



## **Nitro Groups vs. N-Oxide Linkages: Effects Upon Some Key Determinants of Detonation Performance**

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**Abstract:** Increasing the nitrogen/carbon ratios in the molecular frameworks of C,H,N,O explosives has attracted considerable attention because it tends to result in more positive heats of formation and often greater densities. In conjunction with this, there has been a growing interest in N-oxide linkages,  $N^+ \rightarrow O^-$ , as another source of oxygen in these compounds, in addition to or even possibly replacing  $NO_2$  groups. In this study, for a series of polyazines and polyazoles, we have compared the effects of introducing a single N-oxide linkage or  $NO_2$  group upon key properties that affect detonation velocity and detonation pressure. We found that: (1) The heats of formation per gram of compound, which is what is relevant for this purpose, are almost always higher for the N-oxides. (2) The nitro derivatives have greater densities and detonation heat releases. In relation to the latter, it must be kept in mind that increasing detonation heat release tends to be accompanied by increasing sensitivity. (3) The N-oxides produce more moles of gaseous detonation products per gram of compound.

**Keywords:** C,H,N,O explosives, detonation velocity, detonation pressure, N-oxides, polyazines, polyazoles, detonation heat release, crystal density, heats of formation, gaseous detonation products

### **1 Nitro Group vs. N-Oxide Linkage**

Most secondary explosives of general interest are C,H,N,O compounds (*i.e.* composed of carbon, hydrogen, nitrogen and oxygen). The nitro group,  $NO_2$ , has traditionally been the most common source of the oxygens (less often, the nitrate group,  $ONO_2$ ). In recent years, however, in conjunction with an

emerging emphasis upon high-nitrogen compounds (*i.e.*, having high nitrogen/carbon ratios in their molecular frameworks), there has evolved an interest in the N-oxide linkage,  $N^+ \rightarrow O^-$ , as another source of oxygen. Some background for these developments shall be presented.

Our primary objective in this computational study has been to compare the effects of a nitro group and an N-oxide linkage upon several properties that are key determinants of an explosive's detonation performance. We will begin by discussing these properties, focusing particularly upon compounds with high N/C ratios.

## 2 High-Nitrogen Compounds

The heat release  $Q$  in the detonation of an explosive is clearly an important determinant of its performance.  $Q$  depends not only upon the chemical composition of the explosive but also upon physical factors such as its loading density and the extent of expansion of the product gases [1-4]. In assessing proposed new explosives, however,  $Q$  is typically approximated simply as the negative of the enthalpy change per gram of explosive in the overall detonation reaction. Since this reaction is exothermic, the enthalpy change is negative and  $Q$  is therefore positive. Thus for an explosive X,

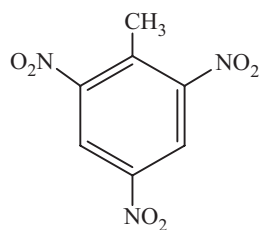
$$Q = -\frac{1}{M_X} \left[ \sum_i n_i \Delta H_{f,i} - \Delta H_{f,X} \right] \quad (1)$$

$M_X$  is the mass of X in g/mol,  $n_i$  is the number of moles of final detonation product  $i$  having molar heat of formation  $\Delta H_{f,i}$ , and  $\Delta H_{f,X}$  is the molar heat of formation of X.

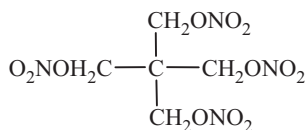
Equation 1 shows that  $Q$  is larger as the heat of formation of the explosive is more positive and as those of the products are more negative. For C,H,N,O explosives, the final detonation products (after a number of intermediate reactions [1, 5]) are normally almost entirely some combination of CO(g), CO<sub>2</sub>(g), H<sub>2</sub>O(g), N<sub>2</sub>(g), H<sub>2</sub>(g) and solid carbon [2, 5, 6-8]. Only the first three of these have negative heats of formation [9]: CO(g), -26.42 kcal/mol; CO<sub>2</sub>(g), -94.05 kcal/mol; H<sub>2</sub>O(g), -57.80 kcal/mol. The heats of formation of the other three – N<sub>2</sub>(g), H<sub>2</sub>(g) and C(s) – are zero by definition, and hence do not contribute to  $Q$ .

