinc sulphate is used. Lead salt can be made by metathesis reaction of 15% solution of sodium salt with 20% solution of lead nitrate at 90-95°C, precipitate is left to settle for 3 hours and then filtered out from solution. Copper salt form when 10% solution of sodium salt is mixed with saturated copper sulphate solution, product is formed in colloidal state, but can be crystallized by passing stream of air to reaction mixture for 3 or more hours. Resulted product is filtered, washed with water, alcohol and either and is dried at 40°C. Mercury and silver salts are almost insoluble, and are easily precipitated by mixing solutions of sodium salt and soluble mercury or silver salt.

Additional Information



1. Dihydrazinium 5,5'- azotetrazolate $(N_2H_5)(N_4C\text{-}N{=}N\text{-}CN_4)(N_2H_5)$. This substance has very large possitive heat formation and contains about 85% nitrogen[5]. Proposed for use as high preformance secondary explosive, with very large volume of explosion products. Salt containing 2 molecules of crystallization water is yellow needle-like crystalls, perfectly soluble in water and alcohol, crystallization water can be removed by heating in vacuum at 100C. Heat of formation is about 858 KJ/mol, heat of explosion is 4.378 MJ/kg, density if hydrate is about 1.564 g/cm3, calcutated detonation velocity is 6330 m/sec, calculated detonation pressure is 247 kbar. Explosion products are: N2, CH4, H2, volume of gaseous explosion products is 974 l/kg. Substance is weakly sensitive to shock (no explosion with 5 kg weight and drop height 50 cm), friction, electrostatic discharge, explodes on rapid heating. Substance is stable in storage at room temperature. May be prepared by action of hydrazine sulphate on hot solution of barium 5,5'-azotetrazolate. Precipitated barium sulphate is removed by filtration and mother liquer is concentrated on water bath until first crystalls appear, mixture is then cooled and product is collected by filtration.



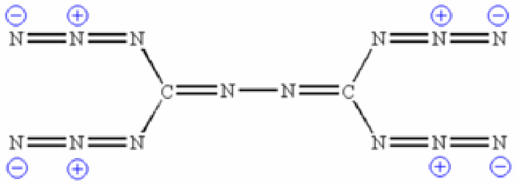
5,5'-Hydrazo-bis-tetrazole

2. 5,5’-Bis-tetrazolyl-hydrazine $H(N_4C)$-NH-NH-$(CN_4)H$. Substance is white amorphous powder with melting point at 240-241°C, explodes then heated to higher temperatures [1,6]. Heat of combustion (in closed volume) is 459.9 kcal/mol, standart heat of formation is 135 kcal/mol. Weakly soluble in boiling water, insoluble in organic solvents, soluble in concentrated hydrochloric acid, addition of ammonia or alkalis to such solution results in precipitation of corresponding salts. Alkaline solutions on exposure to light are readily oxidised salts of 5,5’-Azotetrazole, mercuric and silver salts transform to azotetrazolates on boiling in concenrated hydrochloric acid. 5,5’-Bis-tetrazolyl-hydrazine is sensitive to impact (50% explosions with 2 kg weight and drop height 32 cm), explodes when dropped to hotplate heated to 239°C. Some simple and double salts of 5,5’-bis-tetrazolyl-hydrazine can be used as primary explosives.

Barium salt $Ba(C_2N_{10}H_2)*H_2O$ – pale yellow needle like crystalls, slightly soluble in water, bulk density 1.01 g/cm3, explodes then heated to 265C, heat of decomposition is 1.12 MJ/kg. In form of hydrate has low sensitivity to shock and friction. Lead salt $Pb(C_2N_{10}H_2)$ – yellow amorphous powder with bulk density 1.05 g/cm3, explodes then heated to 160°C, heat of decomposition is 1.22 MJ/kg. Sensitive to shock (50% explosions on 24g ball drop from 125 cm height) and friction (50% explosions with 4kg weight, and slide speed 8 m/sec). Mercuric salt $Hg(C_2N_{10}H_2)$ – brown amorphous powder, bulk density 0.75 g/cm3, explodes then heated to 232°C, heat of decomposition is 1.21 MJ/kg. Has low sensitivity to impact, sensitive to friction (50% explosions with 4kg weight and sliding speed of 32 m/sec) [6].

Synthesis of 5,5’-Bis-tetrazolyl-hydrazine[6]: An amount of 23 g sodium 5,5’-azotetrazole was mixed with 100 ml of distilled water and 50 g of magnesium powder and subjected to gentle reflux for about 3 hours A reaction occurred, at the end of which the yellow solution became almost colourless or sometimes pale yellow. Excess magnesium was removed by filtering the hot solution The filtrate was treated with 50 ml 50% HC1 to precipitate 5,5'-bis-terazolyl-hydrazine as a white crystalline material. The dried material weighed 15 g (89% yield) and decomposed at 518 K when heated in a glass capillary tube in an electrically heated melting point apparatus.

Salts of 5,5’-Bis-tetrazolyl-hydrazine[6]: 5,5’-Bis-tetrazolyl-hydrazine was neutralised to pH 7 with 10% NaOH solution Its concentration was adjusted to 0.1 M and the solution taken into a stainless steel beaker and heated to 60°C on a water bath A 0.1 M solution of an M^{1*} salt (barium, lead or mercury) was placed in a dropping funnel and added dropwise over a period of 10-15 min under stirring. The contents of the beaker were further stirred for a period of 15 min at the same temperature. After cooling to room temperature, they were filtered and washed first with water and then with ethanol (95%). The resulting bis-tetrazolyl-hydrazine salts dried at room temperature for 3 to 4 hours and then in an air oven at 70°C for 1 hour. Yields varied from 70 to 90% in different experiments. In the case of the barium salt, the yield was particularly low and not consistent, this may be due to its moderate solubility in water.

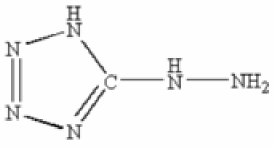


Isocyanogen tetrazide

3. Isocyanogen tetrazide $(N_3)_2C=N-N=C(N_3)_2$. Substance is formed by action of sodium azide on isocyanogen tetrabromide, whitch can be made by action of bromine on solution of sodium 5,5’-azotetrazolate, or better on 5,5’- bis tetrazolyl-hydrazine. Isocyanogen tetrazide is colorless needle like crystalls, melts without decomposition at 89°C, small ammounts on slow heating to 150°C can be sublimed. On shock or fast heating explodes with terrible violence, contais about 89 mass percent of nitrogen. Soluble in acetone, alcohols, either, alyphatic and aromatic hydrocarbons, chlorinated hydrocarbons, weakly soluble in water. Proposed for use as powerfull primary explosive, but is too sensitive for industrial use [7].

