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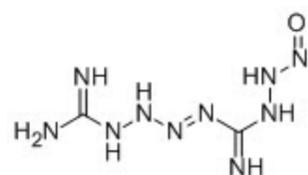
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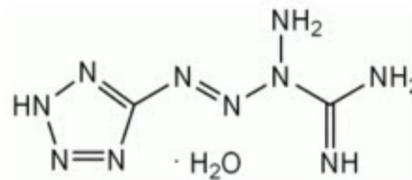
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## Tetrazene



false structure



correct structure

### Tetrazene

"1-guanyl-4-nitrosoaminoguanyltetrazene" was first prepared by Hoffmann and Roth. It is a colorless pale yellow, fluffy material with slight hygroscopic properties. The structure was originally assumed to be  $\text{H}-\text{NC}(=\text{NH})\text{NHNHN}=\text{NC}(=\text{NH})\text{NHNHNO}$ , but this was later corrected (Patinkin, Chem. Zentr. 1955. p8377). Another possible structure was given as  $\text{NH}_2\text{C}(\text{NH})\text{N}=\text{NNHNHC}(\text{NH})\text{NHNHNO}$ . It seems that that early researchers made a false assumption about the structure. The compound known as Tetracene was technically mislabeled. The correct chemical name is actually 1-(5-tetrazolyl)-3-guanyl tetrazene hydrate (tetrazolyl guanyltetrazene hydrate), the structure of which can be seen in the image above. The pure molecule itself does not have an oxygen atom, and the presence of a strongly bound molecule of water probably caused confusion. I do not know whether a "nitrosoamino" group, with the formula  $-\text{NHNHNO}$  can exist. I am unsure if even a primary nitrosamine  $-\text{NHNO}$  can exist. In this case, the structure might be more accurately represented as  $-\text{NH}(+)=\text{NO}(-)$  (since the amine is electron donating to the nitroso, lending such a configuration more stability). Density: 1.7 g/cm<sup>3</sup>. Lead block test: 155cm<sup>3</sup>/10g. It is almost insoluble in water, alcohol, ether, and benzene.

It is stable at normal temperatures when wet or dry, but decomposes in boiling water. Tetrazene is sensitive to friction, shock, and flame. Its brissance is maximized when it has not been compacted, and this compound can easily become dead-pressed. Tetrazene is not suited for blasting caps or alone as an explosive since it does not detonate itself very efficiently. It is best suited for booster charges or in blasting caps mixed with other explosives. It should be detonated by another explosive charge, otherwise if just ignited, it will undergo a lower velocity detonation.

### Preparation:

Prepare a solution of 34 g of aminoguanidine bicarbonate and 12.5 mL of glacial acetic acid with 2500 mL of water in a 3-liter Florence flask. Gently warm the flask on a steam bath and shake periodically until everything is completely dissolved into solution. The solution should be filtered to remove any impurities that may have not dissolved, then cooled to 30° C by running cold water from the faucet over the flask. It is necessary to filter the solution if there are impurities present. Add 27.6 g of sodium nitrite to the solution while swirling to dissolve it. Set the flask aside at room temperature for 3 or 4 hours then shake it vigorously to start precipitation of the product. Let the flask stand for another 20 hours. After standing, decant as much of the solution off as possible and drown the remaining crystals with water. Decant and drown with water several more times to wash the crystals. Filter the washed crystals to collect them and thoroughly wash again with water. Dry the product at room temperature and store in a sealed glass container to keep out the moisture.

Reaction with a strong base causes the compound to hydrolyze into **triazonitrosoaminoguanidine**, which is **significantly more sensitive**. The formula of this is given as  $\text{N}_3\text{C}(=\text{NH})\text{NHNHNO}$ , but I suspect it may actually be  $(\text{N}_3)_2\text{C}=\text{NH}\cdot\text{H}_2\text{O}$  or azidotetrazole hydrate. This compound (with the ambiguous structure) can be reacted with Copper Acetate to form a copper coordination salt, and then with HCl solution (without nitrite this time) to form 5-azido tetrazole in 85% yield.

(1-(5-tetrazolyl)-4-guanyl tetrazene hydrate) is slightly more impact-sensitive than mercury fulminate. When pressed enough, its sensitivity is reduced or destroyed; this is known as dead pressing. It also decomposes in boiling water. In contact with fire, it readily explodes, producing large amounts of black smoke. It is prepared by reacting sodium nitrite with an aminoguanidine salt dissolved in acetic acid at 30–40 °C.  $(\text{HN}_4\text{C})\text{N}=\text{N}-\text{N}(\text{NH}_2)-\text{C}(\text{NH})\text{NH}_2$  Nitrate and perchlorate salts of this are possible and more powerful.

Treatment of aminoguanidine bicarbonate with sodium nitrite and excess HCl solution makes guanylazide, whereas treatment with a solution of acetic acid and sodium nitrite forms mostly  $(\text{HN}_4\text{C})-\text{N}=\text{N}-\text{NH}-(\text{CN}_4\text{H})$ , where the  $(\text{CN}_4\text{H})$  is a tetrazole ring.

Guanylazide reacts with sodium hydroxide to form **sodium azide**, but reacts with a weak base, or weak acid, to form 5-Amino-tetrazole. 5-aminotetrazole will react with nitrogen dioxide to form 5-nitrotetrazole, which is somewhat acidic and forms nitrotetrazolate salts.

Nitrous acid (HONO) oxidizes aminoguanidine nitrate  $\text{H}_2\text{NC}(=\text{NH})\text{NH}_2$  into guanyl azide  $\text{N}=\text{N}=\text{NC}(=\text{NH})\text{NH}_2$ , which cyclizes into aminotetrazole  $\{\text{HN}_4\text{C}\}\text{NH}_2$  when boiled under alkaline conditions. This takes several hours and gives 70–85% yield.

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Č tetrazine-at.bmp (217k)

Anders Hoveland, Nov 19, 2010, 5:14 PM

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### Comments