Explosive compounds with all-carbon frameworks often have heats of formation  $\Delta H_f$  that are negative [3]; some examples are TNT (**1**), -16.0 kcal/mol,

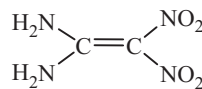
PETN (**2**),  $-128.8$  kcal/mol and FOX-7 (**3**),  $-32.0$  kcal/mol. In such cases, according to Equation 1, it is only the formation of the products CO, CO<sub>2</sub> and H<sub>2</sub>O that is responsible for the heat release  $Q$  that accompanies the detonation process; the  $\Delta H_{f,X}$  of the explosive actually reduces  $Q$ . On the other hand, if the explosive compound has a positive  $\Delta H_{f,X}$ , then by Equation 1 it will increase  $Q$  – a seemingly desirable objective.



1, TNT



2, PETN



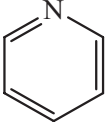
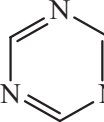
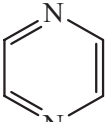
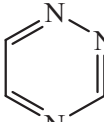
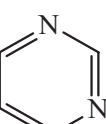
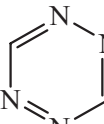
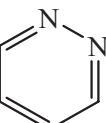
3, FOX-7

One way to achieve a higher, more positive  $\Delta H_{f,X}$  for the explosive is by increasing the N/C ratio in its molecular framework. This follows from the definition of the heat of formation as the overall  $\Delta H$  for producing a compound from its elements in their stable forms. If the compound contains one or more nitrogens, this requires breaking the very strong  $N\equiv N$  triple bond in  $N_2(g)$  and creating much weaker C–N, C=N, N–N and N=N bonds in the compound [10]. This involves a net input of energy and results in a more positive heat of formation, reflecting a greater energy content and therefore less thermodynamic stability. Some examples are in Tables 1 and 2; the  $\Delta H_f$  are higher, more positive, as the N/C ratio is larger.

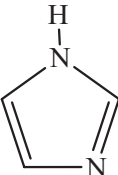
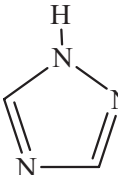
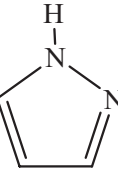
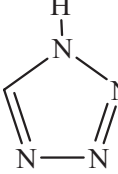
If two or more nitrogens in the molecular framework are linked (catenation), this further reduces stability [11–16] and increases the heat of formation. This is why pyrazole has a larger  $\Delta H_f$  than does imidazole (Table 2), even though both contain two nitrogens, and why the  $\Delta H_f$  of 1,2-diazine is larger than that of 1,3,5-triazine (Table 1) even though the latter has one more nitrogen.

It has sometimes been suggested that increasing the framework N/C ratio leads to not only a more positive heat of formation but also a greater crystal density  $\rho$ . If the larger N/C ratio is due to CH units being replaced by nitrogens, this is plausible, since a nitrogen atom has a larger mass than a CH but a smaller volume [17]. By the same reasoning, replacing a CH<sub>2</sub> by an oxygen should also increase  $\rho$ . Indeed, C<sub>x</sub>H<sub>y</sub>N<sub>z</sub>O<sub>w</sub> compounds do tend to have considerably greater densities than do hydrocarbons [18–20].

**Table 1.** Experimental and computed gas phase heats of formation  $\Delta H_f(g)$  for some polyazines

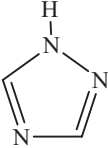
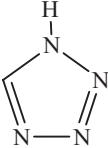
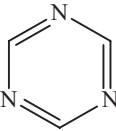
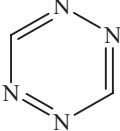
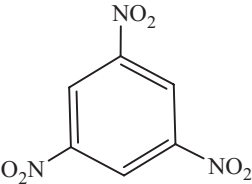
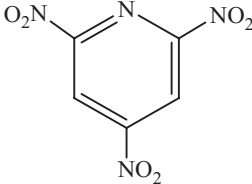
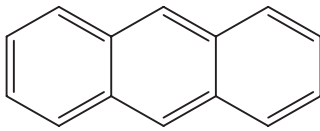
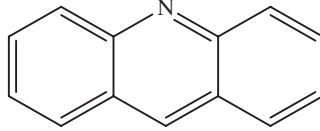
Compound	$\Delta H_f(g)$ , kcal/mol	Compound	$\Delta H_f(g)$ , kcal/mol
	33.50 <sup>a</sup>		53.98 <sup>a</sup>
	46.86 <sup>a</sup>		78 <sup>b</sup>
	46.80 <sup>a</sup>		111 <sup>b</sup>
	66.53 <sup>a</sup>		

