FOX-7 (1,1-Diamino-2,2-dinitroethene)

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Abstract In this paper, the discovery and synthesis of the explosive 1,1-diamino-2,2-dinitroethene (FOX-7) are described, together with an account of its structural, spectroscopic, and explosive properties. The chemical reactivity of FOX-7 towards nucleophilic substitution (transamination), electrophilic substitution, and acid-base properties is explored, as is its thermal behavior (phase transformations and thermal decomposition). The molecular structure and physical properties of FOX-7 are compared with those of its three isomers (as yet unsynthesized), as derived by theoretical calculations. Finally, the physical properties of FOX-7 are compared to those of various energetic molecules that are structurally related to FOX-7.

Keywords 1,1-Diamino-2,2-dinitroethene · FOX-7 · Synthesis · Properties · Reactions · Isomers · Related molecules

1
Introduction

For more than half a century, the main explosive component of artillery shells and other explosive devices has been RDX (1,3,5-trinitro-1,3,5-

triazacyclohexane, **1**). While RDX was not the most energetic material available during most of this period, it was relatively easy to produce, in a single step, from commonly available reagents, namely hexamethylenetetramine (hexamine), nitric acid, and, in most processes, acetic anhydride. However, RDX exhibits several unsatisfactory properties when used as a high explosive. It is sensitive to impact, friction, electrostatic discharge and heat, and it is this sensitivity that has been the cause of many very serious accidents where ordnance has either suffered direct impact by enemy fire or been subjected to heating in fires. Consequently, during the past 25 years there has been a search for replacement explosive materials that are at least as energetic as RDX but at the same time are much less sensitive to external stimuli. One such potential replacement is the simple molecule 1,1-diamino-2,2-dinitroethene, also known as FOX-7 (**2**).
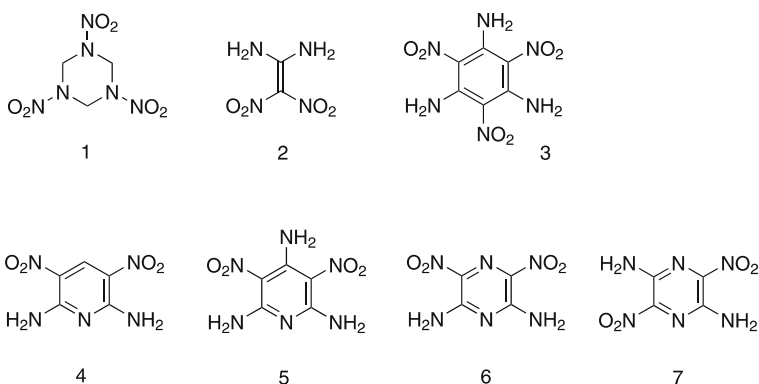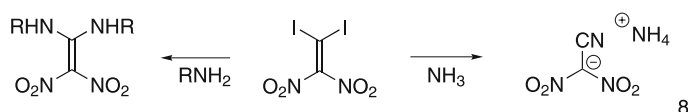

1,1-Diamino-2,2-dinitroethene is structurally similar to several other known energetic molecules. For example, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, **3**) possesses a similar juxtaposition of amino and nitro groups, as do 2,6-diamino-3,5-dinitropyridine (DADNP, **4**), 2,4,6-triamino-3,5-dinitropyridine (TADNP, **5**), 2,6-diamino-3,5-dinitropyrazine (**6**) and 2,5-diamino-3,6-dinitropyrazine (**7**). TATB in particular is known to be extremely insensitive to external stimuli. These relatives of 1,1-diamino-2,2-dinitroethene are however not easily manufactured and involve multi-step processes. What makes 1,1-diamino-2,2-dinitroethene particularly attractive as a replacement for RDX is the relative ease with which it can be synthesized in what is basically a single-step process.

Although 1,1-diamino-2,2-dinitroethene appears to have been originally isolated by Russian workers, its first reported synthesis in the scientific literature was by workers at the Swedish Defence Research Agency (FOI, formerly FOA). Indeed, the name FOX-7 derives from the acronym FOA, with X corresponding to explosive, as in RDX, etc.

2
Historical Development

An initial attempt to synthesize 1,1-diamino-2,2-dinitroethene was made by Baum et al. [1] during their study of the reaction of 1,1-diiodo-2,2-dinitroethene with various amines. Many amines were found to react to give replacement of both iodine atoms by amine functions, the final product being the corresponding 1,1-bis(alkylamino)-2,2-dinitroethene (Scheme 1). It was therefore logical to expect ammonia itself would react in the same manner to give 1,1-diamino-2,2-dinitroethene. However, the product from treatment of 1,1-diiodo-2,2-dinitroethene with ammonia was not 1,1-diamino-2,2-dinitroethene, but the ammonium salt of cyanodinitromethane (**8**).

**Scheme 1** Reactions of 1,1-di-iodo-2,2-dinitroethene

The first successful synthesis of 1,1-diamino-2,2-dinitroethene was reported in 1998 [2] by the group from FOI. It was initially isolated in low yield after hydrolysis of the product mixture obtained from the mixed acid (nitric and sulphuric acid) nitration of 2-methylimidazole (**9**). The choice of reaction conditions is rather critical. Nitration with nitric acid in 101–105% sulphuric acid gave a mixture of parabanic acid (**10**) and 2-methyl-4-
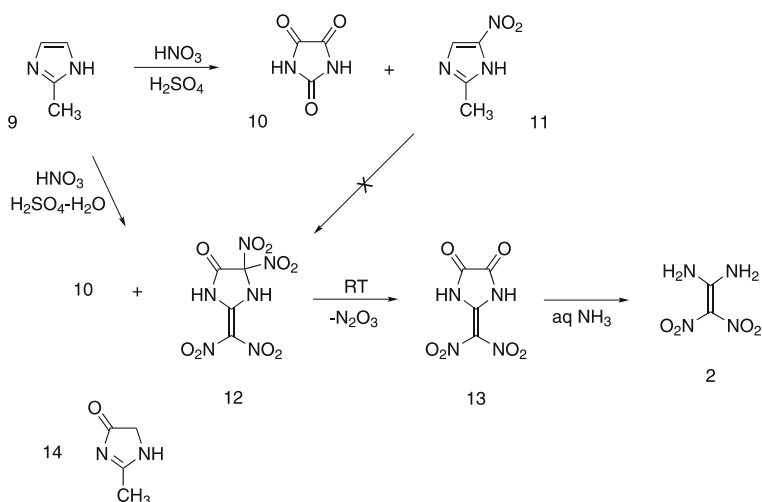
Scheme 2 Nitration of 2-methylimidazole (**9**)

nitroimidazole (**11**), but when 80–100% sulphuric acid was used, the products were parabanic acid and 2-dinitromethylene-4,4-dinitroimidazolidin-5-one (**12**). The latter separated from the reaction medium and was filtered off. It was found to be thermally unstable and lost the elements of N_2O_3 to form 2-dinitromethyleneimidazolidine-4,5-dione (**13**). The dione was subsequently hydrolyzed with aqueous ammonia to give 1,1-diamino-2,2-dinitroethene and oxalate (Scheme 2). A number of control experiments showed that 2-methyl-4-nitroimidazole was not an intermediate in the formation of 2-dinitromethylene-4,4-dinitroimidazolidin-5-one, but that 2-methyl-4,5-dihydro(1*H*)imidazol-4-one (**14**) probably was.

A more direct (but related) route to 1,1-diamino-2,2-dinitroethene was also reported in the same paper [2]. This involved nitration of the methanol adduct of 2-methylimidazolidine-4,5-dione (**15**, synthesized from acetamidine hydrochloride and diethyl oxalate, followed by recrystallization from methanol). This gave 2-dinitromethyleneimidazolidine-4,5-dione (**13**, 67% yield), which, on hydrolysis with aqueous ammonia, gave 1,1-diamino-2,2-dinitroethene (87%; 37% overall from acetamidine hydrochloride, Scheme 3).
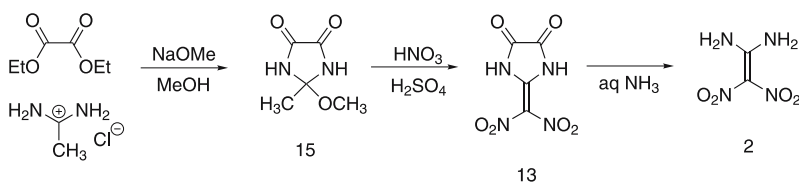
Scheme 3 Synthesis and nitration of 2-methylimidazolidine-4,5-dione (**15**)

Further development work [3, 4] has shown that nitration of the analogous 4,6-dihydroxy-2-methylpyrimidine [**16** ≡ 2-methylpyrimidine-4,6(1*H*,5*H*)-dione], which is commercially available, gives a better overall yield of 1,1-diamino-2,2-dinitroethene than 2-methylimidazolidine-4,5-dione (Scheme 4). In this case, the nitrated intermediate that separates is 2-dinitromethylene-5,5-dinitrodihydropyrimidine-4,6(1*H*,5*H*)-dione (**17**). To effect hydrolysis to 1,1-diamino-2,2-dinitroethene, the unfiltered slurry may be simply added to water and left for several hours. The product separates out as it is formed and is finally filtered off and washed. However, in view of the need to recycle the nitrating acids, it is preferable to filter off the solid intermediate, leaving a controlled amount of sulfuric acid on the solid, and adding the acid-damp solid to water for hydrolysis [5]. Using this modification and optimized conditions, the yield of 1,1-diamino-2,2-dinitroethene is over 90%.

