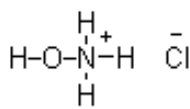




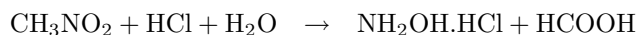
Glyoxime, Diaminofurazan and some Energetic Derivatives, by AXT

1 Hydroxylamine Hydrochloride

Figure 1: Hydroxylamine hydrochloride



Hydroxylamine can be formed by acid hydrolysis of nitromethane[1] forming the acid salt of hydroxylamine and formic acid:



1.1 Hydroxylamine hydrochloride

61 g nitromethane was mixed with 114 g 32% hydrochloric acid in a 300 mL glass bottle (molar ratio $\text{CH}_3\text{NO}_2:\text{HCl}:\text{H}_2\text{O}$ 1:1:4.3). The top was screwed on the bottle and it was immersed in an oil bath heated to 100°C (Figure 2). The solution was left at this temperature for 24 hours whereby the nitromethane and acid layers formed a homogeneous solution.

The solution was then transferred to a wide mouth beaker and left at the same temperature until evaporated to about 1/3 of its initial volume. On cooling the solution to -5°C hydroxylamine hydrochloride precipitated as large white flakes which were filtered and dried. Further concentration and cooling yielded further crystals for a total of 41 g (59%).

A similar process to that described above was used but with a molar ratio of 1:1:10. This allowed the solution to be heated in a non-pressurized vessel without significant loss of HCl. Plastic film and a rubber band was used to cover the flask containing

Figure 2: $\text{CH}_3\text{NO}_2/\text{HCl}$ solution in oil bath (left). $\text{NH}_2\text{OH}\cdot\text{HCl}$ crystals (right).

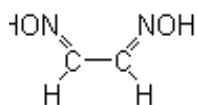


the solution. The solution was heated for 40 hours at 100°C and concentrated and precipitated as before; the yield was 32 g (46%).

When heated on a spoon the $\text{NH}_2\text{OH}\cdot\text{HCl}$ decomposed energetically with release of white smoke but no flame.

2 Glyoxime

Figure 3: Glyoxime



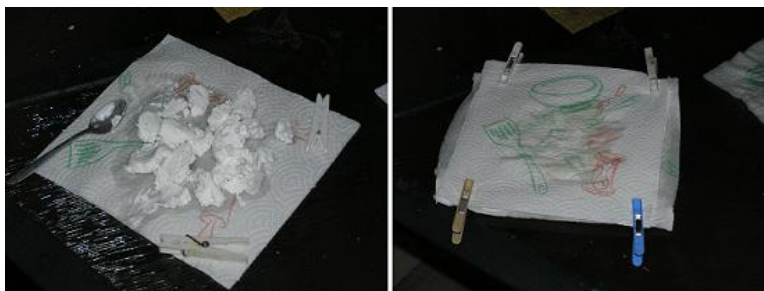
Glyoxime, also known as ethanedial dioxime, is produced by the condensation of glyoxal with hydroxylamine in slightly acidic solution; the following is an adaptation of the literature method[17].

2.1 Glyoxime

27.5 g (0.69 mol) sodium hydroxide was dissolved into 75 mL water and cooled to 0°C . 69.5 g hydroxylamine hydrochloride (1 mol) was then added with stirring. To the still chilled solution was then slowly added 72.5 g (0.5 mol) of 40% glyoxal in 48 mL water while maintaining the temperature below 10°C . The solution was left in the fridge for 15 minutes then removed and allowed to come to room temperature. The solution become solid with precipitate within 1 hour which was scooped out and pressed as dry as possible between absorbent paper. The damp glyoxime was then left sandwiched between 4 sheets of absorbent paper to dry (Figure 4), allowing the salt solution to be wicked out of the glyoxime to deposit the NaCl in the upper layers of paper. The crude

yield of glyoxime was 38 g (86%). The crude glyoxime was recrystallised from ether to form the most pure product, which was used for the lead and silver salts below.