<sup>a</sup>Experimental, Ref. 9.<sup>b</sup>Computed at density functional B3LYP/6-311++G(3d,3p) level, Ref. 35.**Table 2.** Experimental gas phase heats of formation  $\Delta H_f(g)$  for some polyazoles

Compound	$\Delta H_f(g)$ , kcal/mol <sup>a</sup>	Compound	$\Delta H_f(g)$ , kcal/mol <sup>a</sup>
	33.29		46.1
	42.9		76.6

<sup>a</sup>Ref. 9.

**Table 3.** Some experimental crystal densities, in g/cm<sup>3</sup>

<i>Increasing N/C ratio in ring(s)</i>	
→	
 1.456 <sup>a</sup>	 1.529 <sup>a</sup>
 1.38 <sup>b</sup>	 1.501 <sup>a</sup>
 1.76 <sup>c</sup>	 1.751 <sup>d</sup>
 1.28 <sup>b</sup>	 1.005 <sup>b</sup>

<sup>a</sup>Ref. 22; <sup>b</sup>Ref. 44; <sup>c</sup>Ref. 3; <sup>d</sup>Ref. 54.

However generalizations usually require caution. In any specific case, as Table 3 shows, a higher N/C ratio may or may not be associated with a greater  $\rho$ . The masses and volumes of the component units of molecules are not the sole determinants of densities; they depend also upon the strengths of the interactions between the molecules [21, 22].

From the standpoint of detonation performance alone, high values for both the heat of formation  $\Delta H_{f,X}$  of an explosive and its density  $\rho$  are very desirable. The former promotes a larger heat release  $Q$ , Equation 1, and the latter allows more explosive to be packed into the available volume; both of these enhance performance.

Two common measures of explosive performance are the detonation velocity

$D$  (the stable velocity of the shock front that characterizes detonation) and the detonation pressure  $P$  (the stable pressure developed behind the front) [23-25]. The roles of  $Q$  and  $\rho$  in determining  $D$  and  $P$  are shown by the empirical Kamlet-Jacobs equations [6]:

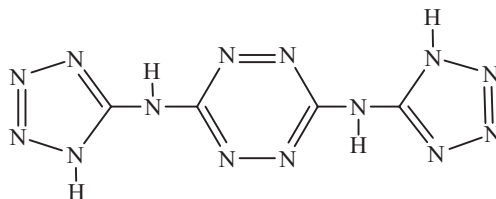
$$D \text{ (km/s)} = 1.01 [N^{0.5}M_{ave}^{0.25}Q^{0.25}(1 + 1.30\rho)] \quad (2)$$

$$P \text{ (kbar)} = 15.58 [NM_{ave}^{0.5}Q^{0.5}\rho^2] \quad (3)$$

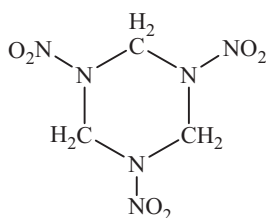
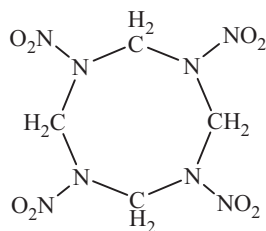
In Equations 2 and 3,  $Q$  is in cal/g and  $\rho$  is in g/cm<sup>3</sup>;  $N$  is the number of moles of gaseous detonation products per gram of explosive and  $M_{ave}$  is their average molecular mass in g/mol. The effectiveness of Equations 2 and 3 is well established [6, 7, 26-29].

By Equations 2 and 3, the larger are  $Q$  and  $\rho$ , the higher will be  $D$  and  $P$  and thus the level of detonation performance. Since a high N/C ratio in the molecular framework is expected to be accompanied by a more positive  $\Delta H_{f,X}$  and therefore larger  $Q$ , as well as possibly a greater  $\rho$ , there has been a growing interest in designing and synthesizing “high nitrogen” compounds as potential explosives [25, 30-37].