Synthesis of isocyanogen tetrabromide[1]: Solution of 1 mol 5,5'-bis-tetrazolyl-hydrazine is added to bromine water containing 8 mol of bromine. Mixture is heated on water bath until all dibromformaltetrazylhydrazone, witch is firs precipitated is converted to brown oil. Brown oil is separated on separation funell and is distilled with water steam, this results in formation of fast solidifying isocyanogen tetrabromide with good yield. Isocyanogen tetrabromide is recrystallized from small ammount of glacial acetic acid, by this firstly slightly yellow colored initial product containing some free bromine crystalizes as completely colorless lustrous plates, quickly loosing luster in dessicator, melting point of product is 42°C.

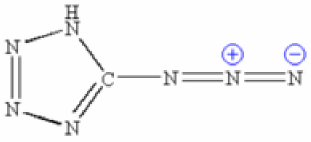
Synthesis of isocyanogen tetraazide[7]: 0.1 g of isocyanogen tetrabromide (purified by steam distillation and sublimation and used immediately after preparation) was dissolved in 1.0 ml. of acetone and cooled at 0°C. A solution of 0.09 g. (about 30% excess) sodium azide (activated by rubbing with a trace of N2H4*H2O and precipitated from a little water with acetone) in 0.6 ml. of water, cooled to about 0°C, was added dropwise while the reaction mixture was stirred by passing therethrough a slow stream of nitrogen. After one hour the cooling bath was removed while stirring was continued for three hours, allowing the reaction mixture to warm up to 30°C. An amount of 5.0 ml. of ice-cold water was added then and the mixture was kept for one half an hour in an ice bath. The formed crystals were filtered, washed with 5.0 ml. of ice-cold water and dried on the filter by air. Yield: 45 milligrams (76 percent). White needles, melting point: 89°C.



5-Hydrazotetrazole

4. 5-Hydrazotetrazole $H(N_4C)-NH-NH_2$. This substance is formed by action of strong acids on salts of 5,5'-azotetrazole. Colorless crystals, soluble in alkali and ammonia, weakly soluble in water, insoluble in ethanol, benzole, either. Melting point is 199C, explodes then heated to higher temperatures[1,8]. Can be made by action of 2 mol of dilute hydrochloric acid on 1 mol of sodium 5,5'-azotetrazole, during this operation one tetrazole ring of azotetrazole is destroyed leaving nitrogen and formic acid. Same reaction takes place with hot diluted sulphuric acid, however then sulphuric acid is cold some brown colored explosive product is formed, it's constitution is unknown. Care should be taken not to use nitric acid for hydrazotetrazole production, because this reaction leads to formation of very dangerous 5-azidotetrazole [8]. Some double salts of tetrazylhydrazine are proposed for use as primary explosives, for example 5-hydrazotetrazolato mercury (II) perchlorate $[Hg(HN_4CNHNH_2)](ClO_4)_2$ is recommended for use in laser initiated detonators, and is extremely sensitive to impulse laser beam in optical an IR areas of spectra and can be used in form of film shape charges with opticaly transparent polymeres[9]. Flash point is 186C (5 sec delay), density is 3.45 g/cm3, detonation velocity is about 6 km/sec at 3.4 g/cm3 density. Minimal ininitating charge vs RDX is 0.015g. Salt is not hygroscopic, insoluble in water and majority of organic solvents, soluble in dimethylsulfoxide. Can be made by action of mercury (II) salt on solution of 5-hydrazotetrazole in 5-70% perchloric acid on heating.

Synthesis of 5-hydrazotetrazole[8]: To a solution of disodium azotetrazole pentahydrate (10.0 g) suspended in water (100 ml.) was added hydrochloric aeid (25 ml 5N). The solution was warmed on a water bath until the gas evolution finished, then was evaporated to dryness from water three times to remove the hydrochloric acid. The residue was dissolved in a minimum of hot water and a hot solution of sodium acetate (10.0 g) in water (10 ml) was added.The apparatus was flushed out with carbon dioxide and the solution allowed to cool to give 5-hydrazino-tetrazole as white prisms with a yield of 2.5g, melting point 195-198°C.

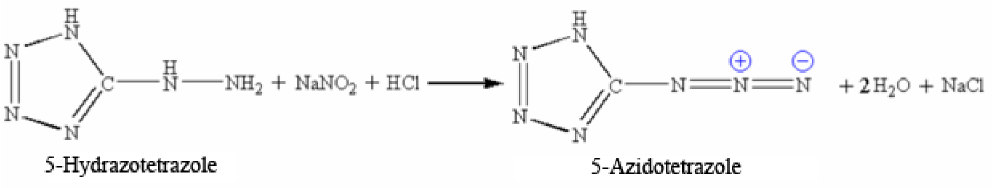


Tetrazylazide

5. 5-Azidotetrazole $H(N_4C)-N_3$. Tetrazylazide is one of organic substances richest in nitrogen. It's crystalline subsance crystallized from benzene, trichloromethane or carbon tetrachloride in form of white needles. Readily soluble in water, acetone, alcohol, slightly soluble in benzene, insoluble in ligroine, either [2,3,10,11,12,13]. On slow heating melts at 72-74C, at 217C explodes without melting. Extremely sensitive to impact and friction, on slight shock or friction explodes with terrible violence demonstrating extreme brisance effect. Stable on storage in pure state, but in presence of some impurities can explode spontaneusly. For example solution of tetrazylazide in acetone in presence of acetic acid can detonate spontaneously on storage, but same solutions in water and alcohol are stable. Density of 5-tetrazylazide, measured from X-Ray diffraction is 1.72 g/cm3, estimated heat of formation is 611 kj/mol, estimated detonation velocity (max) is 8986 m/sec [11].

Ammonium salt NH_4CN_7 – can be made by blowing ammonia gas through solution ot tetrazylazide in benzene. White crystaline powder, readily soluble in water and methanol, slightly soluble in ethanol and benzene[2,4]. Less sensitive to friction and impact than free tetrazylazide, but more sensitive towards heating. Salt is stable at room temperature. Potassium salt KCN_7 – white lustrous plates or needles, exploding without melting at 72-73C. Readily soluble in water, ethanol and acetone, insoluble in benzene and either. Expodes then dropped on hotplate heated above 70C, but on slow heating not explodes until 200C if not touched by spatula. Extremely sensitive to shock, friction and slightest pressure. Explodes with great violence on attemp of vacuum funell filtration or then slighlty pressed by spatula. Brisance effect is so great that even 0.01g ammount can cause dammage [4,10,13]. Sodium salt $NaCN_7$ – lustrous white plates, explode without melting, properties are same as for potassium salt [4,10,13]. Barium salt $Ba(CN_7)_2$ – very hygroscopic crystalls, when ignited by flame deflagrates with red flame and strong sound, soluble in acetone and pyridine, insoluble in absolute alcohol, benzene, trichloromethane and petrol either. Sensitivity to shock is 50% explosions with 500g weight and 35 cm drop height [4]. Lead salt $Pb(CN_7)_2$ – crystaline substance insoluble in water and organic solvents. Explodes with red flash when touched by flame, sensitivity to impact is above 100 cm with 5 kg weight[4]. Mercury salt $Hg(CN_7)_2$ – explosive solid insoluble in water[4]. Copper salt $Cu(CN_7)_2$ – amorphous powder with green color, insoluble in water. Extremely sensitive to impact, impact and flame, flashpoint is 170C [2,4]. Silver salt $AgCN_7$ – insoluble in water, explodes even in wet state on heating or slightest touch. Extremely brisant, unstable on storage – explodes spontaneously [4,12].