The C-5 fragment of the nitrated intermediate (when 4,6-dihydroxy-2-methylpyrimidine is the starting material) is released during the hydrolysis as dinitromethane. If desired, this may be extracted into diethyl ether from the filtrate and precipitated as its potassium salt, or alternatively it may be left to
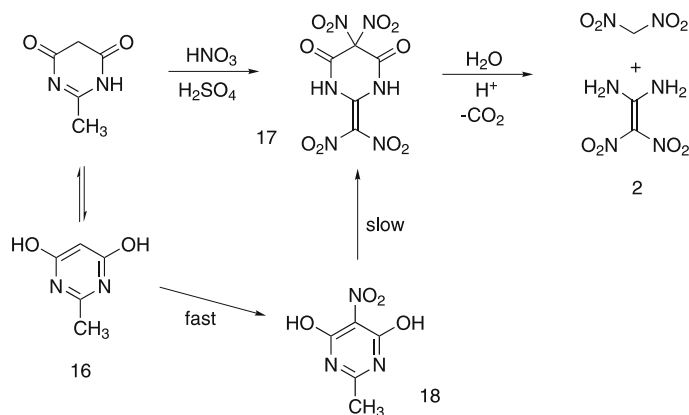
Scheme 4 Nitration of 4,6-dihydroxy-2-methylpyrimidine (**16**)

decompose in the filtrate. However, on a large scale, there may be unacceptable risks involved in either procedure; in theory, there are ~ 7 kg (in practice ~ 5.5 kg) of dinitromethane generated for every 10 kg of 1,1-diamino-2,2-dinitroethene produced. At present, this is probably the major disadvantage in using 4,6-dihydroxy-2-methylpyrimidine as the starting material.

The course of the nitration of 4,6-dihydroxy-2-methylpyrimidine has been shown [6] to involve rapid nitration at C-5 to form 4,6-dihydroxy-2-methyl-5-nitropyrimidine (**18**), followed by slow further nitration, probably initially also at C-5. Further nitration is then rapid, no intermediates other than 4,6-dihydroxy-2-methyl-5-nitropyrimidine being detected.


3
Structural Properties of FOX-7

FOX-7 exists as a canary-yellow solid and may be recrystallized from a variety of solvents, dimethylsulphoxide-water, *N*-methylpyrrolidin-2-one-water and dilute HCl being commonly employed. Scanning Electron Micrograph (SEM) images of FOX-7 crystals, both before and after recrystallization from 0.5 M HCl, are presented in a DSTO report by Lochert [7]. The single-crystal X-ray structure was determined on material that had crystallized from *N,N*-dimethylformamide in the monoclinic form [8, 9]. The molecular structure (Fig. 1 [10]) exhibits bond lengths and angles that are typical for a so-called "push-pull" alkene [1]. Specifically, the $C = C$ bond length is 1.456 Å, intermediate between that of a $C - C$ single bond (1.54 Å) and that of a normal $C = C$ double bond (1.34 Å). Other changes resulting from the effect of the electron-donating amino groups on C-1 and the electron-withdrawing nitro groups on C-2, are the shorter-than-normal $C - NH_2$ bonds (1.31 and 1.32 Å)
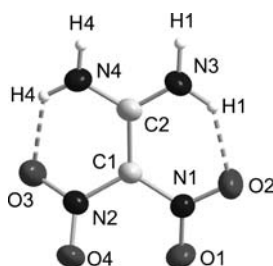
Fig. 1 FOX-7

and C – NO$_2$ bonds (1.42 and 1.39 Å) and the essentially planar structure of the molecule as a whole (average C – C torsion angle 4.8°). Two strong hydrogen bonds exist between NH and NO on both sides of the molecule. There are four molecules per unit cell whose dimensions are: a 6.941 Å, b 6.569 Å, c 11.315 Å, β 90.55°, V 515.9 Å^3, Dx 1.907 Mg m^{-3}.

The supramolecular arrangement of molecules within the crystal is in the form of wave-shaped infinite layers (Fig. 2 [10]), akin to that observed for graphite and triaminotrinitrobenzene (TATB), with intra-layer N – H...O – N hydrogen bonding and inter-layer van der Waals interactions. The distance between layers is $\sim$ 3 Å cf. the layer separation in graphite is $\sim$ 3.5 Å, while that in TATB is $\sim$ 6 Å. The extensive network of hydrogen bonding is probably the reason why 1,1-diamino-2,2-dinitroethene is only slightly soluble in many common solvents (acetone, acetic acid, ethyl acetate, nitromethane, acetonitrile – all < 0.5 g/ml at 20 °C), the greatest solubility being exhibited in *N,N*-dimethylformamide, *N*-methylpyrrolidin-2-one and dimethylsulphox-
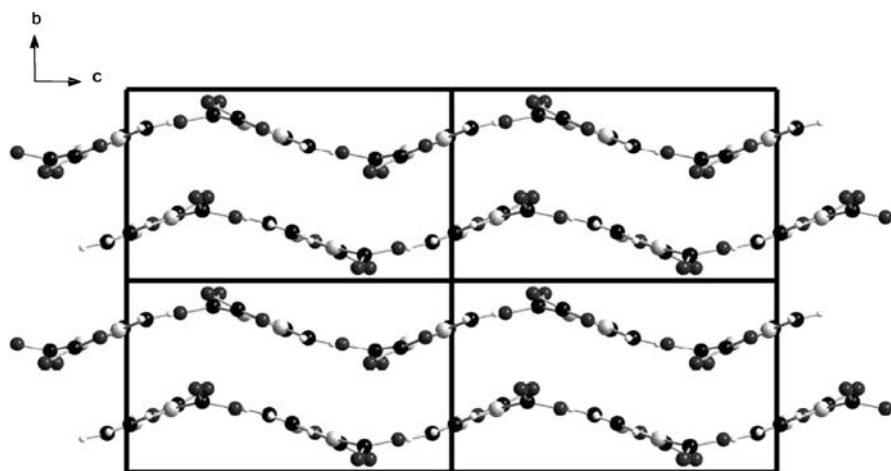
Fig. 2 Crystal structure of FOX-7

ide (21, 32 and $\sim$ 45 g/100ml at 20 °C respectively). It is essentially insoluble in water.

An X-ray diffraction (XRD) study, combined with a range of thermal analysis techniques [differential scanning calorimtery (DSC), thermogravimetry (TG) and thermomechanical analysis (TMA)] [11, 12], has been applied to powdered 1,1-diamino-2,2-dinitroethene [recrystallized from *N*-methyl-pyrrolidinone (NMP)-water]. This has shown that several other crystalline phases exist which are formed on heating the normal α-polymorph. The first phase transition ($\alpha \rightarrow \beta$) is completely reversible (as observed by DSC) and occurs at 113 °C. A second transition ($\beta \rightarrow \gamma$) occurs at 173 °C, but this is only partially reversible (no reverse transition is observed by DSC until the region for the $\beta \rightarrow \alpha$ transition). Above 200 °C the material begins to decompose (Sect. 4 below). This study also reported the crystallographic parameters for both the α- and the β-polymorphs. The data for the former agreed closely with those reported earlier [8, 9]. The β-polymorph is of the orthorhombic type and there are four molecules per unit cell whose dimensions are: *a* 6.978 Å, *b* 6.638 Å, *c* 11.660 Å, β 90°, *V* 540.1 Å^3. The supramolecular arrangement of molecules within the crystal of the β-polymorph is also in the form of wave-shaped infinite layers. The two polymorphs are thus very similar in internal structure. The $\alpha \rightarrow \beta$ transition is accompanied by a volume increase ($\equiv$ density decrease) of 1.9%. This might be of significance during the storage of munitions containing FOX-7, although the temperature required to effect this change is rather high.

Thermogravimetry (TG) indicated a 2% mass loss at around 160 °C on the first heating cycle, with no mass loss on repeated temperature cycling. This was attributed to a possible loss of solvent. NMP is known [13] to become occluded when FOX-7 is recrystallized from NMP-water.

A more detailed crystallographic study of the $\alpha \rightarrow \beta$ transition has recently been published [14]. This gives full crystallographic data for a single crystal (recrystallized from *N,N*-dimethylformamide or dimethylsulphoxide) of FOX-7 at 5 temperatures in the range – 73 to + 120 °C, the α (monoclinic) $\rightarrow \beta$ (orthorhombic) transition being observed between 100 and 120 °C. Powdered FOX-7 was also studied at 130 and 150 °C. Below the transition temperature the thermal expansion of the unit cell is mainly along the *b* axis i.e. between the layers, but during the transition it is the *c* axis which changes most. The volume change at this point is 1.8 cm^{-3} mol^{-1} ($\sim$ 2%). After the transition it is again the *b* axis which is most responsible for the volume change in the unit cell. The crystallographic parameters were unchanged after the $\alpha \rightarrow \beta \rightarrow \alpha$ transitions; after cooling to 20 °C the crystal was still clear and transparent demonstrating that the volume change at the transition had not caused sufficient strain to fracture the crystal. Significantly for the results reported by other workers (see below), no discontinuous changes were observed in the *a*, *b* and *c* cell parameters at temperatures below 100 °C.

In the layered structure (a–c plane) of both polymorphs, the molecular units are held head-to-tail by hydrogen bonds. For the α-polymorph, there are two $N-H...O-N$ hydrogen bonds to each nitro group oxygen (8 in total, of which 6 are intermolecular and 2 intramolecular). For the β-polymorph, one oxygen of each nitro group is involved in 2 hydrogen bonds while the other oxygen is involved in 3 hydrogen bonds (10 in total, of which 8 are intermolecular and 2 intramolecular). Within each FOX-7 molecule both C atoms and both amino N atoms lie within a plane. The two nitro N atoms are slightly out of the plane, while the four oxygen atoms deviate more significantly from the plane.

The $\alpha \rightarrow \beta$ transition is clearly observed by DSC as an endothermic peak at $116.3\,°C$ (onset $114.2\,°C$, $\Delta H = 18.0 \pm 1.5\,\mathrm{J\,g^{-1}}$). The general picture of phase changes for FOX-7 therefore appears to be:

$$\alpha \xrightarrow[113-116\,°C]{} \beta \xrightarrow[173\,°C]{} \gamma\,.$$
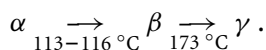
Three other studies, two of them being chronologically earlier than the above work [15–18], report somewhat different observations. Here the temperatures given for the first two transitions are markedly lower, and one further transition is observed. The first phase transition (designated $\alpha \rightarrow \beta$) is here reported to occur at $90\,°C$ and was only detected by X-ray diffraction; it is not visible by DSC. Again a small decrease in density ($1.885 \rightarrow 1.803 \equiv$ increase in volume) is observed. The second transition (designated $\beta \rightarrow \gamma$) occurs at $115\,°C$ (DSC endotherm at $117\,°C$), and a further transition (designated $\gamma \rightarrow \delta$) occurs at $155\,°C$ (DSC endotherm around $155\,°C$). The reverse transitions ($\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$) occur on cooling, but while the $\beta \rightarrow \alpha$ transition is instantaneous, the $\gamma \rightarrow \beta$ (and hence α) transition may take days or even weeks. The second of these studies [16] also demonstrated how particle size can affect the temperature and the rate at which phase transitions occur. For example it was reported that the first transition temperature can vary between $\sim 78\,°C$ (for very fine particles) and $\sim 95\,°C$ (for coarse particles), but the rate ($\sim 3\,h$ for the complete transition) is unaffected by particle size, while the reverse is true for the second transition temperature ($116\,°C$) i.e. the transition temperature is not affected by particle size, but the rate is ($10\,h$ and $14\,h$ for fine and coarse particles respectively). The average enthalpy changes involved in the second and third transitions (those visible by DSC) were reported as 21.6 and $17.1\,\mathrm{J\,g^{-1}}$ respectively [17, 18].

