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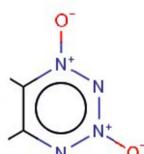
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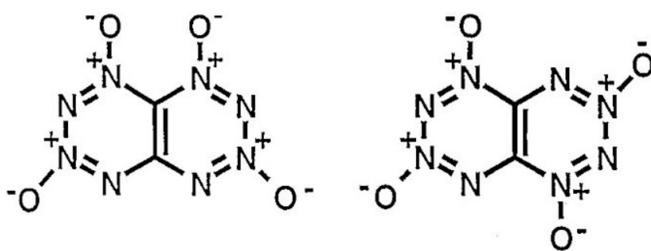
## dioxy-1,2,3,4-tetrazines



1,3-dioxy-1,2,3,4-tetrazolo- structural group

### DTTO

Calculated Density: 1.97 g/cm3  
Calculated Detonation Pressure: 558-567 kbar (compare to only 393 kbar for HMX)  
Calculated Velocity: 10.28 km/sec  
Formula: C2N8O4  
[1,2,3,4-tetrazino-1,2,3,4-tetrazine]-1,3,6,8-tetraoxide / Ditetrazinetetroxide (there are two isomers)



Note that DTTO has not ever been prepared, but researchers are very close to a successful synthesis. It is quite possible that Russian researchers have been successful but did not publish the work because of the potential military value of this extremely powerful compound. If successfully prepared, DTTO is calculated to generate pressures of 558-567 kbar, and that is the downward revised calculation, because the previous ones were thought to be unrealistically high! So that is a very conservative value! For comparison, octonitrocubane, which is generally regarded as the most powerful explosive possible, is calculated to generate pressures of 489 kbar.

It should be noted that the unusual dioxy-tetrazine rings on DTTO have been synthesized into stable compounds, so DTTO should not be seen as completely theoretical. **Dioxy Tetrazolo-benzene (Benzene-1,2,3,4-tetrazine 1,3-N,N-dioxide)** has been prepared and is stable, having a melting point of 172-174 degC. Note that any other arrangement of the two oxygen atoms on the tetrazine, or even the mono-oxide is **not stable**. The mono-(1-N)-oxide, however, can be kept for 6-7 hours before decomposition to benzofurazan and nitrogen gas.

See attachments below.

**Theoretic Synthesis:**  
Oxalamidine (C2N4H6) reacts in a 1:2 molar ratio with monomethyl-hydrazine, ammonia gas is allowed to escape. Next, sodium nitrite and HCl solution are added, this forms a double ringed compound with the formula (C2N8)(CH3)2, with the carbons both being members of both rings. This is then oxidized with peroxyacetic acid, then reacted with acidified permanganate (oxidizing off the methyl groups) to yield the final compound, less two oxygen atoms. A mixture of ozone and pure H2O2 is added (peroxone), then concentrated sulfuric acid slowly added to oxidize this intermediate to the tetraoxide.

Alternatively, fluorine can be bubbled in using an H2O and CH3CN solvent, to add the second oxygen atom to the ring. For the specifics of the procedure, see "*The Tetrazole 3-N-Oxide Synthesis*" *Tal Harel, Shlomo Rozen, School of Chemistry, Tel-Aviv University, Tel-Aviv, Israel. J. Org. Chem., 2010, 75 (9), p3141-3143*

Oxalamidine may be made by heating anhydrous ammonia and cyanogen.

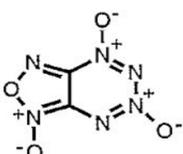
It has also been proposed that 1,2-dinitroso,1,3-diazido ethylene C2(NO)2(N3)2 would spontaneously cyclize into DT*di*-oxide, which could then be oxidized to DTTO. They wanted to first react NaN3 with diiodoacetylene! Then react with nitric oxide.

Normally, such compounds are not very stable, without electron donating hydrogen atoms, but in this case, everything is in a ring and the resonance states add stability. Tetrazine rings alone are not very stable, but become more so when cyclic nitrogens are oxidized.