Synthesis of 5-azidotetrazole[10]: From 5-hydrazotetrazole and nitrous acid. A solution of 2.3 g. (0.023 mole) of tetrazolyl hydrazine and 2 g. (0.029 mole) of sodium nitrite in 100 ml. of water was prepared. It was cooled to 5C and 5 ml. of concentrated hydrochloric acid was added. There was a small amount of gas evolution and the solution turned a cloudy yellow. The mixture was filtered and evaporated to dryness on a steam-bath. The light yellow plates thus obtained were extracted with acetone and the yellow acetone solution on evaporation to dryness at room temperature gave a yellow solid. This solid was heated with benzene and a brown oil formed on the bottom. When the benzene layer was decanted off and cooled, long white needles were obtained. The brown oil was discarded. The yield for two runs was 20-22%. When the brown oil was extracted with more benzene, the yield was raised to 45-48%. The white needles melted sharply without decomposition at 72-73C and exploded when heated in a flame or placed on a hot bar, 217C or over. Tetrazolyl azide is also obtained as fine white needles from chloroform and carbon tetrachloride. It is very soluble in water, absolute ethanol or absolute ether.



Synthesis of potassium 5-azidotetrazolate: From diaminoguanidine and nitrous acid [10]. A solution of 3.04 g. (0.02 mole) of diaminoguanidine nitrate, 1.47 g. (0.015 mole) of potassium acetate and 1.74 g. (0.029 mole) of glacial acetic acid in 30 ml. of water was prepared and cooled to 0C (some solid reprecipitated). A solution of 3.74 g. (0.044 mole) of potassium nitrite in 10 ml. of water was added slowly keeping the temperature at 0-5C. The solution thus obtained was allowed to stand in an ice-box for two to four days. It was then evaporated nearly to dryness under vacuum (water aspirator) and in a stream of pure nitrogen. Long, white, prismatic needles of potassium nitrate were filtered off and washed with ethanol. An additional small amount of potassium nitrate came out of the filtrate on the addition of alcohol and was also filtered off. The filtrate was evaporated to dryness on a steam-bath and the yellow solid obtained was washed with absolute ether to remove the acetic acid and then extracted with acetone. The residue consisted of salts and was discarded. Absolute ether was added to the yellow acetone solution to the cloud point and allowed to stand. Fine cream colored needles formed and were filtered, and the filtrates saved. These needles were dissolved in the minimum amount of acetone and reprecipitated by the addition of absolute ether. This time beautiful, shiny white plates of potassium tetrazolyl azide (11) were obtained. Further purification was effected in the same manner. By adding more absolute ether to the filtrates an additional amount of product was obtained. Potassium tetrazolyl azide explodes violently when heated in a flame, giving a purple color. It will also explode when placed on a hot melting-point bar (60C or above), but when heated slowly it is stable to about 200 unless touched with a spatula. It can also be detonated by light pressure.

Synthesis of sodium 5-Azidotetrazole: From Cyanogen Bromide and Sodium Azide [13].To a solution of sodium azide (3.8 g, 0.058 mol) in water (10 ml) at 0-5C was added (15 min) finely pulverized cyanogen bromide (6.8 g, 0.064 mol). The mixture was stirred at 0-5C for 30 min, and the cold solution was then extracted with ether (2 x 15 ml). The water layer was evaporated to dryness at 50C (I mm). (Caution: The product may detonate if pressure is changed rapidly when the product is dry.) The resulting salt was extracted with hot acetone (3 X 25 ml). The extract was concentrated to about 35 ml and ether was added to precipitate Sodium 5-azidotetrazolate (2.56 g, 66%).

Synthesis of ammonium-5-azidotetrazole: From Cyanogen Bromide and Sodium Azide [13]. An aqueous solution of 5-azidotetrazole is prepared as described from cyanogen bromide (6.2 g, 0.059 mol) and sodium azide (7.6 g, 0.117 mol) was acidified to pH 1 and extracted with ether (3 X 50 ml). The dried ether extract was saturated with anhydrous ammonia and filtered to separate pure ammonium-5-azidotetrazole as a white, crystalline solid (15 2 g, 95%), mp 185-186C.

Hazard note: Tetrazylazide is extremely sensitive and powerfull explosive. Dry potassium salt is extremely sensitive to friction, heat, electric shock, and pressure. For example, a dry sample of potassium 5-azidotetrazole at 1-mm pressure will usually detonate if brought rapidly to atmospheric pressure. Great care and adequate protective equipment (shields, leather gloves, and jacket) should be used when preparing even small quanties of the dry compound. Samples larger than 0.1 g are best handled remotely. The salt can be prepared and handled safely in aqueous solution or as a free-flowing solid when moistened with water or mixed with an equal weight of mineral oil. We have prepared acetone solutions without event, but Lieber reports that such solutions containing traces of acetic acid may detonate and in this respect above procedure is safer. Pure dry 5-azidotetrazole is less sensitive than its potassium salt but the same handling precautions apply. Ammonium-5-azidotetrazole is still less sensitive to shock but detonates when heated rapidly to 190C.

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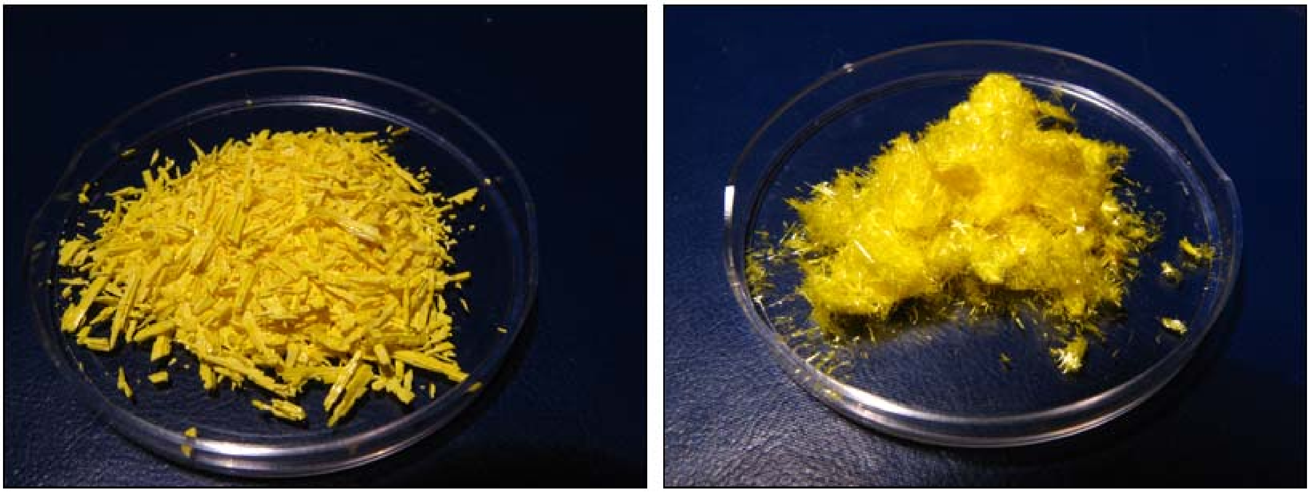
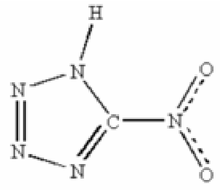
Some photos for this chapter