Figure 4: Drying glyoxime.



The recrystallised glyoxime melts at 178°C with decomposition and ignites easily when touched with the flame of a match, burning mildly with a soft orange flame and faint “hiss.”

2.2 Glyoximate salts

Glyoxime is acidic, and carries the energetic oxime groups, and thus is capable of forming salts that may show notable explosive characteristics. Bretherick[2] lists a basic copper salt ($\text{HOCuON}=\text{CHCH}=\text{NOH}$) which is said to lose weight up to 140°C before exploding.

The silver and lead salts were produced by precipitation of a solution of sodium glyoximate with silver nitrate and lead acetate. These salts were shown to have interesting primary explosive qualities but are unlikely to have, nor were they tested for initiating ability.

2.2.1 Silver glyoximate

Into 2 g (23 mmol) of glyoxime in 50 mL water was added 1.8 g (45 mmol) of sodium hydroxide to produce a solution of sodium glyoximate. Into this solution was added 3.9 g (46 mmol) of silver nitrate in 20 mL water which resulted in the immediate precipitation of a grayish maroon coloured silver glyoximate, which was filtered and dried out of sunlight. The dried salt was found to darken when exposed to sunlight and flash with a “thump” on ignition (Figure 5). Eventually the silver salt exploded by itself when left in direct sunlight.

2.2.2 Lead glyoximate

Lead glyoximate was produced in the same way as the silver salt, except 7.4 g (23 mmol) of lead acetate was used to precipitate the lead glyoximate as a fine, flocculent

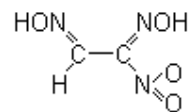
white precipitate. The lead salt on ignition exploded with more vehemence than the silver salt, exploding with a loud report in quantities over about 1 g (Figure 5).

Figure 5: Ignition of 0.8 g lead glyoximate (top) and 0.5 g silver glyoximate (bottom).



3 Nitroglyoxime

Figure 6: Nitroglyoxime



The activated hydrogen of glyoxime is capable of reacting with nitric acid containing HNO_2 [3] or with nitrogen dioxide itself[4] yielding nitroglyoxime, an explosive nitrolic acid.

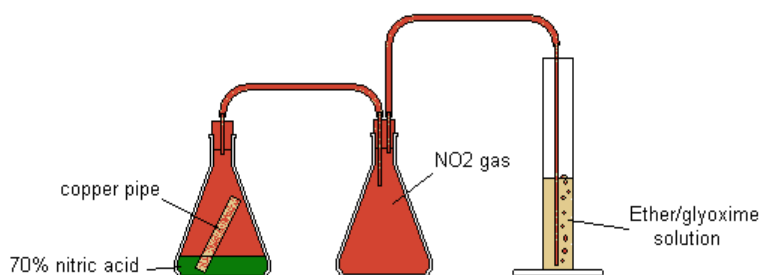
Nitroglyoxime is too unstable to be of any practical use. It melts at 111°C with decomposition and explodes on further heating[4]. It is soluble in water (decomposed by hot water) alcohol, ether and acetone, very slightly soluble in benzene, more so in boiling benzene. It is insoluble in chloroform and petroleum ether[4].

The basic lead salt of nitroglyoxime ($\text{C}_2\text{H}_2\text{N}_3\text{O}_4 \cdot \text{Pb} \cdot \text{O} \cdot \text{Pb} \cdot \text{C}_2\text{H}_2\text{N}_3\text{O}_4$) was first reported by Bamberger[4] as being the yellow precipitate that forms from combining aqueous solutions of nitroglyoxime and lead acetate, and is said to explode when ignited. Bamberger also formed explosive hydrazine, potassium and silver salts.