Although the FOX-7 samples used in the first two of these three studies [15, 16] were stated to have been recrystallized from dimethylsulphoxide, the behavior described is similar to that of unrecrystallized FOX-7. A broad DSC endotherm at $90-110\,°C$ is the normal observation for unprocessed FOX-7 (Latypov, personal communication), and this is replaced by an endotherm at $113\,°C$ on recrystallization. The TG analysis reproduced in one of the studies [16] shows no mass loss i.e. loss of solvent, in the region of $160\,°C$,

which would have been expected if the material had been recrystallized, again suggesting that unrecrystallized material might have been used. The origin, but not the history of the sample used in the more recent study [17, 18] is reported. It may or may not have been recrystallized at source.

In the absence of more definite information on the pre-treatment of the samples used in the earlier work [15, 16], one is tempted to conclude that the differences in the results reported stem from the differences between the crystallographic nature of unrecrystallized and recrystallized material. Unrecrystallized material will have separated from a rather different medium (acidic aqueous medium) to that used in a recrystallized sample, and at a different rate. Its internal structure may therefore be somewhat different. At the present time (2006) some confusion exists regarding which phase change, if any, occurs below 100 °C, but the transition observed at around 115 °C in all studies [11, 12, 14–18] appears to be the $\alpha \rightarrow \beta$ change (but designated $\beta \rightarrow \gamma$ in [15–18]).

4
Thermal Decomposition of FOX-7

The thermal behavior of FOX-7 at temperatures below 200 °C has already been described above. As the temperature is increased above 200 °C, decomposition, without melting, begins to occur. The appearance of the DSC curve in this region is rather variable and appears to depend upon the history of the sample. Even samples from the same batch may give different DSC curves. For example it has been reported [16] that a sample (1.5 mg) of fine crystals (10 K min^{-1}) exhibited two exotherms, one at $\sim$ 235 °C and another at $\sim$ 275 °C, while another sample from the same batch consisting of a single large crystal (1.5 mg) exhibited a single exotherm at $\sim$ 240 °C. Decomposition is normally complete by 300 °C.

The results from several other groups [17–21] support the general picture of two exothermic DSC peaks (Fig. 3, 10 K min^{-1}, recrystallized sample), with the peak positions and relative size being dependent upon the history of the sample. TG and differential thermal analysis (DTA) results indicate that the mass loss and energy evolution associated with the two DSC exotherms are $\sim$ 38% and 909 J g^{-1} for the low temperature peak, and $\sim$ 45% and 518 J g^{-1} for the high temperature peak [21]. However from what has already been reported above, the figures would probably differ for other FOX-7 samples. In order to examine the processes causing the two DSC peaks, Tiemanis et al. [21] heated a 1 g sample of FOX-7 for 3 days at 185 °C, after which the mass loss was 37%. This sample was then examined thermoanalytically and spectroscopically. By DTA it exhibited a single exotherm at approximately the same temperature as the second exotherm of FOX-7, but no lower temperature phase changes were observed. By TG the mass loss associated
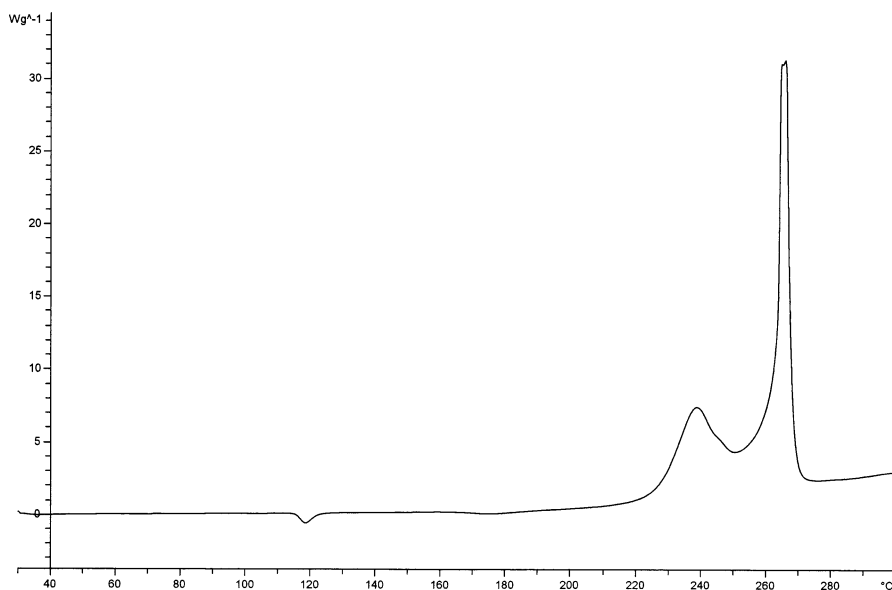
Fig. 3 DSC ($10\,\mathrm{K\,min^{-1}}$) of recrystallized FOX-7

with the exotherm was $\sim 70\%$. Spectroscopic examination (by ^{1}H, ^{13}C and ^{15}N NMR and FTIR) indicated that the material was essentially FOX-7. This was confirmed by HPLC and powder X-ray diffraction. The authors' suggested explanation for these somewhat surprising results is that the original sample of FOX-7 may have consisted of two phases, part crystalline (detected by XRD) and part amorphous (not detected by XRD), and it is the amorphous phase that decomposes during the first DSC peak leaving the original crystalline part. They point out that the relative amounts of these two phases should vary with the previous processing conditions. Their explanation is supported by the observation that recrystallization of the heat treated material gave FOX-7 which exhibited the normal phase changes on DTA analysis, and the double step mass loss at 200–300 °C on TG analysis.

The actual products formed during decomposition in both decomposition steps have been identified [17, 18] by FTIR as CO_2, HCN, N_2O, NO_2, HOCN, H_2O and NO, while HNO_2 and HCOOH are produced in the second decomposition only. The apparent activation energies for the two steps are reported as 238.3 and 322.4 kJ mol^{-1}, respectively.

5
Spectroscopic Properties of FOX-7

Most of the common spectroscopic data for FOX-7 were reported in the original FOI publication [2]. Nuclear Magnetic Resonance (NMR) spectroscopic data were obtained in dimethyl sulphoxide (DMSO–d$_6$). The ^{1}H spectrum (Fig. 4a) shows a single broad peak (at 8.77ppm) for all 4 NH nuclei, while the ^{13}C spectrum (Fig. 4b) exhibits 2 peaks at 128.5 [C(NO$_2$)$_2$] and 158.8 ppm
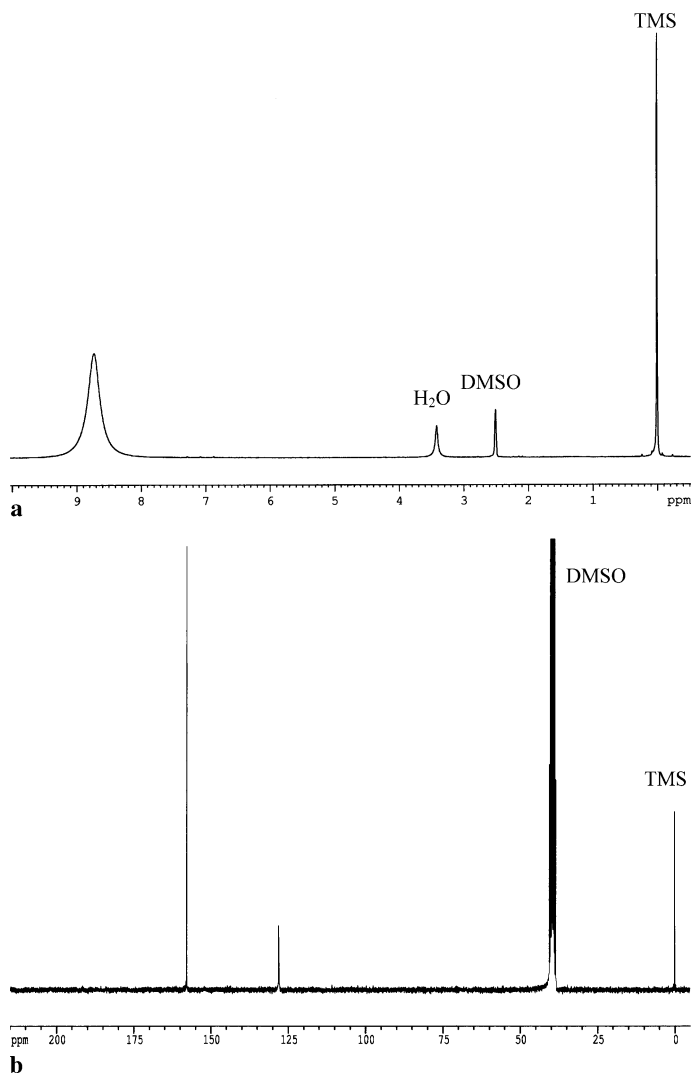
Fig. 4 a ^{1}H NMR spectrum of FOX-7, **b** ^{13}C NMR spectrum of FOX-7