However this enthusiasm for high nitrogen content needs to be tempered by some important considerations. A high  $\Delta H_{f,X}$  does not necessarily translate into a large  $Q$ . For example, BTATz (**4**) has an “exceptionally large heat of formation”, measured to be 211 kcal/mol [34]. Since it contains no oxygens, its final detonation products consist largely of N<sub>2</sub>, H<sub>2</sub> and C(s), all of which have zero heats of formation. By Equation 1, its detonation heat release comes entirely from the heat of formation of **4**, and despite the fact that this is very large on a molar basis, the resulting  $Q$ , which is on a gram basis, is quite low: just 0.85 kcal/g. This is less than any of the  $Q$  values in a recent listing of the properties of 30 known secondary explosives [38]. For instance, TNT (**1**), PETN (**2**) and FOX-7 (**3**) have calculated  $Q$  equal to 1.29, 1.51 and 1.20 kcal/g, respectively, despite their negative heats of formation (mentioned earlier).



**4**, BTATz

**5, RDX****6, HMX**

Furthermore, the density of **4**,  $1.76 \text{ g/cm}^3$  [31], although among the highest known for C,H,N compounds, is less than the  $1.80 \text{ g/cm}^3$  that has been suggested as being “an essential requirement for advanced energetic materials” [39]. The low  $Q$  and  $\rho$  of **4** result in relatively poor predicted values of detonation velocity and detonation pressure,  $D=7.52 \text{ km/s}$  and  $P=223 \text{ kbar}$  [31]. For comparison, RDX (**5**) has experimental  $D$  and  $P$  of  $8.754 \text{ km/s}$  and  $347 \text{ kbar}$ , and for HMX (**6**) they are  $9.1 \text{ km/s}$  and  $393 \text{ kbar}$  [5].

This example demonstrates the desirability of having some oxygen atoms in the explosive compound, to allow the detonation products to include those with negative heats of formation:  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$ . This will increase  $Q$  and possibly  $\rho$ . Furthermore, converting some of the carbons to  $\text{CO}_2$  and/or  $\text{CO}$  will result in more moles of gaseous products,  $N$ , and thus, by Equations 2 and 3, larger  $D$  and  $P$ .

An established means of including oxygen is by the substitution or addition of  $\text{NO}_2$  groups. However this leads to another concern. If there is a sufficient number of oxygens to produce a significant amount of  $\text{CO}_2$ , the detonation product with by far the most negative heat of formation, then the detonation heat release  $Q$  may be quite large. While increasing  $Q$  does improve detonation performance, as measured by  $D$  and  $P$ , it also tends to be accompanied by the very undesirable feature of increasing sensitivity – the vulnerability of the explosive to accidental detonation due to unintended stimuli, such as impact, shock, *etc.* There is an overall trend for larger heat release to be associated with greater sensitivity [38, 40-43, 49]. Thus the price for better detonation performance has often been a more sensitive explosive [31, 42, 43, 45, 46].

The fact that a high oxygen content and subsequent large  $Q$  are likely to go together with high sensitivity is the basis for Kamlet’s approximate correlations between oxygen balance and sensitivity [47, 48]. To avoid high sensitivity, therefore, the detonation heat release needs to be restricted to a moderate level – which appears to contradict the whole concept of a high explosive! In reality,

however, it does not [38, 49]. Equations 2 and 3 show that the dependence of  $D$  and  $P$  upon  $Q$  is rather weak. Thus, a large  $Q$  is not necessary, and from the standpoint of sensitivity should be avoided. High  $D$  and  $P$  can be obtained with a moderate  $Q$ ; this has been demonstrated by a number of examples [38, 49].

To summarize the preceding discussion, some oxygens are needed but their number should be limited. One way of achieving this is for at least some of the oxygens to come from N-oxide linkages,  $N^+ \rightarrow O^-$ . Each of these introduces just one oxygen, compared to the two of the  $NO_2$  group. The N-oxide linkage is formally a coordinate covalent bond in which both electrons are provided by the nitrogen. In addition to being a source of oxygen, there is evidence that it somewhat counters the destabilizing effect of nitrogen catenation [15, 16, 50, 51].

In recent years, N-oxides have in fact attracted a great deal of interest as energetic materials [31, 32, 34-37, 52-59]. With the current emphasis upon high N/C ratios, there are more nitrogens in the molecular frameworks that are available for forming N-oxides. The question then arises: How does a single  $NO_2$  group compare to a single  $N^+ \rightarrow O^-$  linkage in its effect upon the key properties of an explosive that determine its performance, as measured by its detonation velocity and detonation pressure. Answering this question is our present objective.