Description: 5-aminotetrazole solution is oxidized by alkline solution of potassium permanganate, precipitated manganesse dioxide is filtered, leaving orange solution of 5,5'-azotetrazole, witch is concentraded and cooled to precepitate perfect orange lustrous crystalls of sodium 5,5'-azotetrazolalate pentahydrate, collected by filtering.

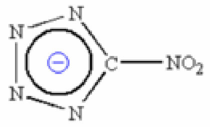


Description: Left photo shows perfect crystalls of sodium 5,5'-azotetrazolate separated from solution, rigth photo shows dihydrazinium salt made by metathesis reaction from barium azotetrazolate, badly soluble in cold water.

5-Nitrotetrazole and derivatives



5-Nitrotetrazole



5-Nitrotetrazolate anion

From 5-substituted tetrazoles 5-nitrotetrazole attracts special attention, because nitro group gives this molecule some unique properties. Combination of tetrazole nucleus and C-nitrogroup supply 5-nitrotetrazole with powerfull energetical properties, as well as very high N-H acidity and ability to produce powerfull explosions (this is caused by highly electronegative character of nitrogroup, see genereal properties of tetrazoles in beginning of article). Taking to account large theoretical and practicial interest in 5-nitrotetrazole, there was many attemps to prepare it, but for a long time they remained unsuccessful. Dirrect nitration of tetrazole is imposible because of acidity of tetrazole ring, attempts to oxidize aminogroup in 5-aminotetrazole vere insuccessfull too, because it leads to formation of azotetrazole instead of nitro compound. Only 47 years after discovery of tetrazole by Bladin, Von Herz first succeded to prepare 5-nitroderivative by Sandmeer reaction[1].

Herz prepared and described properties of 5-nitrotetrazole salts, witch are shown to be powerfull primary explosives. At time of second world war he patented 5-nitrotetrazolates for use in primary devices as replacement for conventional primary explosives, however due to the end of the war plans of it's production never come to reality. Later studies of 5-nitrotetrazole were preformed in many countries, but mass production was found to be imposible due too unaffordable hazards during synthesis (extreme instability of tetrazolediazonium intermediate). In recent years interest to 5-nitrotetrazole has rearisen and new safer methods of synthesis has been found. Now 5-nitrotetrazole is produced in pre-production experimental scale and believed to soon enter mass production.

Neverless of large interest to 5-nitrotetrazole, information about this compound is very limited. Fundamental review by Boyer, gives only few citations, article on nitroazoles not mentioned 5-nitrotetrazole at all. Due to 100-th anniversary of famous russian primary explosive researcher – proffesor L.I.Bagal, russian yournal of organic chemistry published article made by his followers, with first measured properties of individual 5-nitrotetrazole and preparation of several organic derivatives[2].

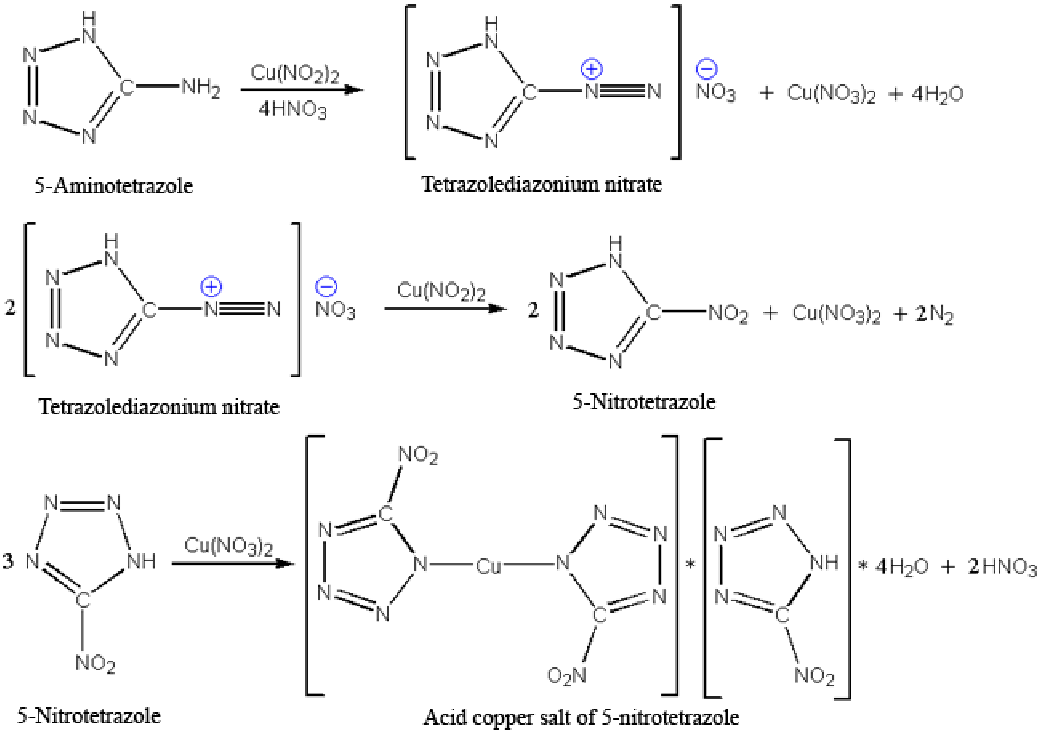
Free 5-nitrotetrazole is colorless very higroscopic crystaline plates, with melting point 101°C, violently exploding then heated above 115-120°C. Measured heats of formation are +62.3 kj/mol in solid state and +89.2 kj/mol in gas. Extremely sensitive to external stimulus – impact, friction or fast heating. 5-Nitrotetrazole is strong monobasic N-H acid (pKa = -0.8) and weak base (pK_{BH+} = -9.2). Impact sensitivity (K-44-II) is 100%, sensitivity to friction (K-44-III) has lower limit at 250 kg/cm3, detonation velocity at density 1.73 g/cm3 is 8900 m/sec, crystall density is 1.77 g/cm3. Forms stable salts with yellow color in solution, whitch transforms to lime green on standing, without any visible change of properties.