3.1 Nitroglyoxime

5 g glyoxime was dissolved into 150 mL diethyl ether and poured into a 250 mL measuring cylinder. Nitrogen dioxide was produced by reacting a piece of copper pipe with 85 mL of 70% nitric acid. This red gas was piped using PVC tubing into another flask to cool the gas and condense and trap any liquid, and from that flask into the measuring cylinder holding the glyoxime solution (Figure 7). The nitrogen dioxide was passed through the solution until the reactor was exhausted. The ether solution was filtered and evaporated in a 1000 mL wide form beaker in the sun until dry.

Figure 7: Nitroglyoxime apparatus



The only product obtained was a yellowish red explosive oil that smelled of nitrogen oxides and flashed when heated on a spoon.

To reclaim any nitroglyoxime that may have been present in the oil, it was poured into an aqueous solution of lead acetate. This produced a red solution and a small quantity of yellow precipitate that was filtered and dried. In small quantities the putative lead nitroglyoximate flashed when ignited from a flame (Figure 8). Glyoxime itself will not form a precipitate from lead acetate.

Figure 8: Ignition of 0.1 g putative lead nitroglyoximate

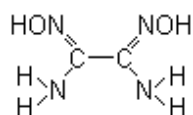


The synthesis of nitroglyoxime was also attempted by the action of N_2O_4 on solid glyoxime, when a stream of NO_2 was piped over the glyoxime in an improvised glass condenser cooled by NH_4NO_3/H_2O . The reaction was hypergolic, bursting into flames.

A review article by Riebsomer[6] shows reactions of nitrogen oxides with oximes, which mentions that the oxime/glyoxime groups themselves are open to attack from NO_2 . For example, the primary product of nitrogen dioxide acting on dimethyl, methyl, ethyl methyl and phenyl glyoxime in ether was a glyoxime peroxide containing a $\text{R}-\text{C}=\text{N}-\text{O}-\text{O}-\text{N}=\text{C}-\text{R}$ ring bound through the carbons. The reactions of glyoxime itself are not mentioned and no references to the glyoxime peroxide structure could be found in recent literature. In more recent literature[26] it is mentioned that the action of N_2O_4 on dinitroxyoxime forms dinitrofurazan. Dinitrofurazan is a sensitive liquid explosive that decomposes slowly at room temperature. This suggests that the explosive oil obtained above may have been an unstable nitrofurazan.

4 Diaminoglyoxime (DAG)

Figure 9: Diaminoglyoxime



Diaminoglyoxime, also known as oxamidoxime, has been prepared by numerous methods, such as from cyanogen and hydroxylamine[15], ammonolysis of dichloroglyoxime diacetate, from dibromofurazan and ammonia, by the reaction of dithiooxamide (rubeanic acid) with hydroxylamine[23], or glyoxime with hydroxylamine[24], but most conveniently in one step through the condensation of glyoxal and hydroxylamine[16]. DAG is soluble in hot water though difficultly soluble in cold water and alcohol[7] so is readily precipitated and recrystallised from aqueous solution.

4.1 Diaminoglyoxime from glyoxime

Into a beaker containing a solution of 20 g (0.5 mol) sodium hydroxide in 90 mL water was added 17.6 g (0.2 mol) glyoxime. 27.8 g (0.4 mol) hydroxylamine hydrochloride was then added in one portion. An improvised reflux condenser was added to the beaker (Figure 10) and it was heated in an oil bath at 90°C for 6 hours. After 6 hours the solution was cooled to room temperature which precipitated diaminoglyoxime as small fine needles (Figure 11) which were filtered and dried. The yield was 12.2 g (51%).