### 3 Properties Governing Detonation Velocity and Detonation Pressure

Equations 1-3 identify the properties that determine the detonation velocity and detonation pressure of an explosive: (a) its density  $\rho$ , (b) its detonation heat release  $Q$ , (c) its heat of formation  $\Delta H_{f,X}$ , (d) the number of moles  $N$  of the final gaseous detonation products per gram of explosive, (e) their average molecular mass  $M_{ave}$ , and (f) the heats of formation  $\Delta H_{f,i}$  of the final detonation products.

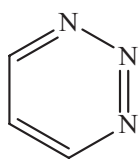
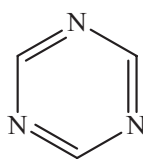
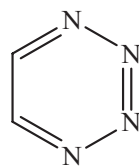
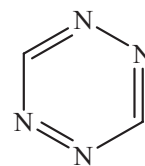
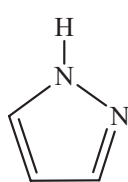
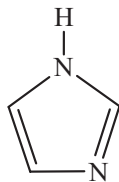
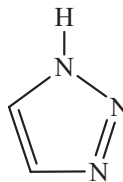
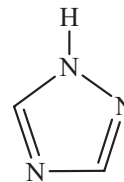
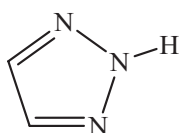
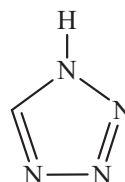
The roles of the  $\Delta H_{f,i}$  of the detonation products have already been discussed.  $M_{ave}$  varies roughly inversely with  $N$  [60], so that  $N$ , which appears in Equations 2 and 3 to a higher power than  $M_{ave}$ , is partially cancelled. The net result is that  $D$  and  $P$  depend only weakly upon  $N$  and  $Q$  (and therefore  $\Delta H_{f,X}$ ) and much more strongly upon  $\rho$ .

Our focus has accordingly been upon  $\rho$ ,  $\Delta H_{f,X}$ ,  $Q$  and  $N$ . How do they change in going from the parent compounds to (a) their nitro derivatives, and (b) their N-oxides? For  $\rho$ ,  $\Delta H_{f,X}$  and  $Q$ , these questions have been addressed to some extent by Lai *et al.* [61]. However they did not compare the effects of the  $NO_2$  group and the  $N^+ \rightarrow O^-$  linkage directly on a one-to-one basis, as we do in the present work.



## 4 Procedure

Our study has encompassed the polyazines **7-10**, the polyazoles **11-16**, and all of their mono-nitro and mono-N-oxide derivatives. The Gaussian 09 program [62] was used at the density functional B3PW91/6-31G(d,p) level. Molecular electrostatic potentials were obtained with the WFA-SAS code [63].

**7**, 1,2,3-triazine**8**, 1,3,5-triazine**9**, 1,2,3,4-tetrazine**10**, 1,2,4,5-tetrazine**11**, pyrazole**12**, imidazole**13**, 1*H*-1,2,3-triazole**14**, 1*H*-1,2,4-triazole**15**, 2*H*-1,2,3-triazole**16**, 1*H*-tetrazole

Densities were estimated from the molecular masses and volumes, and the electrostatic potentials on the molecular surfaces [21, 22]. They will be presented only for the polyazines **7-10** and their derivatives; the procedure is less reliable for the polyazole systems due to the distorting effects of the very strong positive potentials of the N–H hydrogens.

To obtain the solid phase heats of formation  $\Delta H_{f,X}(s)$ , the first step was determining the gas phase values  $\Delta H_{f,X}(g)$ . This was done for each compound by finding the change in enthalpy for producing it from the stable forms of its elements and then adding empirical correction terms [64].  $\Delta H_{f,X}(g)$  was converted to  $\Delta H_{f,X}(s)$  by subtracting the heat of sublimation  $\Delta H_{sub,X}$ , which was estimated from the molecular surface area and electrostatic potential [64].