[C(NH$_2$)$_2$] [2], the former being significantly less intense (can be as low as 10–15% relative intensity) than the latter. Carbon atoms with nitro groups attached normally give low intensity peaks. The relative peak positions reflect the strong polarization of the electrons of the C $=$ C bond towards the carbon with nitro groups attached, causing greater shielding of that carbon
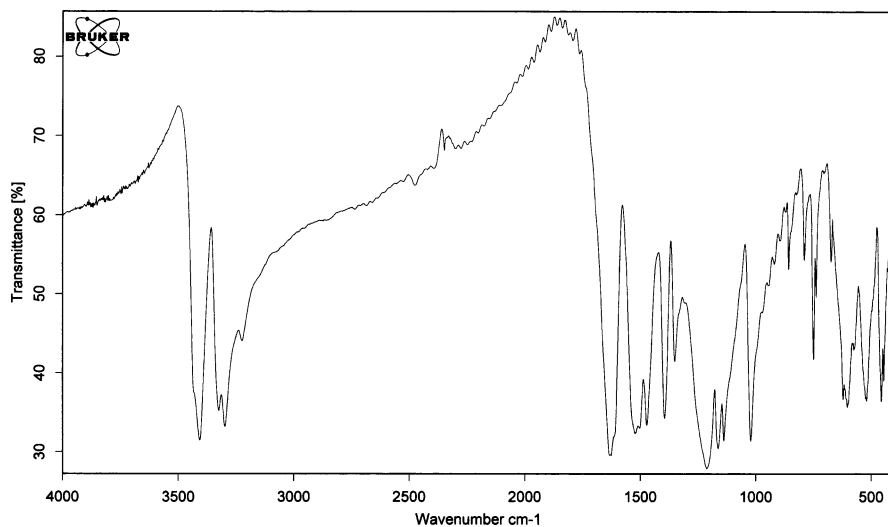
Fig. 5 FTIR spectrum of FOX-7
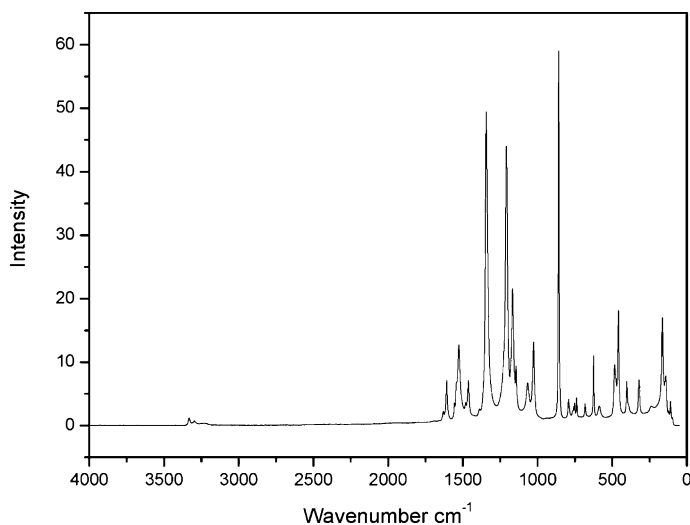
Fig. 6 Raman spectrum of FOX-7

relative to that of the carbon bearing the amino groups. In the ^{15}N spectrum absorptions occur at – 24.0 (NO_2) and – 276.6 ppm (NH_2) [21].

The infrared spectrum of solid FOX-7 (KBr disc, Fig. 5) exhibits [2] peaks at 3417 (NH_2), 3315 (NH_2), 3200 (NH_2), 1638 (NH_2), 1524 (NO_2), 1471, 1400, 1356 (NO_2), 1234, 1176, 1143, 1027, 752, 652, 521, 462 cm^{-1}. The Raman spectrum of solid FOX-7 (neat) is shown in Fig. 6 [10].

FOX-7's ultraviolet spectrum (in water) exhibits three maxima, 210 (ε9500), 278 (ε5000) and 346 nm (ε11 300) (Latypov, unpublished results).

The mass spectrum (70 eV) exhibits a very strong molecular peak at m/z 148 (M$^+$). A more detailed study [16] reported that the intensity of the parent ion peak indicated that this species was more stable than those encountered with other energetic molecules e.g. RDX, TNT. At both 20 and 70 eV there were peaks at m/z 148, 130 and 18, indicative of loss of H_2O, as also observed with TATB.

6
Explosive Properties of FOX-7

As mentioned in an earlier section, the main international interest in FOX-7 has been as a replacement for the secondary explosive RDX [22]. This section will therefore compare the explosive properties and performance of FOX-7 against that of RDX. Table 1 lists some of the relevant explosive properties for FOX-7 and RDX, and these should help to demonstrate why FOX-7 is an attractive alternative to RDX.

The main reason for requiring a replacement for RDX is that it is a rather vulnerable explosive material with relatively high sensitivity to both impact and friction. By contrast, FOX-7 is much less sensitive to impact and very insensitive to friction. But it is not just sufficient for a replacement explosive to be less sensitive. It must also be capable of performance comparable to that of RDX. In this regard, FOX-7 is a good candidate. While the detonation velocity and detonation pressure are slightly below those of RDX, the maximum density is greater (1.88 versus 1.82 g cm^{-3}), which means that a greater mass ($\sim$ 3%) of explosive material, and potentially more energy, can be contained within a given volume. However, this must be set against the enthalpy of formation of FOX-7 which is negative, while that of RDX is positive. Since both FOX-7 and RDX have the same oxygen balance (– 21.6%), having the atom ratios [$C_nH_{2n}N_{2n}O_{2n}$; $n = 2 \rightarrow$ FOX-7, $n = 3 \rightarrow$ RDX], it appears that FOX-7 contains less energy than RDX. So how large is this difference and in practice is it significant? An attempt to estimate this is made below, but it should be remembered that the actual ΔH_f° values used for FOX-7 and RDX in these calculations may be critical. The values of ΔH_f° that have been reported [25] are surprisingly variable [ΔH_f° (FOX-7) – 53 to – 134 kJ mol^{-1} and ΔH_f° (RDX) + 60 to + 79 kJ mol^{-1}]. The values selected for use below [– 130

Table 1 Some relevant explosive properties of FOX-7 and RDX

Property	FOX-7	RDX
Molecular formula	$C_2H_4N_4O_4$	$C_3H_6N_6O_6$
Molecular mass	148	222
Density (g cm^{-3})	1.88	1.82
Enthalpy of formation (kJ mol^{-1})	– 130 [23]	+ 67 [23]
Oxygen balance (to CO_2, %)	– 21.6	– 21.6
Decomposition temperature (ARC onset, °C)	219–223 [24]	195–199 [24]
Detonation velocity (experimental, m s^{-1})	8870 [22]	8930 [22]
Detonation pressure (calculated, GPa)	33.96 [22]	34.63 [22]
Impact sensitivity		
Dropweight test (BAM, 2 kg, cm)	126 [16]	38 [16]
Rotter Impact (F of I)	110–140 [7]	80 [7]
Friction sensitivity (Julius–Petri, > 35 kp)	> 350 [16]	120 [16]
Electrostatic Discharge Test	4.5 J ignition, 0.45 J no ignition [7]	4.5 J ignition, 0.45 J no ignition [7]

FOX-7: 1,1-diamino-2,2-dinitroethene
RDX: 1,3,5-trinitro-1,3,5-triazacyclohexane

and + 67 kJ mol^{-1}, respectively] were selected because they were both from the same reference [23].

In order to estimate the amount of energy available for release on detonation, we need to apply the Wilson–Kistiakowsky rules [26], which state that (for an explosive with an oxygen balance not below – 40%; FOX-7 and RDX, with oxygen balances of – 21.6%, both fall within this group):

(i)   carbon atoms are converted to CO
(ii)   any remaining oxygen is used to convert hydrogen atoms to H_2O
(iii) any oxygen remaining after (ii) is satisfied is used to convert CO to CO_2
(iv) all nitrogen atoms are converted to N_2.

Thus, applying these rules to FOX-7 and RDX, the following ratios of detonation products are predicted:

FOX-7: $C_2H_4N_4O_4 \rightarrow 2CO + 2H_2O + 2N_2$

RDX: $C_3H_6N_6O_6 \rightarrow 3CO + 3H_2O + 3N_2$.

The energy released in these two processes is then calculated by subtracting the enthalpy of formation of the explosive from the sum of the enthalpies of

formation of the detonation products (all in units $kJ\,mol^{-1}$):

$$\Delta H_{det}^{\circ}(\text{FOX-7}) \quad = 2\Delta H_f^{\circ}(CO) + 2\Delta H_f^{\circ}(H_2O) - \Delta H_f^{\circ}(\text{FOX-7})$$
$$= 2 \times (-110) + 2 \times (-242) - (-130)$$
$$= -574\,kJ\,mol^{-1} = -3.88\,MJ\,kg^{-1} = -7.29\,MJ\,dm^{-3}$$

$$\Delta H_{det}^{\circ}(\text{RDX}) \quad = 3\Delta H_f^{\circ}(CO) + 3\Delta H_f^{\circ}(H_2O) - \Delta H_f^{\circ}(\text{RDX})$$
$$= 3 \times (-110) + 3 \times (-242) - (+67)$$
$$= -1123\,kJ\,mol^{-1} = -5.06\,MJ\,kg^{-1} = -9.21\,MJ\,dm^{-3}\,.$$

An experimental value for ΔH_{det}° (FOX-7) is $-4.86 \pm 0.06\,MJ\,kg^{-1}$ [27], significantly larger than the above calculated value. Selection of a less negative value for ΔH_f° (FOX-7) in the above calculation would have resulted in a calculated ΔH_{det}° (FOX-7) closer to the experimental value. An experimental value for ΔH_{det}° (RDX-wax 94/6), using the same technique, is $-5.28\,MJ\,kg^{-1}$ [28]. The calculated value for ΔH_{det}° (RDX) would have been closer to the experimental value if a more positive value for ΔH_f° (RDX) had been chosen. As already stated, the values of ΔH_f° chosen for the calculations were selected because they were both from the same reference and were therefore assumed to be mutually consistent. The experimental values for ΔH_{det}° suggest that this assumption may be incorrect.