4.2 Diaminoglyoxime from glyoxal

140 g (3.5 mol) sodium hydroxide was dissolved into 400 mL water, the solution was cooled down to 0°C and 222 g (3.2 mol) hydroxylamine hydrochloride was added in portions with stirring. To the still cold solution was added 116 g (0.8 mol) of 40%

Figure 10: Reflux apparatus for glyoxime/glyoxal to diaminoglyoxime condensation

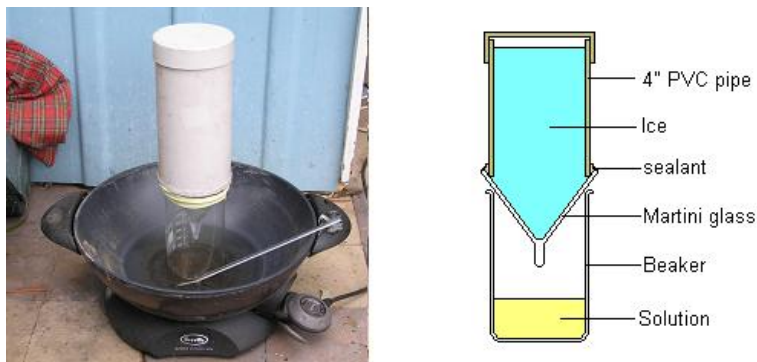


Figure 11: Precipitate of diaminoglyoxime



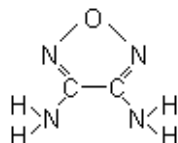
glyoxal in one portion. The solution was left in the freezer for 10 minutes then placed in an oil bath heated to 90-100°C (Figure 10) for 5 hours. After this time a precipitate had formed in the solution. It was taken off the heat and cooled to 0°C. The large crystalline precipitate was filtered, placed in another beaker and enough water was added to make up 400 mL of solution. This was boiled to redissolve the DAG then on slow cooling long straw-like crystals formed in the solution (Figure 12). These were filtered and dried. Yield after recrystallisation was 38 g (40%).

Figure 12: Recrystallisation of diaminoglyoxime



5 3,4-Diaminofurazan (DAF)

Figure 13: 3,4 Diaminofurazan



Diaminofurazan is the precursor to a wide range of energetic substances carrying the furazan ring. Furazans have many desirable properties for an energetic material such as its dense planar structure, stabilizing aromatic nature and energetic oxygen in the ring; many furazan derivatives also have a very high heat of formation.

DAF is formed from the base catalysed dehydration and cyclisation of diaminoglyoxime by aqueous sodium[23] or preferably potassium hydroxide[24, 18] at 180°C. Recently a convenient microwave mediated synthesis has also been reported[22].

DAF melts at 180°C, decomposes at 240°C and has a density of 1.61 g/cm³ [25].

5.1 Diaminofurazan

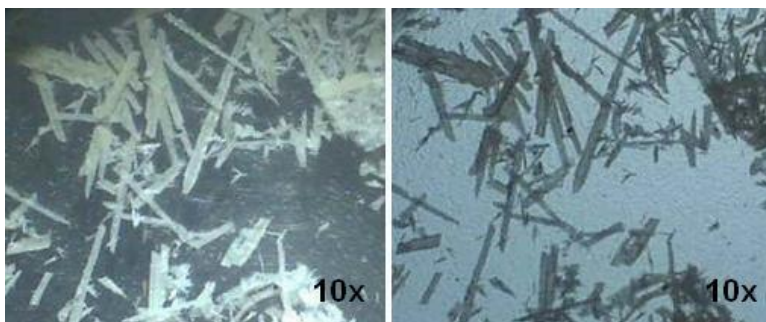
9 g potassium hydroxide was dissolved into 76 mL water, then poured over 24 g diaminoglyoxime in a stainless steel reactor (Figure 14). The reactor was made by weld-

ing together stainless steel water pipe fittings and had a capacity of 270 mL. The reactor was immersed into oil and heated up to 180°C. Cover 30 minutes and then left for two hours at 170-180°C. After this time the hotplate was then turned off and allowed to cool slowly. On opening the reactor a small amount of pressure was released and the solution smelled strongly of ammonia. A quantity of small white needle-like crystals (Figure 15) had precipitated which were filtered and dried. The yield was 8.6 g (42%) of DAF.