Salts of alkali, alkaline earth and ammonium are readily soluble in water, salts of cobalt, nickel, mercury, lead, silver and copper are very badly insoluble[3]. Mercury salt is more soluble then silver salt, lead and copper salts are soluble in hot water. Sodium salt is soluble in acetone. Salts are stable on storage in usual conditions, water and carbon dioxide not affect them in any visible ammount. Many salts form hydrates, witch are less sensitive then anhydrous salts. In wet state salts are relatively safe, but then dry they explode on shock, friction and fast heating. Many salts have excelent initiating power and strong brisance.

5-Nitrotetrazole is chemicaly stable to action of oxidizers and prolonged heating of solution, is readily acylated on atom N-2 forming numerous organic derivatives, reaction is regioselective N-1 derivatives are found only in trace ammounts. Electron density in 5-nitrotetrazolate anion is deeply common with one of it's isoelectronic analogue – cyclopentadienyl cation, and forms sandwich type complexes with Fe (II) in same way. 5-nitrotetrazole forms complexes with copper, iron, cobalt and nickel, witch are usualy not volatile, unsoluble in most of solvents and can form polymers.

5-Nitrotetrazole can be successfully obtained, by original Herz method[1], but method is dangerous in terms of “micro explosion” hazard. Later Gilligan and Kamlet[4], reviewed original Herz procedure to eliminate minor detonations, increase yield and ease filtration of product, this method is shown below.

Synthesis of Sodium 5-Nitrotetrazolate[4]: Place solution 104g (1.5 mol) sodium nitrite and 55g (0.22 mol) copper sulphate pentahydrate in 300 ml water in a 2L beaker and cool to 5°C. Add solution of 51.5g (0.5 mol) 5-aminotetrazole monohydrate, 2g copper sulphate pentahydrate and 64 ml 70% nitric acid in 700 ml water to solution of sodium nitrite/copper sulphate, dropwise with efficient stirring over a period of about 90 minutes holding the temperature at 15° to 18°C (watch hazard notes below). Stir for 15 minutes, add solution 70 ml 70% nitric acid in 30 ml water dropwise and then stir for an additional 30 minutes. Filter with suction and wash the copper acid salt with 250 ml 1.8 N nitric acid and three times with 250 ml of water. Do not allow the cake to dry during the filtration and washing. Transfer the wet cake to a 1500 ml beaker and adjust the volume to about 600 ml with water. Adjust the pH of the slurry to ca 9 with 50% sodium hydroxide solution to precipitate copper hydroxide and then heat the efficiently stirred slurry to 100°C on water bath and digest for 30 minutes (Note 1). Allow the precipitate to partially settle and filter with suction through a packed layer of "celite" (Note 2). Wash the precipitate twice with 100 ml of water. Adjust the pH of the combined filtrate and washes to 4, with concentrated nitric acid. Reduce the volume to ca 350 ml using slow evaporation on water bath. Cool to 2°C and filter the sodium 5-nitrotetrazole (Note 3). Reduce the filtrate to 200 ml and take a second crop...etc. Combine the crops, redissolve in water and recrystallize a second time. Air dry the product. Dissolve the sodium 5-nitrotetrazole in acetone on a steam bath and filter to remove inorganic salts. Cool the filtrate in an ice bath and remove the sodium 5-nitrotetrazole by filtration. Recrystallize a second time from acetone and air dry (Note 4). The yield is about 45-55% of theory based on 5-aminotetrazole. Reaction scheme:



Summary reaction equation

$$\boxed{\begin{array}{c} 3ATZ + 3CuSO_4*5H_2O + 6NaNO_2 + 4HNO_3 \longrightarrow \\ Cu(NT)_2*HNT*4H_2O + 2Cu(NO_3)_2 + 3N_2 + 3Na_2SO_4 + 17H_2O \end{array}}$$

General notes:

1. The blue hydrated cupric hydroxide is converted to the brownish-black cupric oxide at temperatures above 70°C.

2. Without, "celite" the filtration and washing requires several hours since the finely divided cupric oxide clogs the filter.
3. Sodium 5-nitrotetrazole crystallizes from water as a voluminous hydrated mass. After air drying, the salt contains two to five moles of water of crystallization depending on ambient humidity.
4. Sodium 5-nitrotetrazole crystallizes from acetone as a dihydrate. This appears to be stable at ambient conditions.

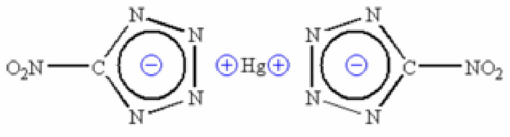
Hazard notes:

During the diazotization of 5-aminotetrazole nitrogen oxide fumes are given off from the reaction solution. This step should be carried out in an efficient hood. Reaction goes through extremely unstable diazotetrazolium intermediate, witch can spontaneously detonate in solution then the concentration exceeds 1%, causing so called “minor detonations” , which while not harmful in themselves, were pschologically disturbing and did on occasion break glassware. There was the possibility that the potentially dangerous (in the dry state) acid copper nitrotetrazole salt would be spilled over adjacent surfaces. Minor detonations occurring during the diazotization were caused by nitrogen oxide fumes arising from the reaction solution and reacting with droplets of 5-aminotetrazole solution on various surfaces of the apparatus. Since copper salts catalyze the reaction of 5-diazotetrazole with nucleophiles, it was felt that the addition of small amounts of copper sulfate to the 5-aminotetrazole solution would eliminate any build-up of the diazotetrazole by catalyzing its conversion to 5-hydroxytetrazole. This proved to be the case since the addition of small amounts (~2g) of copper sulphate to the 5-aminotetrazole solution completely eliminated the detonations previously experxenced. However one should remember that minor detonations can still take place occasionously in some cases.

The copper acid salt of 5-nitrotetrazole, CuHNT*(NT)2, can be handled safely in the wet state; however in the dry state, it is very sensitive to shock and electrostatic discharge. Air dried sodium 5-nitrotetrazole containing two or more mole-equivalents of water of crystallization is relatively insensitive to shock; it cannot be detonated with a hammer blow. However when completely dry, it is also a sensitive explosive. Both compounds will detonate violently if dropped on a hot plate. All precautions consistent with the handling of potentially dangerous explosive materials should be observed throughout this operation.

Synthesis of free 5-Nitrotetrazole[2]: 5.48g (0.026 mol) of sodium 5-nitrotetrazolate tetrahydrate is dissolved in 30 ml of water at 5-10°C and 19.6 ml 20% sulphuric is added cautiously by drops with stirring. Reaction mixture is extracted with either (3 portions 50 ml each), extract is washed with water (50 ml) and dried with magnesium sulphate. Either is distilled off in vacuum, 1.9g (63%) of colorless crystalline 5-nitrotetrazole is obtained, melting point is 101°C (from benzene).
Warning!!! 5-Nitrotetrazole is very sensitive and powerfull explosive, it’s sensitive to friction, shock and fast heating, readily attacks metals forming explosive salts, work should be done with great care, using all nececary precautions.