Using the calculated rather than the experimental values for ΔH_{det}°, it is clear that on a mole basis only about half the amount of energy is released by FOX-7 compared to RDX. However, it is volume that limits the mass of energetic material that can be contained within a piece of ordnance, and on the basis of volume (via mass and then density) $\sim 21\%$ less energy is released by FOX-7 relative to an equal volume of RDX. [Using the experimental values for ΔH_{det}° instead, FOX-7 would release only 5% less energy than an equal volume of RDX]. Thus, although it looked initially as though FOX-7 might be greatly inferior to RDX regarding energy output, from an energy density viewpoint, the position of FOX-7 looks significantly closer to that of RDX. And, as has already been stated, the detonation velocity and detonation pressure are only slightly below those of RDX. It is also worth noting that the volume of gas generated on detonation (per mole of explosive) is greater for RDX (9 mol versus 6 mol $\equiv$ 202 dm^3 versus 134 dm^3 at STP), but per unit mass they are the same (0.91 $dm^3\,g^{-1}$), and per unit volume of explosive, FOX-7 generates slightly more gas (1.66 $dm^3\,cm^{-3}$ versus 1.71 $dm^3\,cm^{-3}$).

Of course these calculations are based on rather idealized behavior. In reality, other factors, such as actual density of the charge (which may be significantly lower than the crystal density, the latter being the maximum value attainable) and non-ideal detonation behavior, have a bearing on the comparison. Some actual performance testing has been reported ([29, 30], Sect. 10) and indicates that FOX-7 is comparable with RDX in its explosive output.

Other reported testing has included the range of tests that are normally conducted in order to ascertain the suitability of an energetic material for service. This includes production of crystals of the desired size and shape, large-scale sensitivity and thermal stability tests, and compatibility with other components in an explosive formulation. The overall picture from these tests is that the future for FOX-7 as a replacement for RDX seems very promising.

7
Chemical Reactions of FOX-7

The location of two electron-donating, amino groups on one carbon, and two electron-withdrawing, nitro groups on the other carbon should make 1,1-diamino-2,2-dinitroethene a good example of a push-pull alkene [31], with strong polarization of the double bond (Scheme 5).
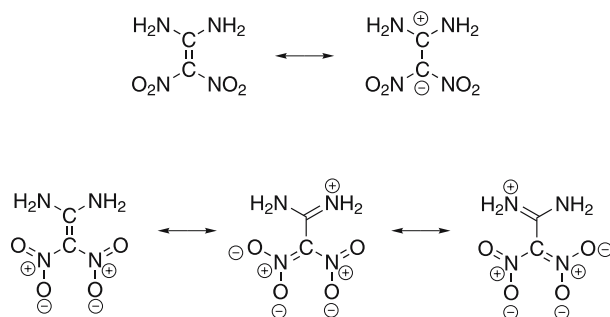
Scheme 5 FOX-7 as a "push-pull" alkene

The main consequences of this polarization are (i) the carbon bearing the amino groups (C-1) should be relatively electron deficient and susceptible to attack by nucleophiles, (ii) the H atoms should be more acidic than those of simple amines, and (iii) the amine N atoms should be poor nucleophiles. All of these aspects have been demonstrated to be present in the chemistry of 1,1-diamino-2,2-dinitroethene.

Simple nitro-enamines have been reported to undergo transamination reactions via an addition-elimination mechanism. For example, 1-dimethylamino-2-nitroethene reacts with amines to release dimethylamine, accompanied by the formation of a new nitro-enamine (Scheme 6 where R^1R^2NH = piperidine, morpholine and pyrrolidine) [32, 33].

1,1-Diamino-2,2-dinitroethene, which is a double nitro-enamine, reacts with primary alkylamines in N-methylpyrrolidin-2-one (NMP) at 90 °C to give both single and double substitution products [34–36], with loss of ammonia. 3-Aminopentane reacts quantitatively to give the mono-substituted
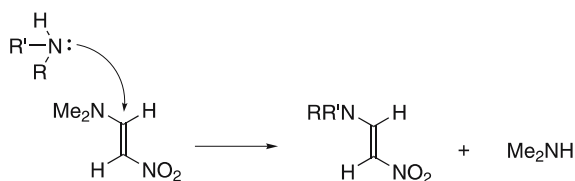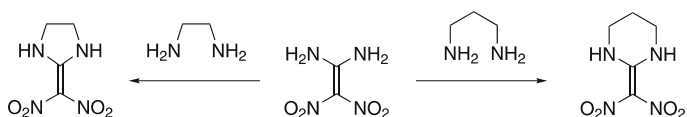
Scheme 6 Transamination of a nitro-enamine

product 1-amino-1-(pent-3-ylamino)-2,2-dinitroethene, while less hindered primary amines, e.g., 1-aminobutane, 2-aminoethanol, 3-aminopropanol, give mixtures of both mono- and bis-substitution (Scheme 7), the ω-aminoalkan-1-ols affording water-soluble products.
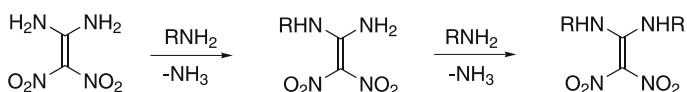

Scheme 7 Transamination of 1,1-diamino-2,2-dinitroethene with a primary alkylamine

The di-amines 1,2-diaminoethane and 1,3-diaminopropane react at both amine functions to give the same cyclic products (Scheme 8) that Baum et al. [1] had obtained by reacting the same di-amines with 1,1-diiodo-2,2-dinitroethene.

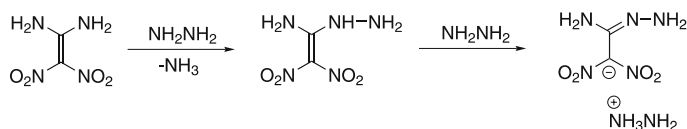**Scheme 8** Transamination of 1,1-diamino-2,2-dinitroethene with α,ω-diamines

In the absence of solvent, 1,2-diaminoethane reacts further to effect displacement of both nitro groups (Scheme 9).
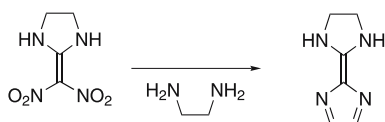
Scheme 9 Further reaction of 2-dinitromethyleneimidazolidine

A similar transamination reaction occurs with hydrazine, but in this case only mono-substitution is achieved. Reaction with excess hydrazine only serves to form the hydrazinium salt of the conjugate base of the mono-substituted product (Scheme 10).

Reaction with guanidine, instead of effecting transamination, causes de-protonation of 1,1-diamino-2,2-dinitroethene to give its guanidinium salt

Scheme 10 Transamination of 1,1-diamino-2,2-dinitroethene with hydrazine

(Scheme 11), and thus exhibits another aspect of the reactions of 1,1-diamino-2,2-dinitroethene.
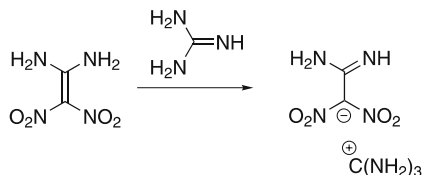
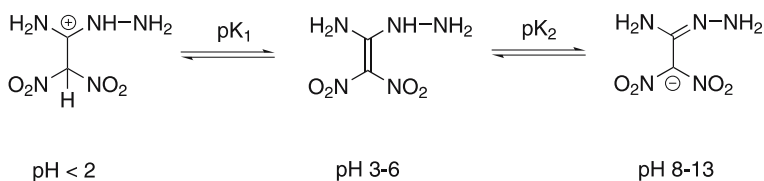**Scheme 11** Reaction of 1,1-diamino-2,2-dinitroethene with guanidine

Indeed, this is a general reaction with common bases like KOH. The potassium salt of 1,1-diamino-2,2-dinitroethene may be isolated as a white, crystalline solid on treatment with cold aqueous KOH, and the free 1,1-diamino-2,2-dinitroethene may be regenerated on acidification. The pKa of 1,1-diamino-2,2-dinitroethene was found [36, 37] to be approximately 10.6, the conjugate base existing in the pH range 11–13 (Scheme 12). Both 1,1-diamino-2,2-dinitroethene and its conjugate base may be detected by UV and ^{13}C NMR spectroscopy.

pH 1-9   pH 11-13
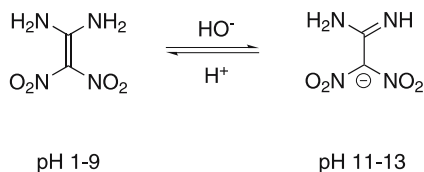
**Scheme 12** Acid-base equilibria of 1,1-diamino-2,2-dinitroethene

The corresponding pKa of the mono-hydrazino derivative (see above) is lower (value ~ 6.7) than that of 1,1-diamino-2,2-dinitroethene and explains why excess hydrazine causes deprotonation of the initial mono-transamination product. At pH < 2 the protonated form appears to be generated (Scheme 13). Again UV and ^{13}C NMR spectroscopy may be used to detect the interconverting species [36, 37].