Figure 14: Stainless steel reactor



Figure 15: Crystals of 3,4-diaminofurazan in transmitted and reflected light



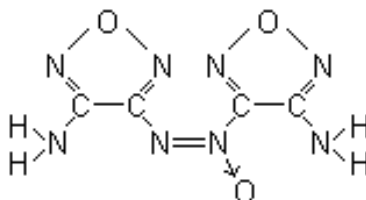
DAF, being a weak base, has been shown to form a nitrate salt. However, the weakly bound nitric acid is lost when drying under vacuum[5]. It also will form stable complexes with some metal salts such as with copper nitrate, $\text{Cu}(\text{DAF})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2$ [5].

Table 1: Comparative Properties of Explosives

	NM	TNT	DAAF	PETN	HMX	AAAF	HNIW	DNAF
Empirical Formula	CH ₃ NO ₂	C ₇ H ₅ N ₃ O ₆	C ₄ H ₄ N ₈ O ₃	C ₅ H ₈ N ₄ O ₁₂	C ₄ H ₈ N ₈ O ₈	C ₄ H ₂ N ₁₀ O ₃	C ₆ H ₆ N ₁₂ O ₁₂	C ₄ N ₈ O ₇
MW	61.04	227.14	212.15	316.15	296.18	238.16	438.23	272.12
Density (g/cm ³)	1.14	1.64	1.747	1.77	1.89	1.74 (calc.)	1.98 (beta cryst.)	1.91 (cryst.)
MP (°C)	-29	80.9	249 (dec.)	140	285	150 (dec.)	260	111
%OB	-39.31	-65.84	-52.79	-10.12	-21.61	-40.31	-10.95	-5.88
%N	23.0	18.5	52.8	17.7	37.8	58.8	38.4	41.2
Impact sensitivity (cm @ 2.5 ^{1/2} wt)	>320	148	>320	13	32		17-21	7.8
Friction sensitivity (kg)				6.4				6.4
Electrostatic sensitivity (J)				1.25				0.45
VOD (m/s)	6350	6930	8020 (meas.)	8260	9110	9400 (calc.)	9380 (calc.)	9800 (calc.)
P _c (kbar)	144 (calc.), 125 (meas.)	223 (calc.), 210 (meas.)		332 (calc.), 390 (meas.)	394 (calc.), 390 (meas.)	426 (calc.)	428 (calc.)	458 (calc.)
ΔH _f (kcal/mole)	-27	-16	+100.8	-128	+17.93		+99.9	+154
ΔH _f (cal/g)	-442	-70.5	+475.1	-407	+60.5		+228	+568.5
References	[13]	[13]	[8, 9, 14]	[11, 13]	[13]	[18]	[12]	[10, 11]

6 3,3'-Diamino-4,4'-azoxyfurazan (DAAF)

Figure 16: 3,3'-Diamino-4,4'-azoxyfurazan



While DAAF is yet to find commercial or military use due to limited commercial production, its explosive properties (Table 1) show it to be a practical and powerful explosive. DAAF has a relatively high density, low sensitivity to impact and a high velocity of detonation. DAAF also has acceptable thermal stability, melting with decomposition at 249°C[14].

DAAF is formed by the oxidation of DAF by a mixture of hydrogen peroxide and sulphuric acid[9].

6.1 3,3'-Diamino-4,4'-azoxyfurazan

Into 15 g 50% hydrogen peroxide was added 10 g crushed ice, then 14 g sulphuric acid was dripped in while maintaining the temperature below 20°C. This solution was then poured over 2.5 g diaminofurazan in a 80 mL beaker. The suspension was stirred by use of a drill press, whereby the DAF went into solution imparting a green colour from the formed soluble nitroso compound. Within an hour the green colour gave way to orange due to a fine precipitate of DAAF (Figure 17). The solution was stirred for 9 hours then left for a further 15 for a total of 24 hours. The mixture was then diluted with an equal volume of water, filtered to recover fine orange crystals (Figure 18), washed with 200 mL of cold water and dried. Yield after bottling was 1.5 g (57%).