Additional materials

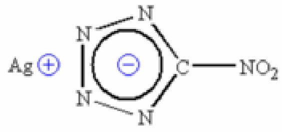


Mercury (II) 5-nitrotetrazolate

1. Mercury (II) 5-nitrotetrazolate $Hg(N_4C\text{-}NO_2)_2$ – dense white rhombic crystals, exploding without melting at 205°C. Soluble in 20% solution of ammonium acetate, very spartingly soluble in water, insoluble in nitric acid. This compound is one of the most powerfull and efficient primary explosives known at this time. Proposed as lead azide replacement for US Navy[3]. Heat of decomposition is 2.59 MJ/kg, minimal initiating charge for tetryl is 0.006g (at loading pressure 160 kg/cm2), deflagration to detonation transition takes 2 microsec time (lead azide 9 microsec) [7]. Sensitive to friction, impact and fast heating, sensitivity is on mercury fulminate level. Sensitivity to impact: 50% explosions with 5kg weight and 5 cm drop height, sensitivity to electrostatic discharge (5000V twenty sequential ignition falures) >= 12.5J. Stable in storage in usual conditions, presence of carbon dioxide, moisture and light not affects this material[3]. There are many synth procedures, generally using sodium 5-nitrotetrazolate as starting product (references [1] [3] [4] [5] [8]) one of them is shown below:

Synthesis of mercury (II) 5-nitrotetrazolate[5]: A solution of 11.6 g of sodium 5-nitrotetrazolate dehydrate in water (195 ml) and concentrated nitric acid (22 ml) was heated to 80°C. A solution of mercuric nitrate dihydrate (18 g) in water (100 ml) and concentrated nitric acid (2 ml) was added with stirring over 50 min, then the reaction allowed to cool to 20°C.

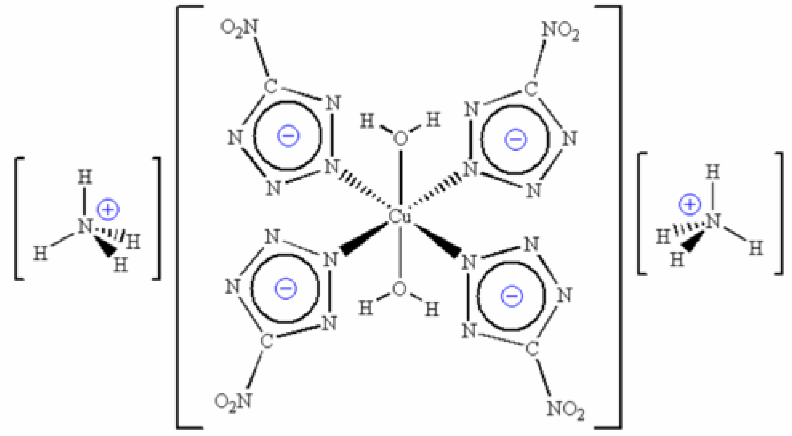
Product was obtained by filtration as agglomerations of tiny white crystals; ignition temp. 205(2x) °C, 207°C (literature: 205°C, 208°C).



Silver 5-nitrotetrazolate

2. Silver 5-nitrotetrazolate $Ag(N_4C\text{-}NO_2)$ – small white needle like crystals, explodes without melting at 230°C. Insoluble in water and nitric acid. Heat of decomposition is 1.94 MJ/kg, minimal initiating charge for tetryl is 0.005g (at loading pressure 160 kg/cm2), deflagration to detonation transition takes 2 microsec time (lead azide 9 microsec) [7]. Salt is quite sensitive to friction, impact and fast heating, slightly more sensitive then mercury fulminate. Stable in storage in usual conditions, presence of carbon dioxide, moisture and light not affects this material[3]. In wet state significantly less sensitive, but action of open flame still causes violent explosion. Silver 5-nitrotetrazolate is one of the most powerfull primary explosives up to date, and should be handled with great caution and in small quantities. There are many synth procedures, generally using sodium 5-nitrotetrazolate as starting product (references [1] [3] [5] [8]) one of them is shown below.

Synthesis of silver 5-nitrotetrazolate[5]: A solution of silver nitrate (2.35 g) in water (55 ml) was added over 30 min to a stirred solution of sodium 5-nitrotetrazolate dehydrate (1.7 g) in water (50 ml). After complete addition, 1 M nitric acid (10 ml) was added in one lot and the reaction stirred for a further 10 min. The reaction was allowed to cool and filtered to give product as small irregular white crystals; ignition temp. 261°C (3x) (literature 262°C, 265°C).



Ammonium diaquatetrakis-(5-nitrotetrazolato-N2) cuprate (II) (NH4CuNT)

3. There is a group of complex 5-nitrotetrazole complexes, witch is proposed as replacement for common primary explosives, called "Green Primaries" [9]. Chemical constitution of this complex compounds can be described by general formula $(Cat)_z[Me(NT)_x(H_2O)_y]$, Me is complex forming central atom (Fe,Co,Ni or Cu), Cat is some inorganic cation (NH4,Na,K). Constitution of complexes allows carefull tweaking of explosive properties and sensitivity, by varying content of energetic tetrazole ligands (e.g x value) and content of coordinated inert water molecules (e.g. y value). Most profitable properties achived for complexes with 3-4 nitrotetrazole ligands (x=3,4) and 2-3 water ligands respectively (y=2,3), total number of ligands is always six (x+y=6). Exposive properties of some of these complexes are shown in table below, values marked with green color are estimated, friction sensitivity is measured as mass witch must be applied to two parallel porcelain surfaces with 1 mg explosive sample between them, so slide of surfaces against each other cause 50% chance of explosion. Impact sensitivity is measured by drop test (25% explosions, 2.5 kg weight).