Another route for oxalamidine might be to fuse P2O5 with ammonium phosphate, forming phosphamic acids, then fuse this with oxalamide NH2C(=O)C(=O)NH2, which can be made by heating ammonium oxalate in a sealed tube, or by reacting ethyl oxalate ester with a concentrated solution of NH4OH, with constant stirring, for several days. The ethyl oxalate ester may also be a useful precursor for DADNE.

Alternatively, 1,1-dichloro-ethylene could react with nitrosyl sulfate to form 1,1-dichloro-2,2-dinitroso-ethylene. This could then be reacted with anhydrous monomethyl-hydrazine to replace the chlorines with --NHNHCH3 groups. There should be no more than 2 moles of methylhydrazine for each mole of the ethylene derivative. The HCl forms a salt with the hydrazine groups.. Then reaction with propyl nitrite ester may cyclize the intermediate into a double ring.

### 1,3-dioxytetrazolofuroxan



$\rho = 2.191 \text{ g cm}^{-3}$   
 $\Delta H_f = 128.6 \text{ kcal mol}^{-1}$   
 $P_{CJ} = 61.8 \text{ GP}_a$

Below is a tested synthesis for the furoxan of dioxytetrazine, which is a less powerful version of DTTO and has already been prepared. This compound is still calculated to generate more pressure than HMX, a realistic estimate being 406 kbar. The given calculated value is actually 618 kbar, but this is actually greater than that of DTTO. The explanation for this paradox is that DTTO was initially over-optimistically calculated to generate 1318 kbar, before the value was later revised downward. Doing my own calculations, I am estimating that the more realistic value for the furoxan compound is around 406 kbar, which is still slightly above the value for HMX. (My estimate assumed that the errors in the initial calculations for the dioxytetrazine components in the two compounds are proportional, but since the furoxan-dioxytetrazine also contains a furoxan group, only 6/10ths of the 618 value was proportionally adjusted downward) The calculation for the density of this furoxan compound was later revised down to around 1.7 g/cm3.

RDX produces only 346 kbar of pressure and HMX produces 390 kbar, for comparison. Dioxytetrazine compounds could be mixed with some other highly energetic, but fairly insensitive compound for safety, that is why TNAAZ or DADNE are so useful, if you were wondering why anyone would bother with these. A composition of dioxytetrazine compound and DADNE, for example, could potentially be both 50% more powerful than HMX and be more resistant to impact.

### Incomplete Synthesis of DTTO:

(this is basically a synthesis for dioxytetrazolofuroxan, which the researchers were then going to use as a precursor to DTTO, but they never completed the full synthesis)

#### Step 1

Cyanogen is bubbled in into aqueous phenyl hydrazine (10%) in an ice batch, until no longer absorbed, forming an insoluble compound, which is then isolated by filtration, and crystallized from 20% ethanol. At the end of the cyanogen addition, filtration of the thick milky reaction mixture produced a large quantity of solid, which decreased to one third of its initial volume after washing with water. Too much cyanogen reacts further, but more slowly than the first reaction, to form a darker byproduct, which required activated charcoal for removal. Yield after crystallization from ethanol was 25%.

The cyanogen flow rate should be half that of the phenylhydrazine for best yields, which then gives a much whiter product.

The below is a modified publication of K. Christe, et. al. This site has not attempted any of the below. The opinion of this site is that the procedure Christe adapted from Japanese researchers in unnecessarily complex, and therefore it is not recommended. However, it still may be an interesting read.

#### Step 2

The procedure described by Thiele is reasonably straightforward, rapid and readily reproducible. The reaction was conducted by combining near saturated solutions of 2-amino-2-phenylhydrazonoacetonitrile (I) in refluxing ethanol with equimolar quantities of hydroxylamine prepared from stoichiometric amounts of hydroxylamine hydrochloride and sodium carbonate in a minimum amount of water. The significantly smaller 72-78% yield of product could be increased to the reported range (90-100%) by secondary recovery from the product mother liquor and washings, but with slightly lower purity. This difference in the initial yield may be due to a lower water concentration than that used by Thiele who probably worked with 95% ethanol rather than 100% and may have used more water for the hydroxylamine preparation in order to dissolve the by-product sodium chloride. The solid oxime undergoes slow oxidation on exposure to air at ambient temperature, particularly when wet, and more rapidly at higher temperatures to give black char. Oxime solutions oxidize rapidly turning wine red.