Further oxidation of amine groups on DAAF results in the extremely powerful explosive 3,3'-dinitroazoxyfurazan. DNAF's explosive properties rate it as one of the most powerful of the conventional explosives with exceedingly high velocity of detonation, very high heat of formation and good oxygen balance. DNAF is also castable, melting at 110-112°C and boiling at 270°C[18]. However, its main fault is its high sensitivity to impact, being nearly twice as sensitive as PETN, which would limit practical use. DNAF's explosive properties are listed in Table 1.

The literature methods for DAAF oxidation to DNAF require ammonium persulphate[18, 19] or sodium persulphate[8]; with hydrogen peroxide and sulphuric acid, yield was 60%. DNAF can also be formed in by direct oxidation of 3,3'-diamino-4,4'-azofurazan or DAF, but with reduced yield (15% & 4% respectively[18]).

7.1 3,3'-Dinitro-4,4'-azoxyfurazan

Into a 250 mL conical beaker was added 27.5 g 50% hydrogen peroxide diluted with 17.5 mL water. It was then chilled to 5°C. 30 g ammonium persulphate was then dissolved into the peroxide solution and left to cool in the freezer. Another solution was made by dissolving 2.5 g DAAF into 32 g 98% sulphuric acid and was slowly added to the cooled peroxide solution while maintaining the temperature below 20°C. On addition the DAAF precipitated as a very fine orange suspension. The beaker was then placed in an oil bath heated to 40°C and stirred by use of a drill press (Figure 20). Good stirring must be used to churn the foam that is created during the oxidation. This was maintained for 8 hours, the orange solution turning bright yellow. The solution was then drowned in 200 mL ice cold water and filtered, flushed with more water then dissolved into 150ml dichloromethane, the DCM solution was then washed with dilute sodium bicarbonate/water solution. The yellow DCM solution was then separated and evaporated to yield yellow crystals of DNAF (Figure 20). Yield was 1.3 g (40%).

The DNAF was pressed into a drinking straw, taped to a lead block, buried under sand and detonated. PETN detonating cord was used for comparison (Figure 21). When touched with a match DNAF will melt then ignite and burn vigorously with a luminous smokeless flame (Figure 22).

Figure 20: Oxidation of DAAF to DNAF (left); DNAF crystals (right).



Figure 21: DNAF & PETN detonated against lead block

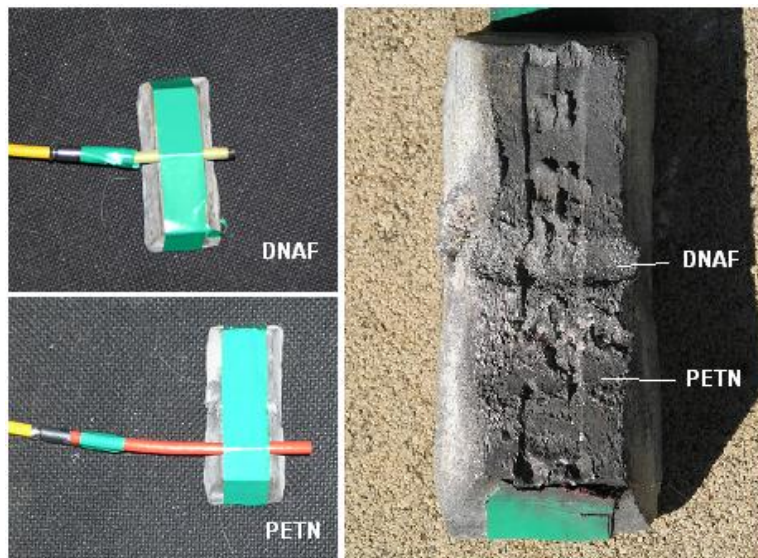
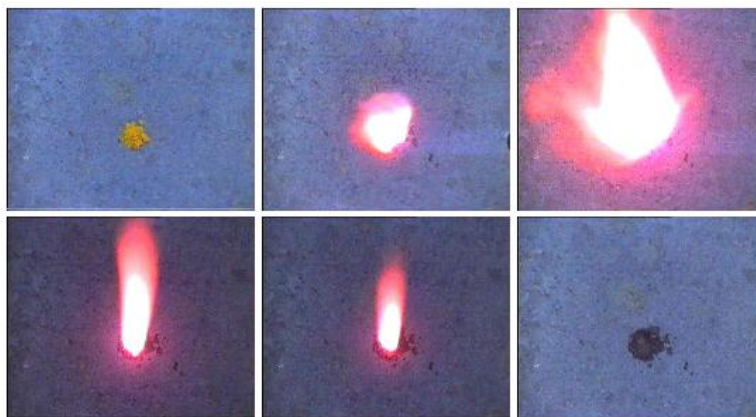
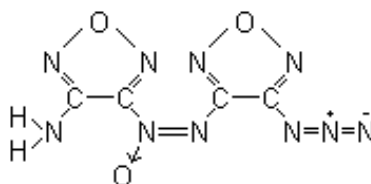