Heating 1,1-diamino-2,2-dinitroethene in the presence of aqueous KOH (70 °C) causes hydrolytic cleavage of the C = C bond, presumably via nucleo-

Scheme 13 Acid-base equilibria of 1-amino-1-hydrazino-2,2-dinitroethene

philic attack by HO$^-$ at C-1, and generates the potassium salt of dinitromethane (Scheme 14).
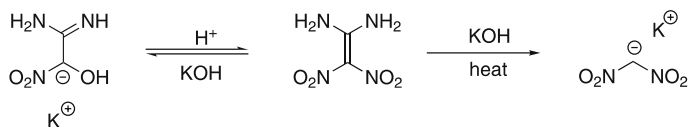
**Scheme 14** Base hydrolysis of 1,1-diamino-2,2-dinitroethene

The observation by Baum et al. [1] that the ammonium salt of cyanodinitromethane (**8**) and not 1,1-diamino-2,2-dinitroethene is formed when 1,1-diiodo-2,2-dinitroethene is treated with ammonia (Scheme 1), prompted a study of the behavior of ammonium cyanodinitromethanide (**8**) and 1,1-diamino-2,2-dinitroethene in liquid ammonia, in the hope that ammonium cyanodinitromethanide might isomerize to 1,1-diamino-2,2-dinitroethene (Scheme 15) (Bellamy et al., unpublished results).
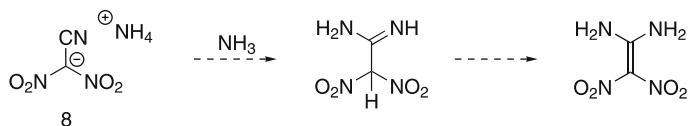

Scheme 15 Hypothetical isomerization of ammonium cyanodinitromethanide (**8**) to 1,1-diamino-2,2-dinitroethene

It was found that 1,1-diamino-2,2-dinitroethene reacts with liquid ammonia, albeit under more extreme conditions (100 °C/110 bar) than used by Baum et al. [1], to give a mixture of ammonium cyanodinitromethanide (**8**) and the guanidinium salt of dinitromethane (**19**), the latter predominating (ratio 1 : 20, $t_{1/2} \sim 6$ h). Furthermore, treatment of ammonium cyanodinitromethanide under the same conditions gave back starting material containing only a small amount of 1,1-diamino-2,2-dinitroethene (0.25%), and no guanidinium dinitromethanide. Thus conditions which would appear to offer the possibility for 1,1-diamino-2,2-dinitroethene to be formed from ammonium cyanodinitromethanide, appear to favor the latter. Moreover, since no guanidinium dinitromethanide was formed when ammonium

cyanodinitromethanide was subjected to pressure and heat, it must be formed from 1,1-diamino-2,2-dinitroethene alone. One has to conclude therefore that the desired isomerization to 1,1-diamino-2,2-dinitroethene is both unfavorable <u>and</u> slow. The formation of ammonium cyanodinitromethanide from 1,1-diamino-2,2-dinitroethene presumably results from the reverse of the intended reaction (Scheme 16), while guanidinium dinitromethanide is formed by conjugate addition of ammonia to 1,1-diamino-2,2-dinitroethene (the initial step in a transamination reaction), followed by C – C bond cleavage (Scheme 17), reflecting both the basic and the nucleophilic properties of ammonia, respectively.
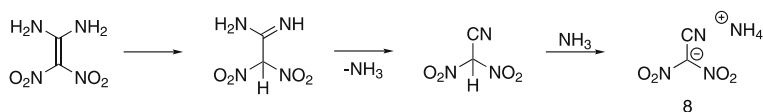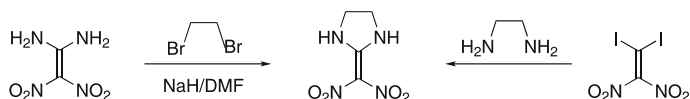

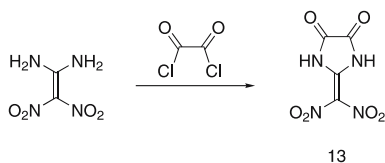**Scheme 16** Isomerization of 1,1-diamino-2,2-dinitroethene to ammonium cyanodinitromethanide (**8**)
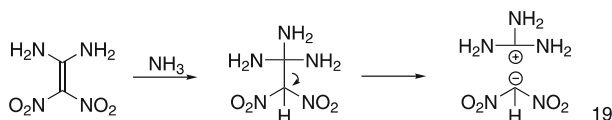
Scheme 17 Isomerization of 1,1-diamino-2,2-dinitroethene to guanidinium dinitromethanide (**19**)

An indication of the low reactivity of the amino nitrogen atoms in 1,1-diamino-2,2-dinitroethene was evident from the original FOI publication [2]. It was reported that 1,1-diamino-2,2-dinitroethene would not react with 1,2-dibromoethane, even in hot *N*,*N*-dimethylformamide (DMF), without prior activation to the conjugate base with sodium hydride (2 equivalents). Thereafter reaction at 115 °C gave 2-dinitromethyleneimidazolidine, the same product that was prepared by Baum et al. [1] by reacting 1,1-diiodo-2,2-dinitroethene with 1,2-diaminoethane (Scheme 18). However, 1,1-diamino-2,2-dinitroethene was found to react more readily (without NaH activation) with oxalyl chloride to give 2-dinitromethyleneimidazolidine-4,5-dione, the intermediate isolated from the nitrations of 2-methylimidazole and 2-methylimidazolidine-4,5-dione (Scheme 19).
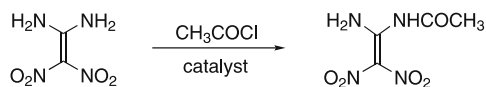

Scheme 18 Alkylation of 1,1-diamino-2,2-dinitroethene

Scheme 19 Acylation of 1,1-diamino-2,2-dinitroethene with oxalyl chloride

The chemical reactivity of 1,1-diamino-2,2-dinitroethene has been further explored in a joint investigation by FOI (Sweden) and SNPE (France) [38]. No evidence was found for the participation of the $C = C$ bond of 1,1-diamino-2,2-dinitroethene in [2 + 1] cycloadditions (with Cl_2C:) or [3 + 2] cycloadditions (with benzyl azide, ethyl diazoacetate and benzonitrile oxide). Furthermore, acetylation on the amino groups with acetyl chloride only succeeded if a catalyst was present, the mono-*N*-acetyl derivative being produced (Scheme 20).

Scheme 20 Acetylation of 1,1-diamino-2,2-dinitroethene

More successful reactions involved treatment with (i) *N*-chlorosuccinimide (CBS), (ii) *N*-bromosuccinimide (NBS) and (iii) nitric acid in trifluoroacetic anhydride/trifluoroacetic acid (HNO_3/TFAA/TFA). All three reagents gave products in which the electrophilic species (Cl, Br and NO_2 respectively) had added at both an amino N-atom and C-2 to produce 1-chloro/bromo/nitro-1,1-dinitro-2-(*N*-chloro/bromo/nitro-amidino)ethane, respectively (Scheme 21). In the case of the nitration, this product is analogous to those obtained on nitration of 1,1-bis(alkylamino)-2,2-dinitroethenes by K. Baum and N.V. Nguyen [39].


Reagents: (i) X = Cl, NCS/MeOH/20°C/3h
(ii) X = Br, NBS/MeOH/20°C/3h
(iii) X = NO_2, HNO_3/TFAA/TFA/-5 to 5°C

Scheme 21 Halogenation and nitration of 1,1-diamino-2,2-dinitroethene

8
Alternative Attempts to Synthesize FOX-7

At the present time (2006) the preferred starting material for the manu-
facture of FOX-7 is 4,6-dihydroxy-2-methylpyrimidine, despite the fact that
for every 10 kg of FOX-7 there is > 5 kg of unwanted dinitromethane pro-
duced as a by-product and two equivalents of nitric acid are wasted. It would
obviously be preferable if these disadvantages could be avoided and con-
sequently the nitration of a number of other, closely related heterocyclic
systems has been studied as potential alternative precursors [40–42]. These
were chosen because they were unable or unlikely to nitrate at position 5. Per-
haps the most obvious candidate to investigate was 6-methyl-1,3,5-triazine-
2,4(1H,3H)-dione (**20**), since this molecule has nitrogen instead of carbon
between the carbonyl groups.

When 6-methyl-1,3,5-triazine-2,4(1H,3H)-dione (**20**) was nitrated under
the conditions normally used for the 2-methylpyrimidine derivative (mixed
acid, 25 °C), there was no evidence for nitration even after several days.
When the temperature was raised to 80 °C, nitration did occur, but not to
give the anticipated product. After 20 h at 80 °C, a quantitative yield of 2,4,6-
trihydroxy-1,3,5-triazine (**21**, cyanuric acid) was obtained, accompanied by
tetranitromethane (Scheme 22). Thus it appears that nitration has occurred
initially as anticipated, but then the nitration has progressed further with
cleavage of the original C – CH$_3$ bond and full nitration of the methyl car-
bon. This cleavage is analogous to that which occurs in the nitration of
2-methylimidazole (**9**, Scheme 2), where parabanic acid (**10**) is a major prod-
uct. It is likely that cleavage to parabanic acid also occurs to some extent
in the nitration of 2-methylimidazolidine-4,5-dione (**15**, Scheme 3) since the
yield of the intermediate **13** is only 67%. It is possible that cleavage does not
occur in the methylpyrimidine case because the tetra-nitrated derivative **17**
(Scheme 4) separates from the nitration medium. When the methyltriazine **20**
was nitrated with nitric acid alone at 20 °C, cyanuric acid was still the product
isolated.
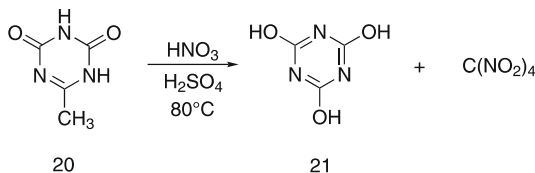
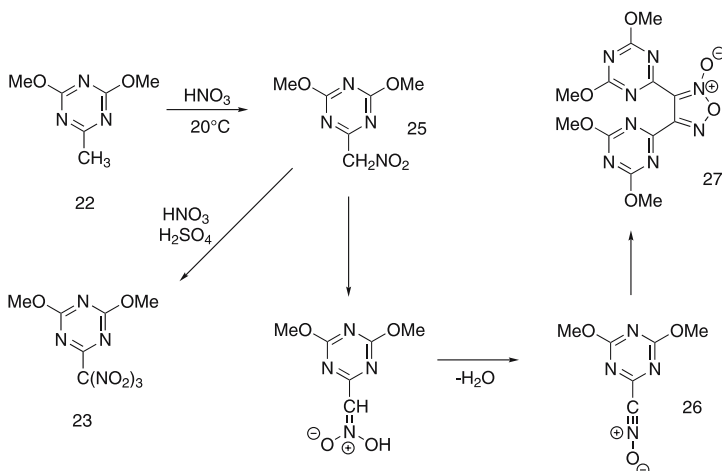**Scheme 22** Nitration of 6-methyl-1,3,5-triazine-2,4(1H,3H)-dione (**20**)