The quantities  $\Delta H_{f,X}(g)$ ,  $\Delta H_{f,X}(s)$ ,  $Q$  and  $N$  all depend upon the composition of the final detonation products. For explosive loading densities near their crystal densities, it was shown by Kamlet *et al.* [6, 26, 27] and subsequently confirmed by others [5, 7, 60] that good results are obtained for C,H,N,O explosives by taking the final products to be  $N_2(g)$ ,  $H_2O(g)$ ,  $CO_2(g)$  and  $C(s)$ , with oxygens forming  $H_2O(g)$  before  $CO_2(g)$ . We shall proceed accordingly. If there are no oxygens in the compound, as in the polyazoles and polyazines themselves, the hydrogens will be assumed to form  $H_2(g)$  [5, 8].

Taking  $CO_2$  rather than  $CO$  to be a final product yields a higher value of  $Q$ , because the former has the more negative heat of formation,  $-94.05$  kcal/mole vs.  $-26.42$  kcal/mole [9]. This larger  $Q$  has been labeled  $Q_{max}$  [4, 42]. It is  $Q_{max}$  that is related to sensitivity [38, 40-43, 49].

## 5 Results

### 5.1 Densities

Experience has shown that the introduction of  $NO_2$  groups into a molecular framework generally produces greater densities. For example, those of the polynitrocubanes increase progressively from  $1.662$  g/cm<sup>3</sup> for 1,4-dinitrocubane to  $2.024$  g/cm<sup>3</sup> for heptanitrocubane [22], before dipping slightly to  $1.978$  g/cm<sup>3</sup> for octanitrocubane. It has been anticipated that N-oxide linkages would have similar effects, and experimental data cited recently by Lai *et al.* [61] support this expectation, as does the more extensive compilation in Table 4.

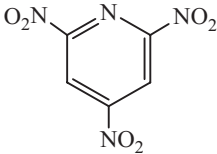
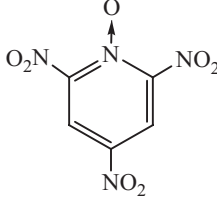
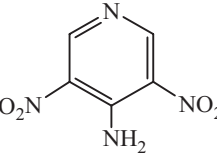
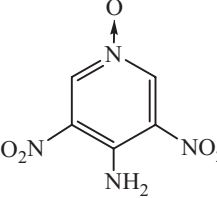
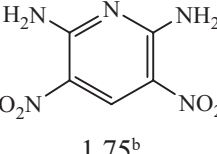
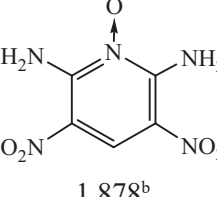
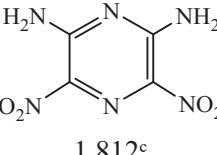
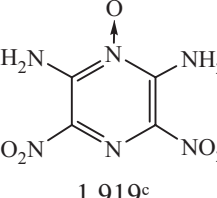
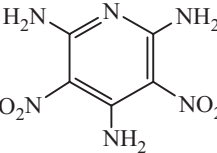
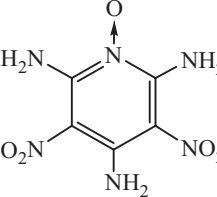
To directly compare the effects of  $NO_2$  groups and  $N^+ \rightarrow O^-$  linkages upon density, Table 5 gives our predicted values for the mono-nitro and mono-N-oxide derivatives of the polyazines **7-10**. The N-oxide densities are greater than those of the respective parent polyazines, by about  $0.1$  g/cm<sup>3</sup>, but the densities of the nitro derivatives similarly exceed those of the N-oxides.

### 5.2 Heats of formation: gas phase

Gas phase heats of formation are sometimes viewed as measures of the intrinsic energy contents of molecules. For the polyazines (Table 5), the  $\Delta H_{f,X}(g)$  of the N-oxides are generally lower than those of the parent compounds, while those of the nitro derivatives are in all instances higher than the respective polyazines.