The phenylazo- group is substituted for the first amino group introduced and subsequently by a further modification (Steps 4,8 and 9)

#### Step 4. Synthesis of 2-Phenylazo-2-phenylhydrazonoacetonitrile (IV) from Cyanoacetic Acid and Phenyl diazonium Chloride

The material is produced in near quantitative yield as an extremely fine and voluminous solid which required extensive washing to remove inorganic salts and vacuum drying near ambient temperature to prevent air oxidation and/or thermal decomposition. Most of the water insoluble compound (91%) is produced as a thick floating foam over the remainder which occurs as a thin slurry. Both forms were shown to be identical on analysis. The thoroughly washed wet product isolated by filtration had an inordinately high water content namely 78% for the foam and 83% for the slurry. Extraction of the crude dry product with chloroform was performed and left less than 1% residual salts. However, two recrystallizations from ethanol were required to raise the melting point to the reported value with recovery of only 60% of the material in each crystallization. An attempt to purify the material by vacuum sublimation was unsuccessful due to extensive decomposition.

#### Step 5. Synthesis of 2-Phenylazo-2-phenylhydrazonoacetamide Oxime (V) from 2-Phenylazo-2-phenylhydrazonoacetonitrile (IV) and Hydroxylamine

A series of seven experiments was carried out with variations in reaction conditions in the conversion of the title nitrile (IV) to the oxime (V). The principal differences among syntheses reported in the literature were the solvents used, reactant concentrations, reaction time, temperature and the preparative method for hydroxylamine from its hydrochloride. An attempt to follow the procedure of Henderson<sup>25</sup> failed to give any solid product. A reinvestigation of Henderson's procedure by Nikitin<sup>26</sup> reported a 98% oxime yield but in our hands over 80% of the starting nitrile was recovered. Much better results were obtained with the procedure of Thiele (see Step 2 above) with some modifications namely extending the reaction time and adding a 2.5-fold excess of hydroxylamine to the nitrile (reverse addition) under a nitrogen atmosphere. With these modifications pure product was obtained in 70% yield.

#### Step 6 Phenylazo-2-phenylhydrazonoacetamide Oxime (V) and Acetic Anhydride

Two attempts were made to reproduce the synthesis by Nikitin wherein acetic anhydride is used as the reaction solvent for this ring closure instead of water as was used in Step 3 above. In this process the by-product water forms acetic acid which acetylates the initially formed amino group. In each attempt the reaction did not proceed as rapidly as reported leaving the product contaminated with much starting material. Rather than trying to improve the synthesis of the 4-acetamido- derivative which then requires a basic hydrolysis Step 7 to form the 4-amino- derivative, a newly reported process which could be adapted for a single step conversion of 2-phenylazo-2-phenylhydrazono-acetonitrile (IV) to the title compound was investigated (see Step 8).

(Using water as a solvent, the oxime was cyclized into a triazine at 150degC under pressure)

#### Step 7. Synthesis of 4-Amino-5-phenylazo-2-phenyl-1,2,3-triazole (VI) from 4-Aceto-amido-5-phenylazo-2-phenyl-1,2,3-triazole (VI) and Aqueous Base

Despite the low purity of the 4-acetamido-derivative available it was subjected to basic hydrolysis to obtain a crude sample of the corresponding 4-amino- derivative following the Nikitin's report. Separation of the mixture was accomplished on a thin layer chromatographic plate and the components were identified as the desired product (VII) and the starting material (VI).