A second triazine system that was also investigated was 2,4-dimethoxy-6-
methyl-1,3,5-triazine [**22**, the synthetic precursor of 6-methyl-1,3,5-triazine-
2,4(1H,3H)-dione]. Mixed acid nitration of this at 20 °C again gave over

nitration at the methyl carbon, but in this case the product, 2,4-dimethoxy-6-trinitromethyl-1,3,5-triazine (**23**), had not undergone C – C bond cleavage. Reductive removal of one of the nitro groups (KI/MeOH) did produce the potassium salt of 2,4-dimethoxy-6-dinitromethyl-1,3,5-triazine (**24**) but this could not be hydrolyzed to FOX-7, cyanuric acid again being the final product (Scheme 23).
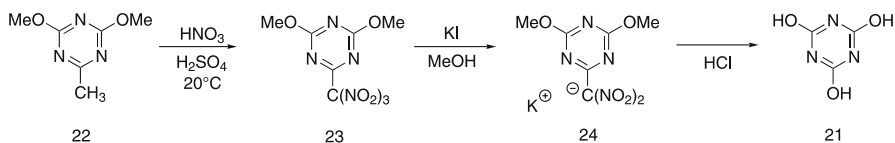

Scheme 23 Mixed acid nitration of 4,6-dimethoxy-2-methyl-1,3,5-triazine (**22**)

Finally, when 2,4-dimethoxy-6-methyl-1,3,5-triazine was nitrated with nitric acid alone at 20 °C, the product was 3,4-bis(3′,5′-dimethoxy-1,3,5-triazinyl)-1,2,5-oxadiazole 2-oxide (**27**). This product was presumably formed by the normal dimerisation of a nitrile oxide to a furazan N-oxide, the nitrile oxide in this case being 3,5-dimethoxy-1,3,5-triazinonitrile oxide (**26**). The latter would be formed by tautomerism and elimination of water from the mono-nitration product 3,5-dimethoxy-2-nitromethyl-1,3,5-triazine (**25**) before it could be further nitrated to the product formed under mixed acid conditions (Scheme 24).


Scheme 24 Alternative modes of nitration of 4,6-dimethoxy-2-methyl-1,3,5-triazine (**22**)

Two other 2-methylpyrimidine systems have been studied, 5,5-dimethyl- and 5,5-diethyl-2-methylpyrimidine-4,6-dione (**28** and **29** respectively) [42]. These systems are more closely similar to the parent system, but here

28 R = Me

29 R = Et
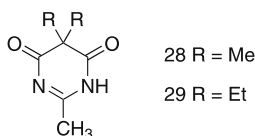
nitration at C-5 is blocked by the alkyl groups. Unfortunately, neither system gave FOX-7 on nitration. Interestingly, nitration of 4,6-dihydroxy-2,5-dimethylpyrimidine (30), a system which is structurally even closer to 4,6-dihydroxy-2-methylpyrimidine (16) was reported [42] to give trinitromethane, plus presumably 2-methylbarbituric acid, instead of the expected 2-dinitromethylene-5-methyl-5-nitrodihydropyrimidine-4,6(1H,5H)-dione (31) (Scheme 25).
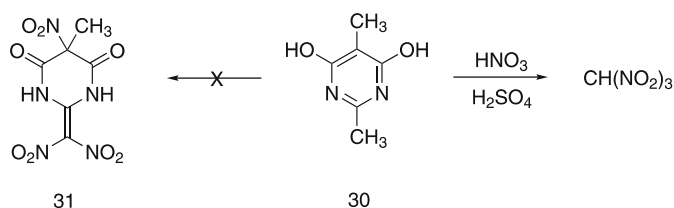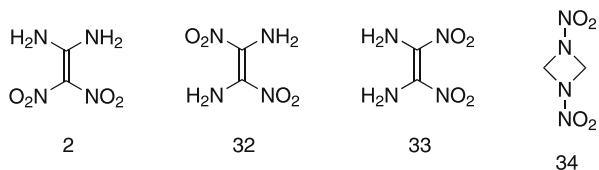

Scheme 25 Nitration of 4,6-dihydroxy-2,5-dimethylpyrimidine (30)

Thus, 4,6-dihydroxy-2-methylpyrimidine (16) still remains the preferred precursor of FOX-7, and its success probably hinges on the insolubility of its tetranitro derivative, this preventing further nitration at the methyl carbon.

9
Isomers of FOX-7

While FOX-7 (2) shows great promise as a secondary explosive, it is not ideal and it is interesting to compare its properties with other, structurally related molecules. How does it compare for example with its isomers, *trans-* (32) and *cis-*(33) 1,2-diamino-1,2-dinitroethene and 1,3-dinitro-1,3-diazacyclobutane (34)? Would they be more or less energetic than FOX-7? Would they have more desirable physical properties, e.g., higher density, greater thermal sta-

bility, lower sensitivity to impact etc? Unfortunately, despite various attempts, none of these has, as yet, been synthesized. Therefore the best that can be done is to compare their theoretically calculated properties.

Several groups have attempted to address this problem and although this approach may have limitations, it can be used as a pointer for future synthetic targets. Politzer et al. [43] were the first to compute the relative energies of the three isomeric diaminodinitroethenes. In fact, their seminal paper was accepted for publication three months before the first successful report [2] of the synthesis of FOX-7 was submitted. They concluded that the relative stabilities and molecular geometries of all three molecules are largely dictated by the available "push-pull" electronic delocalizations and intramolecular hydrogen bonds. Their computed structures are shown in Fig. 7 [44].
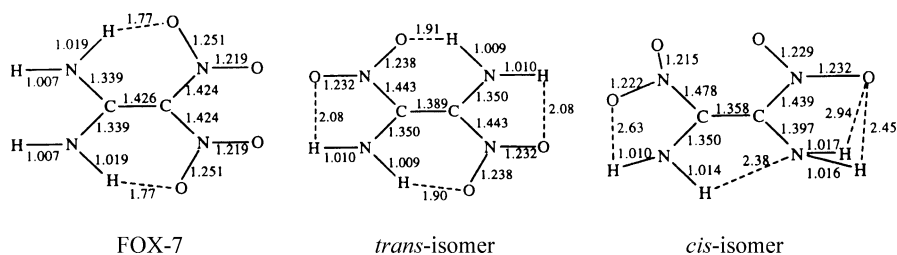
Fig. 7 Computed structures of the isomeric diaminodinitroethenes

In the gas phase, the heats of formation are – 4, + 4 and + 63 kJ mol^{-1} for FOX-7, *trans-* and *cis-*diaminodinitroethene, respectively, which, by means of the calculated heats of sublimation, translates to – 113, – 80 and – 29 kJ mol^{-1} respectively for the solids. FOX-7 is thus calculated to be the solid of lowest energy. Conversely, since all three molecules are isomeric, FOX-7 would liberate the least amount of energy on decomposition (detonation) to CO, H$_2$O and N$_2$. The heats of such a reaction are calculated to be – 592, – 630 and – 680 kJ mol^{-1}, respectively, roughly half that emitted by RDX (experimental value – 1134 kJ mol^{-1}). However, on a kJ g^{-1} basis, which is the more important parameter for energetic performance, *cis-*diaminodinitroethene is much closer to RDX (– 4.59 vs – 5.11 kJ g^{-1}).

Regarding the molecular geometries, all of the bonds attached to each carbon are essentially coplanar in all three diaminodinitroethenes. The bonds to the oxygen-bearing nitrogen atoms are also coplanar, but those to the hydrogen-bearing nitrogen atoms are somewhat pyramidal. For FOX-7 and the *trans-*isomer, the molecules are almost planar, but the *cis-*isomer has one nitro group and one amino group which are rotated out of the plane in order to facilitate weak hydrogen bonding and to avoid steric interactions between neighboring *syn* nitro groups. FOX-7 has two relatively strong (short, both 1.77 Å) intramolecular hydrogen bonds, the *trans-*isomer has four weaker (longer, two each at 1.90 and 2.08 Å) ones, while the *cis-*isomer also has four

hydrogen bonds but these are very weak (2.38–2.94 Å). The "push-pull" effect exerted by the electron donating amino groups and the electron withdrawing nitro groups, is, as expected, strongest in FOX-7 and least in the *cis*-isomer, where non-planarity of one nitro group and one amino group reduces the orbital overlap.

Two further theoretical studies of the isomers of diaminodinitroethene [45, 46] gave similar results to those found by the Politzer group. The study by Sorescu et al. [45] was particularly detailed and gave good agreement with the parameters calculated by Politzer et al. for molecules in vacuo. In the case of FOX-7, the study was also extended to the crystalline state and these results were in accord with the previously reported crystallographic data [8, 9]. This agreement adds confidence to the results obtained for the other two isomers. However, calculation of the lattice parameters for FOX-7 at 25 K intervals over the temperature range 25–450 K failed to detect the experimentally observed phase change ($\alpha \rightarrow \beta$) in the region of 373–393 K.

A comparison of the various bond lengths, bond angles and crystallographic data for FOX-7 as calculated by the studies of Politzer et al. [43] and Sorescu et al. [45], and those found experimentally [8, 9, 14] is given in Table 2. The largest error appears to be in the estimation of the length, and hence strength, of the intramolecular hydrogen bonds. The more recent study is somewhat better in this respect, but still underestimates the length. However there is some divergence on the crystallographically determined length also.

One further theoretical study [30] on FOX-7 alone, in addition to using CHEETAH to calculate the detonation velocity and detonation pressure for FOX-7, also reported the experimentally determined performance of both FOX-7 [velocity of detonation 8870 m s^{-1}, detonation pressure 34.0 GPa, 91% performance compared to RDX] and RDX [8930 m s^{-1} and 35.64 GPa, respectively].