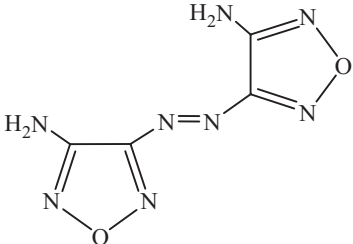
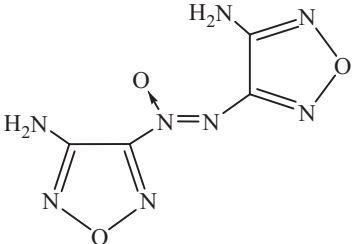
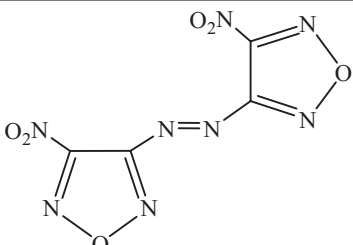
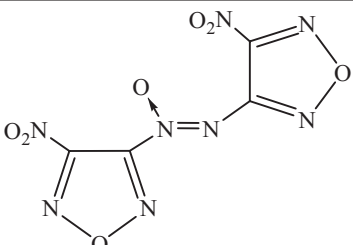
In contrast, the  $\Delta H_{f,X}(g)$  of the polyazole systems (Table 6) are usually greater for *both* the nitro and the N-oxide derivatives than for the polyazoles themselves. The nitropyrazoles and nitroimidazoles are exceptions, having  $\Delta H_{f,X}(g)$  similar to those of pyrazole and imidazole.

**Table 4.** Effects of N-oxide linkages upon experimental crystal densities, in g/cm<sup>3</sup>

<i>Without N-oxide linkage</i>	<i>With N-oxide linkage</i>
 1.751 <sup>a</sup>	 1.875 <sup>a</sup>
 1.76 <sup>b</sup>	 1.83 <sup>b</sup>
 1.75 <sup>b</sup>	 1.878 <sup>b</sup>
 1.812 <sup>c</sup>	 1.919 <sup>c</sup>
 1.819 <sup>d</sup>	 1.876 <sup>d</sup>

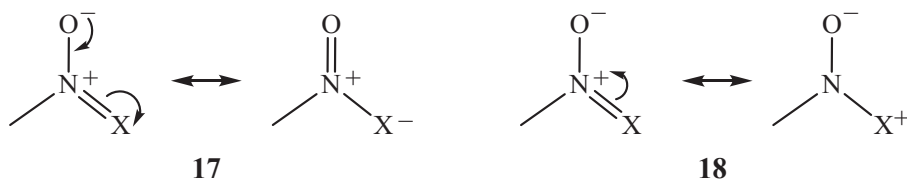
(continued)

**Table 4.** (continued)

<i>Without N-oxide linkage</i>	<i>With N-oxide linkage</i>
 <p>1.70<sup>c</sup></p>	 <p>1.747<sup>c</sup></p>
 <p>1.73<sup>f</sup></p>	 <p>1.82<sup>f</sup></p>

<sup>a</sup>Ref. 54; <sup>b</sup>Ref. 61; <sup>c</sup>Ref. 72; <sup>d</sup>Ref. 36; <sup>e</sup>Ref. 31; <sup>f</sup>Ref. 56.

Why are the N-oxides of the polyazines the only derivatives that have  $\Delta H_{f,x}(g)$  less than those of the parent compounds? One possible reason relates to the interactions between the substituents and the heterocyclic rings. The  $\text{NO}_2$  group is strongly electron-withdrawing, primarily through induction [65]. The  $\text{N}^+ \rightarrow \text{O}^-$  linkage is also electron-withdrawing through induction [66] but it can be either donating or withdrawing via resonance delocalization, *e.g.* structures **17** and **18**, respectively, depending upon the nature of X [15, 16, 66-69]. The electron-donating character, as in **17**, appears to be dominant in the N-oxides of polyazoles and polyazines, judging from the  $\text{N}^+ \rightarrow \text{O}^-$  bond lengths in these molecules [15, 16, 69]. Since polyazines are generally viewed as being more aromatic than polyazoles [16, 70], the  $\pi$  electron delocalization shown in **17** may occur to a larger extent in the polyazine N-oxides. Indeed the  $\text{N}^+ \rightarrow \text{O}^-$  bond lengths tend to be slightly shorter in the polyazine N-oxides [15] than in those of the polyazoles [16]. Greater delocalization implies greater stabilization and consequent diminished energy content; this could at least partially account for the lower gas phase heats of formation of the polyazine N-oxides.