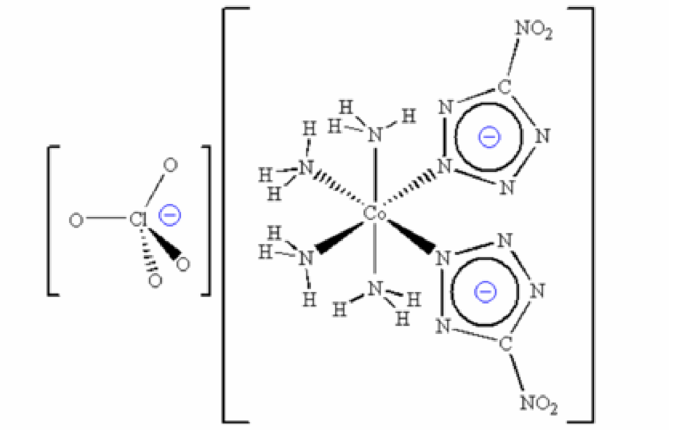
Composition	Name	Tign	Impact	Friction	Spark	Denstity	VOD (Density)
$(NH_4)_2[Fe(NT)_4(H_2O)_2]$	NH4FeNT	255	25 cm	2800 g	>0.36 J	2.18 g/cm3	7140 m/s (1.71)
$(NH_4)_2[Ni(NT)_4(H_2O)_2]$	NH4NiNT	270	18 cm	1500 g	>0.36 J	2.44 g/cm3	7020 m/s (1.73)
$(NH_4)_2[Co(NT)_3(H_2O)_3]$	NH4CoNT	270	22 cm	800 g	>0.36 J	2.04 g/cm3	6749 m/s (1.64)
$(NH_4)_2[Cu(NT)_4(H_2O)_2]$	NH4CuNT	265	23 cm	600 g	>0.36 J	1.94 g/cm3	7390 m/s (1.71)

$Na_2[Fe(NT)_4(H_2O)_2]$	NaFeNT	259	12 cm	20 g	>0.36 J	2.20 g/cm3	6962 m/s (1.71)
$Na_2[Ni(NT)_4(H_2O)_2]$	NaNiNT	265	8 cm	<<500 g	>0.36 J	2.46 g/cm3	6906 m/s (1.71)
$Na_2[Co(NT)_3(H_2O)_3]$	NaCoNT	264	10 cm	<<500 g	>0.36 J	2.05 g/cm3	6574 m/s (1.71)
$Na_2[Cu(NT)_4(H_2O)_2]$	NaCuNT	250	12 cm	40 g	>0.36 J	2.10 g/cm3	6848 m/s (1.71)
$(NH_4)[Fe(NT)_3(H_2O)_3]$	NH4FeNT-3	261	15 cm	4200 g	>0.36 J	2.10 g/cm3	6769 m/s (1.71)
$(NH_4)_2[Fe(NT)_4(H_2O)_2]$	NH4FeNT-4	255	12 cm	2800 g	>0.36 J	2.20 g/cm3	7140 m/s (1.71)
$(NH_4)_3[Fe(NT)_5(H_2O)]$	NH4FeNT-5	253	10 cm	1300 g	>0.36 J	2.34 g/cm3	7388 m/s (1.71)
$(NH_4)_4[Fe(NT)_6]$	NH4FeNT-6	252	8 cm	800 g	>0.36 J	2.45 g/cm3	7568 m/s (1.71)
$Pb(N_3)_2$	Lead Azide	315	10 cm	6 g	0.0047 J	4.80 g/cm3	5300 m/s (4.10)
$PbC_6N_3H_4O_8$	Lead Styphnat	282	14 cm	40 g	0.0002 J	3.00 g/cm3	5200 m/s (2.90)
$C(CH_2ONO_2)_4$	PETN	-	14 cm	5800 g	-	1.77 g/cm3	8350 m/s (1.72)

Table above shows good performance and small sensitivity of these complexes, compared to conventional explosives, in addition this complexes are non toxic and give non toxic, envourimentaly friendly explosion products. This set of new primary explosives, commonly refered as “Green Primaries”, were patented by Los-Alamos laboratory in 2006. All this substances can be produced in common way, from solution of corresponding 5-nitrotetrazolate and solution of good soluble inorganic salt.

Synthesis of green primary complexes[10]: All complexes can be made in same manner, solution of 0.5g salt (A) is dissolved in 30 ml of water and (B) gram of (C) 5-nitrotetrazolate is added with stirring, (D) colored precipitate is formed imidately. Suspension is brought to reflux and stirred for 2-hours, precipitate is filtered, washed with small amount of ice cold water, alcohol and dried. Yield is (E) gram ((F) percent).

Комплекс	A	B	C	D	E	F
NH4CoNT	$Co(ClO_4)_2*6H_2O$	0.682	NH4	Pale yellow	0.74	91
NH4NiNT	$Ni(NO_3)_2*6H_2O$	0.912	NH4	Lavender	0.94	93
NH4FeNT	$Fe(ClO_4)_2*6H_2O$	0.727	NH4	Orange	0.77	96
NH4CuNT	$Cu(NO_3)_2*6H_2O$	1.090	NH4	Blue	1.14	93
NaCoNT	$Co(ClO_4)_2*6H_2O$	0.892	Na	Pale yellow	0.76	92
NaNiNT	$Ni(NO_3)_2*6H_2O$	1.190	Na	Lavender	0.92	90
NaFeNT	$Fe(ClO_4)_2*6H_2O$	0.954	Na	Orange	0.77	94
NaCuNT	$Cu(NO_3)_2*6H_2O$	1.430	Na	Blue	1.18	95



Tetramino-cis-bis-(5-nitrotetrazolato-N2) cobalt (III) pechlorate (BNCP)

4. BNCP laser ignited primary eplosive complex. Teramino-cis-bis-(5-nitrotetrazolato-N2) cobalt (III) perchlorate or simply BNCP is orange red needle like crystals, insoluble in cold water[11]. Density is 2.05 g/cm3, thermally stable up to 200°C, flash point is 269°C. Heat of explosion 3.32 MJ/kg, detonation velocity at 1.97 g/cm3 is 8100 m/sec (calculated), deflagration-detonation transition takes 10-11 microseconds, minimal initiating charge vs RDX is 0.05g. Substance is not toxic, non hygroscopic, sensitive to flame, impact and friction. Sensitivity to impact by drop test is 50% with 2.5 kg weight and 17cm height (PETN – 12 cm), insensitive to electrostatic discharge. Sensitive to light, ignites by neodymium

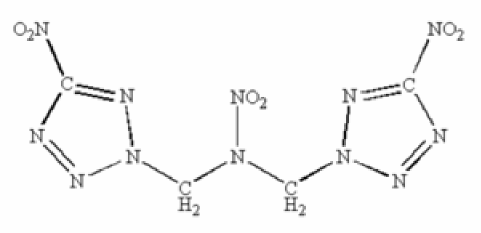
laser (wavelength 1.06 micrometers, impulse time 1 ms, diameter of ray 0.5 mm, impulse energy 1.5 J). Compound has clear deflagration-detonation transition zone and has optimall loading pressure value. Then weakly pressed compound fails to detonate, if loading pressure is too high compound can be overpressed. BNCP is entering to use as primary explosive in some modernistic laser initiated devices and in safe electrodetonators, can be used without secondary boosting charge. There are also copper and nickel analogous witch have familiar properties[12].