Returning to the third, un-synthesized isomer of FOX-7, 1,3-dinitro-1,3-diazacyclobutane (**34**), the four-membered ring analogue of RDX, its molecular geometry and heat of formation have been calculated by the Politzer group [47]. The bond lengths were computed to be: C–C 1.466 Å, N–N 1.355 Å, N–O 1.191 Å; the bond angles were: N–C–N 87.3°, C–N–C 92.7°, C–N–N 119.9°, N–N–O 116.4°, O–N–O 127.2°; and the dihedral angles were: N–C–N–N 127.1°, C–N–N–O 34.6° and 147.7°. The heat of formation at 25 °C was calculated to be + 218 kJ mol^{-1}, 26 kJ mol^{-1} greater than that for RDX. 1,3-Dinitro-1,3-diazacyclobutane therefore contains considerably more energy than FOX-7 (– 113 kJ mol^{-1}) and its other isomers (*trans* – 80 kJ mol^{-1}, *cis* – 29 kJ mol^{-1}). These data enable one to estimate the heat of reaction to form CO, H$_2$O and N$_2$ (detonation) as about – 922 kJ mol^{-1} [$\equiv$ – 6.23 kJ g^{-1} vs – 5.28 kJ g^{-1} (experimental) for RDX]. Thus, from an energy release viewpoint 1,3-dinitro-1,3-diazacyclobutane would appear to be a worthwhile target molecule for synthesis. However it is most probable that

Table 2 Measured and computed bond lengths, bond angles and crystallographic data of FOX-7

	Bemm et al. [8] 173 K	Evers et al. [14] 200 K	Gilardi [9] 294 K	Politzer et al. [43] 0 K	Sorescu et al. [45]
Interatomic distances (Å)					
C2 – N3	1.399	1.389	1.400	1.424	1.410
C2 – N4	1.426	1.417	1.418	1.424	1.423
C1 – C2	1.456	1.460	1.446	1.426	1.465
C1 – N1	1.319	1.309	1.310	1.339	1.331
C1 – N2	1.325	1.320	1.324	1.339	1.336
N3 – O2	1.249	1.243	1.247	1.251	1.271
N3 – O1	1.252	1.254	1.239	1.219	1.262
N4 – O4	1.242	1.237	1.237	1.251	1.262
N4 – O3	1.242	1.238	1.231	1.219	1.264
O2…H2	1.97	1.87	1.96	1.77	1.88
O4…H3	2.03	2.04	1.98	1.77	1.92
Bond angles (°)					
N3 – C2 – N4	116.3	116.5	115.9	–	116.7
N3 – C2 – C1	123.9	124.1	123.7	–	123.5
N4 – C2 – C1	119.8	119.4	120.3	–	119.9
N1 – C1 – N2	118.4	118.2	118.2	–	118.2
N1 – C1 – C2	120.8	120.7	121.3	–	121.0
N2 – C1 – C2	120.7	121.1	120.4	–	120.7
O1 – N3 – O2	120.9	120.3	121.0	–	120.7
O2 – N3 – C2	118.9	119.1	118.6	–	119.0
O1 – N3 – C2	120.1	120.5	120.4	–	120.7
O3 – N4 – O4	121.0	121.7	120.7	–	120.6
O4 – N4 – C2	118.6	118.4	118.3	–	118.8
O3 – N4 – C2	120.4	119.9	121.0	–	120.6
Crystallographic data					
a (Å)	6.941	6.921	6.940	–	6.978
b (Å)	6.569	6.552	6.637	–	6.776
c (Å)	11.315	11.274	11.341	–	11.336
β (°)	90.55	90.06	90.61	–	90.80
Z	4	4	4	–	4
V (Å^3)	515.9	511.2	522.3	–	536.0

it would be less thermally and chemically stable than either its other isomers or RDX. Nevertheless one must never allow tentative theoretical arguments to persuade one not to attempt to synthesize a promising molecule.

Other properties of 1,3-dinitro-1,3-diazacyclobutane (**34**) have been predicted in a series of publications by Zeman et al. [48–52]. By using data collected for a wide range of energetic nitramines and other polynitro com-

pounds, and by seeking trends in various properties as a function of different structural parameters, it was possible to predict the same properties for the un-synthesized 1,3-dinitro-1,3-diazacyclobutane (**34**). For example, the DSC melting point was predicted to have an onset of 161 °C and a peak at 163 °C, with a heat of fusion of 26.32 kJ mol^{-1} [48]. Other predicted properties included heat of sublimation (94.2 kJ mol^{-1}), Arrhenius parameters for thermal decomposition (Ea 153.10 kJ mol^{-1}, log A 14.1), impact sensitivity, detonation characteristics (detonation velocity 8.46 km s^{-1}), and ^{15}N NMR chemical shifts (nitro – 27.83 ppm, amino – 203.62 ppm).

10
Compounds Structurally Related to FOX-7

It was stated in Sect. 1 that 1,1-diamino-2,2-dinitroethene is structurally similar to several other known energetic molecules viz. 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, **3**), 2,6-diamino-3,5-dinitropyridine (DADNP, **4**), 2,4,6-triamino-3,5-dinitropyridine (TADNP, **5**), 2,6-diamino-3,5-dinitropyrazine (**6**) and 2,5-diamino-3,6-dinitropyrazine (**7**). All of these molecules possess a similar juxtaposition of amino and nitro groups, and it is the interplay, predominantly through hydrogen bonding, of these two groups that is believed to be responsible for decreased sensitivity towards external stimuli e.g. impact and friction, high melting points and high thermal stability. TATB (**3**) in particular is known to be extremely insensitive to impact and has a high decomposition temperature. One could think of these related structures as FOX-7 with extra carbon and/or nitrogen atoms inserted between the carbon atoms bearing the amino and nitro groups. In some cases, there are extra nitro and/or amino groups present. That these molecules are structurally related to FOX-7 is reflected in their crystal structures, most, if not all, existing as sheets of molecules with strong intermolecular hydrogen bonding. In addition, there is strong intramolecular hydrogen bonding between vicinal N – H and N – O groups.
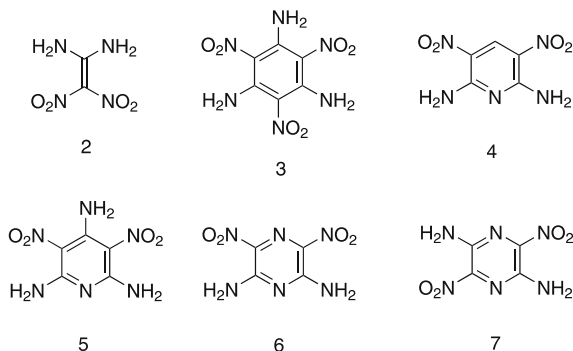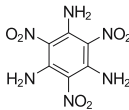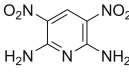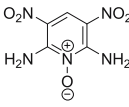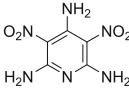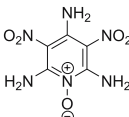
Since one of the objectives in designing a new energetic molecule is to incorporate as much oxygen as possible into the molecule, so that a maximum number of the carbon atoms are converted to CO_2, rather than CO or even C, during d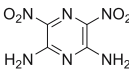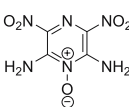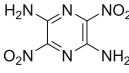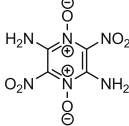etonation, it is the *N*-oxide derivatives of the above listed N-heterocycles that are greater interest as explosives. Thus it is 2,6-diamino-3,5-dinitropyridine 1-oxide (DADNP-O, **35**) rather than 2,6-diamino-3,5-dinitropyridine (DADNP, **4**) [53, 54], 2,4,6-triamino-3,5-dinitropyridine 1-oxide (TADNP-O, **36**) rather than 2,4,6-triamino-3,5-dinitropyridine (TADNP, **5**) [54], 2,6-diamino-3,5-dinitropyrazine 1-oxide (**37**) [55–57] rather than 2,6-diamino-3,5-dinitropyrazine (**6**), and 2,5-diamino-3,6-dinitropyrazine 1,4-dioxide (**38**) rather than 2,5-diamino-3,6-dinitropyrazine (**7**) [58] that are of greater interest as explosives. In all of these cases the un-oxidized form is an intermediate in the synthesis of the *N*-oxide. However, it is the un-oxidized forms that are closer structurally to 1,1-diamino-2,2-dinitroethene.

Apart from FOX-7, only one of the energetic molecules in this list, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, **3**), is already established as an important, widely used explosive. Two of the others, 2,6-diamino- (**35**) and 2,4,6-triamino-3,5-dinitropyridine N-oxide (**36**), and have been around for 10–15 years and have yet to become widely used. This is in part because they are not much better than TATB in terms of explosive properties and thermal stability. One molecule which does promise to be significantly better than TATB is 2,6-diamino-3,5-dinitropyrazine 1-oxide (**37**). This has only relatively recently appeared on the scene and has yet to be fully investigated.

So how does FOX-7 compare, in terms of its explosive performance, physical properties and ease of manufacture, with these related molecules (see Table 3)? Only 2,6-diamino-3,5-dinitropyrazine 1-oxide (**37**) has potential explosive performance comparable with FOX-7, and it also has a higher density than FOX-7, but its production involves, at present, four synthetic steps. The other molecules show inferior explosive performance, partly due to their poor
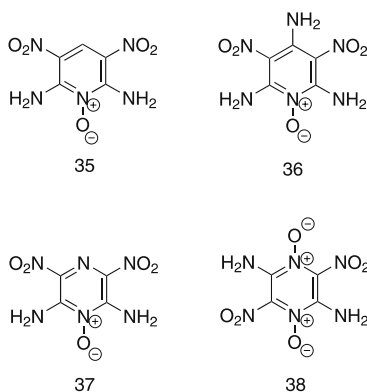
Table 3 Comparison of the physical properties of FOX-7 and structurally related energetic molecules

Compound	Melting or decomposition temperature (°C)	Density (g cm^{-3}) obs (calc)	Detonation velocity (m s^{-1}) calc* (obs)	Detonation pressure (kbar) calc* (obs)
	235	1.88	8740 (8870)	360 (340)
	350	1.93	7870 (7620 at 96% max density)	278 (285)
	345	1.75	7480 (6800 at 97% max density)	242
	> 340	1.84	7840 (7030 at 94% max density)	276
	353	1.82	7670	260
	308	1.88	8010	291
	357	–	8465	334
	343	1.91	8730	358
	288	(1.88)	8465	334
	–	(1.91)	8930	397

* Calculated according to Rothstein and Petersen's method [59–61]

oxygen balance, a consequence of which is that the oxygen which is available in the molecule, is insufficient to oxidize the carbon atoms beyond the CO stage. A considerable amount of the potential energy (if sufficient oxygen were present to oxidize all carbon atoms to CO_2) is thus not released. Perhaps the only deficiency which FOX-7 has is its lower thermal stability. All of the N-oxides in this list have decomposition temperatures well in excess of $300\,^{\circ}C$ and are potential high temperature explosives. However none can be manufactured, in high yield, in a single step from a readily available precursor and for a general purpose explosive that is a great advantage.

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