Figure 22: Ignition of DNAF

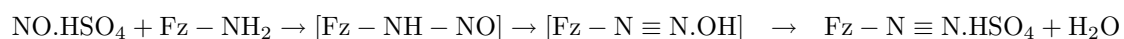


8 3-amino-3'-azido-4,4'-azoxyfurazan (AAAF)

Figure 23: 3-amino-3'-azido-4,4'-azoxyfurazan



DAAF, being a basic, aromatic primary amine is open to diazotisation and subsequent reactions. The azido and diazido derivative of DAF is known to the literature[18, 21]. DAAF like DAF has only weakly basic properties thus diazotisation must be carried out in nitrosylsulphuric acid, and the formed diazonium sulphate salt of these furazans is not stable enough to be isolated[20]. AAAF is formed by reacting a 3-amino-4,4'-azoxyfurazan-3'-diazonium sulphate solution with sodium azide[18].



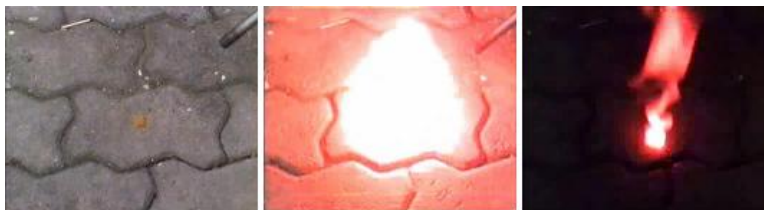


The substitution of one amino group with an azido group greatly increases the energetic potential of DAAF with AAAF having calculated explosive properties similar to that of HNIW (Table 1). The crude un-neutralized product on drying turned from light yellow to orange, and flashed on ignition by flame (Figure 24).

8.1 3-amino-3'-azidoazoxyfurazan

1 g (15 mmol) sodium nitrite was dissolved in 28 g 98% sulphuric acid and combined with a solution of 1.1 g (5 mmol) DAAF in 18 g 98% sulphuric acid while keeping temperature at 0-5°C. Maintaining the temperature at 0-5°C the combined solution was diluted with 26 g glacial acetic acid, then with good cooling was treated with 1 g (15 mmol) sodium azide in 20 g water drop by drop over 30 minutes, not letting the temperature rise over 5°C. On addition of the sodium azide the solution foamed with release of nitrogen and turned from dark orange to light yellow. The solution was then left for a further 15 minutes then drowned in 300 mL cold water. A light yellow precipitate of AAAF was filtered, flushed with water and dried. The yield was 0.6 g.

Figure 24: Ignition of AAAF



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*Thanks go to CHRIS THE GREAT for sourcing references [8, 11, 19, 24].
Thanks also go to CHEMOLEO for translating references [1] and [3].*