Synthesis of BNCP[11]. 47g cobalt (II) sulphate heptahydrate is dissolved in 125 ml of water and slowly stirred into solution of 100g ammonium carbonate in 500 ml of water + 250 ml of 25% ammonia solution. Resulted dark-violet solution is oxidised by 14 ml 30% hydrogen peroxide, added by drops with intense stirring. Mixture is allowed to stand for 30 minutes, and evaporated to 300 ml, with many occasional additions of ammonium carbonate (5g at one time). Solution is filtered from any solid precipitate and concentrated further to 200 ml, and slowly cooled to 0°C. Apon cooling dark red crystalls of carbonatotetraminocobaltisulphate are precipitated, theese are filtered and dried, yield is about 16g (Note 1). 16g of sodium perchlorate is dissolved in 40 ml of water and stirred to solution of 16g carbonatotetraminocobaltisulphate in 320 ml of water, mixture is then cooled on ice for several hours. Precipitate of small lustrous violet sharp-edged prysms of carbonatotetraminocobaltiperchlorate is filtered, washed with small ammount of ice-cold water and dried, yield is 14g (Note 2) [13]. 26.5g of sodium 5-nitrotetrazolate dihydrate is dissolved in 450 ml of water and slowly added to solution of 14 g carbonatotetraminocobaltiperchlorate in 140 ml of 10% perchloric acid, reaction mixture is placed on boiling water bath, allowed to sit for 4 hours and cooled to 15°C. Bright orange-red precipitate of BNCP is filtered off, washed with two 70 ml portions of ethyl alcohol and recrystalized from 1% perchloric acid, yield is 12.9g[11].

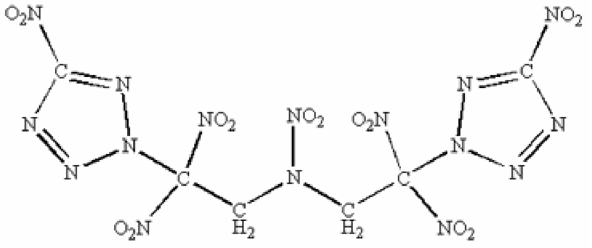
Notes:

1. Furher concentration of solution with additions with ammonium carbonate will allow to separate another 16g of complex compound. Some more product may be separated without concentration, by strong cooling of solution, but in this case product will be less pure. Compound formula is $[Co(NH_3)_4CO_3]_2SO_4*3H_2O$.

2. Carbonatotetraminocobaltiperchlorate complex $[Co(NH_3)_4CO_3]ClO_4$ is badly soluble in cold water, solubility data from literature is 13.3g in 1000 ml of water at 20°C [13]. Part of reaction product stays in solution, so yield is slightly lower then theoretical. Further concentration or strong cooling should be avoided, because it can cause precipitation of sodium sulphate.



1,3-di(5-nitrotetrazolato-N2)-2-nitro-2-azapropane



1,1,3,5,5-pentanitro-1,5-di(5-nitrotetrazolato-N2)-3-azapentane

5. There are numerous organic derivatives of 5-nitrotetrazole, some of them are interesting as high performance explosives, for example 1,3-di(5-nitrotetrazolato-N2)-2-nitro-2-azapropane (left formula) and 1,1,3,5,5-pentanitro-1,5-di-(5-nitrotetrazolato-N2)-3-azapentane (right f-la). 1,3-di(5-nitrotetrazolato-N2)-2-nitro-2-azapropane – experimental explosive, first prepared in soviet union in 1972, is colorless crystalline compound with melting point 165C, density is 1.9 g/cm3, heat of formation 476 ccal/kg (other sources give 388 ccal/kg), heat of explosion is 1430 ccal/kg. Detonation velocity is 9350 m/sec (1.86 g/cm3), 9940 m/sec (1.9 g/cm3), critical diameter 0.82 mm, thermal stability is acceptable. Can be prepared by action of silver 5-nitrotetrazolate on 1,3-dichloro-2-nitro-2-azapropane in organic solvent (solid AgCl is filtered and solution is evoparated to get product). 1,1,3,5,5-pentanitro-1,5- di-(5-nitrotetrazolato-N2)-3-azapentane is another experimental explosive, first produced in soviet union in 1983, colorless crystalline substance with melting point at 65C, density is 2.06 g/cm3, heat of formation is 296.9 ccal/kg, impulse against HMX is 113%, detonation velocity is 9000 m/sec (1.78 g/cm3), 10600 (2.06 g/cm3, estimated). Substance can be made by scheme: $K[(N_4C-NO_2)-C(NO_2)_2] + (CH_2)_6N_4 + H_2SO_4$ => … + HNO_3/H_2SO4 => product.

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Some photos for this chapter

Description: Synthesis of acid copper salt of 5-nitrotetrazolate by Sandmeer's reaction, first photo shows solution of reagents, next two are taken in the middle of reaction process, characteristic malachite like colored solid of acid copper salt is floating in mixture, forming greenish slurry. Microexplosions usualy take place in this stage, causing serious, nervousness during this - the most responsible moment of all process. After addition of reagents is complete, solution is acidified and precipitate is allowed to settle at the bottom of reaction wessel, reaction mixture is then filtered on vacuum filter to get reaction product – hydrate of acid copper 5-nitrotetrazolate Cu(NT)2*HNT*3H2O.

Description: This series of photos shows some solid 5-nitrotetrazolates and complexes. Top left photo is lustrous perfectly formed crystalls of solid sodium 5-nitrotetrazolate dihydrate, obtained from acetone solution, top right photo shows greyish-white lumps of silver 5-nitrotetrazolate, made by metathesis of sodium 5-nitrotetrazolate with silver nitrate. Two photos in the middle are green primary complexes – NH4CuNT and NH4CoNT, produced from solution of ammonium 5-nitrotetrazolate and corresponding metall salts. Lower left photo demonstrates characteristic yellow/lime color of 5-nitrotetrazolates in solution (in this case sodium 5-nitrotetrazolate), final shows crystalls of free 5-nitrotetrazole, obtained by metathesis strontium 5-nitrotetrazolate and sulphuric acid.

Description: This series of photos shows synthesis of tetramino-cis-bis-(5-nitrotetrazolato-N2) cobalt (III) perchlorate, (BNCP) complex. Top left photo shows initial carbonatotetraminocobaltisulphate complex, obtaned from cobalt sulphate ammonium carbonate and ammonia, then it is converted to carbonatotetraminocobaltiperchlorate by action of conc. solution of sodium perchlorate and colling to get dark violet crystalls of product shown on top right photo. This complex is used as one of reagents to get BNCP in coordination process with sodium 5-nitrotetrazolate solution (reaction mixture is shown on middle-left photo). After reaction is allowed to go for sufficent time and reaction mixture is cooled, crystalls of BNCP begin to appear at the bottom of reaction flask (middle right and lower-left photos) theese are separated by filtering washed by two portions of ethyl alcohol, recrystalized from 1% perchloric acid and dried on the air, to give crystalls of pure tetramino-cis-bis-(5-nitrotetrazolato-N2) cobalt (III) perchlorate complex, shown on lower-right photo.