#### Step 8. Synthesis of 4-Amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII) from 2-Phenyl-azo-2-phenylhydrazonoacetonitrile (IV) and Hydroxylamine

A procedure reported by Badahdah for the one step conversion of 2-(heterocyclic radical)-2-phenylhydrazonoacetonitrile to the 4-amino-5-(heterocyclic radical)-2-phenyl-1,2,3-triazole was adapted by substituting the title nitrile (IV) for the nitrile containing the heterocyclic radical in this process. The nitrile (IV) reacts with hydroxylamine (generated *in situ* as its acetate salt from its chloride salt and sodium acetate) to produce the amide oxime (V) which in turn cyclizes to the title triazole (VII) in the refluxing dimethylformamide solvent. A series of seven experiments using purified nitrile indicated that the yield of the recrystallized triazole was increased from 16% to 39% when the reaction time was extended from 2 to 4 hr but further extension to 8 hr was without effect. In one 4 hr experiment where crude nitrile was used in place of recrystallized material the yield was only 15% although up to an additional 8-15% yield of a slightly less pure triazole derivative could be obtained from the concentrated mother liquor.

#### Step 9 Synthesis of 4,5-Diamino-2-phenyl-1,2,3-triazole (III) from 4-amino-5-phenylazo-2-phenyl-1,2,3-triazole (VII) and Zinc/Sulfuric Acid

Three experiments were conducted following the procedure of Nikitin reported to give an 80% yield (88% with secondary recovery). The reduction was far from complete in the first experiment where 29% of the starting material was recovered. The product yield was 60% based on reacted starting material. On repetition of the reaction the reduction was virtually complete with only about 4% of the starting material contaminating the diamino- derivative obtained in 69% yield and on scale-up in 76% yield.

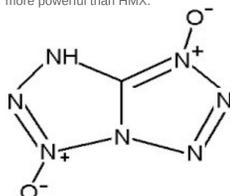
#### Step 10. Synthesis of 4,5-Triazolo-2-phenyl-1,2,3-triazole (IX) from 4,5-Diamino-2-phenyl-1,2,3-triazole (III)

The procedure of Thiele was followed wherein 4,5-diamino-2-phenyl-1,2,3-triazole (III) was diazotized to form 4-amino-5-diazo-2-phenyl-1,2,3-triazole (VIII) which without being isolated was allowed to decompose to give a 75% yield of 4,5-triazolo-2-phenyl-1,2,3-triazole (IX). The net yield for the entire chain to this final intermediate was 13%.

The research team did not carry their investigation any further than this last intermediate. The idea was that the triazole ring would be converted by ring expansion into a triazine ring and then be oxidized. Apparently oxidizing the double ring further than two oxygen atoms requires an oxidizer on the order of FOH, or F2 being bubbled into an alkaline aqueous solution of the oxytetrazine..

For the FTDOsynth attachment, N2O5 can substitute for the NQ2NF4 in the second step, formation of a ring from this reaction generally gives yields of 40-55%.

A similar compound could possibly be formed from diaminotetrazole. Reaction with nitrous acid (HNO2) gives a double acid, or H2O2 in the presence of cyano groups (-CN , these civate the H2O2, but the cyano is rapidly degraded, so the cyano compound should be added last). The resulting compound, dioxy-triazolotetrazine, should be highly energetic, and slightly more powerful than HMX.



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Č	DTTO-s.bmp (719k)	Anders Hoveland, Nov 8, 2010, 1:03 PM	v.1	d'
Č	DTTOresonance.bmp (909k)	Anders Hoveland, Nov 8, 2010, 12:15 PM	v.1	d'
Č	FTDOsynth.bmp (2949k)	Anders Hoveland, Nov 8, 2010, 12:52 PM	v.1	d'
Č	cleavage.bmp (684k)	Anders Hoveland, Nov 10, 2010, 3:47 PM	v.1	d'
Č	furazanDTO.bmp (238k)	Anders Hoveland, Nov 8, 2010, 12:20 PM	v.1	d'
Č	longreactionD.bmp (755k)	Anders Hoveland, Nov 8, 2010, 4:39 PM	v.1	d'

### Comments