### 5.3 Heats of sublimation

The heats of sublimation were estimated from the computed electrostatic potentials on the molecular surfaces [64], and are larger as these potentials are stronger and more variable. Accordingly they are usually somewhat greater for the more polar nitro and N-oxide derivatives than for the parent polyazoles and polyazines (Tables 5 and 6). The 5-nitropolyazoles are an exception, having lower  $\Delta H_{\text{sub},X}$  than the respective polyazoles. This may reflect some neutralization between the positive electrostatic potentials of the N–H hydrogens and the negative ones of the nearby nitro oxygens.

The  $\Delta H_{\text{sub},X}$  of the polyazines and their derivatives vary from 12 to 19 kcal/mol, with most between 13 and 18 kcal/mol (Table 5). For the polyazole systems, the values are higher, probably due to the strongly positive electrostatic potentials of the N–H hydrogens; they range from 16 to 27 kcal/mol, with the majority between 18 and 26 kcal/mol (Table 6).

### 5.4 Heats of formation: solid phase

On a molar basis, the trends in  $\Delta H_{f,X}(s)$  are similar to those observed for the gas phase values. For the polyazine systems (Table 5), the  $\Delta H_{f,X}(s)$  of the nitro derivatives are usually greater than for the respective polyazines, those of the N-oxides are less. For the polyazole systems (Table 6), the  $\Delta H_{f,X}(s)$  are generally greater for all of the derivatives than for the parent compounds, with the nitroimidazoles and nitroimidazoles again being exceptions.

Note however that when  $\Delta H_{f,X}(s)$  is larger for the derivative than for the parent compound, the difference is often less than it was for the gas phase. This is because the heat of sublimation, which is subtracted from  $\Delta H_{f,X}(g)$  to obtain  $\Delta H_{f,X}(s)$ , is usually larger for the derivative than for the parent compound.

In the context of detonation velocity and detonation pressure, it is really more relevant to look at  $\Delta H_{f,X}(s)$  on a gram rather than a molar basis, since this is how  $Q_{\text{max}}$  enters Equations 2 and 3. Accordingly Tables 5 and 6 also list the values of the  $\Delta H_{f,X}(s)$  in kcal/g.

**Table 5.** Calculated properties for polyazines **7-10** and their mono-N-oxide and mono-nitro derivatives. Properties are density  $\rho$ , gas phase heat of formation  $\Delta H_f(g)$ , heat of sublimation  $\Delta H_{sub}$ , solid phase heat of formation  $\Delta H_f(s)$  in both kcal/mol and kcal/g, maximum heat of detonation  $Q_{max}$  and number of moles of gaseous detonation products per gram of explosive  $N$ . Experimental values, when available, are in parentheses

Compound	$\rho$ , g/cm <sup>3</sup>	$\Delta H_f(g)$ , kcal/mol	$\Delta H_{sub}$ , kcal/mol	$\Delta H_f(s)$ , kcal/mol	$\Delta H_f(s)$ , kcal/g	$Q_{max}$ , kcal/g	$N$ , mol/g
1,2,3-triazine, <b>7</b>	1.44	91.6	17.2	74.4	0.918	0.92	0.0370
1,2,3-triazine-1-oxide	1.56	83.9	18.4	65.5	0.675	1.27	0.0309
1,2,3-triazine-2-oxide	1.55	76.6	17.9	58.7	0.605	1.20	0.0309
4-nitro-1,2,3-triazine	1.68	96.1	19.1	77.1	0.612	1.44	0.0278
5-nitro-1,2,3-triazine	1.66	96.0	18.0	78.0	0.619	1.45	0.0278
1,3,5-triazine, <b>8</b>	1.38 (1.38) <sup>a</sup>	50.2 (53.98) <sup>b</sup>	11.8 (13.0) <sup>c</sup>	38.4 (41.03) <sup>b</sup>	0.474	0.47	0.0370
1,3,5-triazine-1-oxide	1.51	52.3	14.5	37.9	0.390	0.99	0.0309
2-nitro-1,3,5-triazine	1.67	55.2	17.8	37.4	0.297	1.13	0.0278
1,2,3,4-tetrazine, <b>9</b>	1.53	122.4	16.6	105.8	1.29	1.29	0.0366
1,2,3,4-tetrazine-1-oxide	1.62	112.0	16.7	95.3	0.972	1.56	0.0306
1,2,3,4-tetrazine-2-oxide	1.62	108.7	16.8	91.9	0.937	1.53	0.0306
5-nitro-1,2,3,4-tetrazine	1.72	129.4	16.4	113.0	0.889	1.67	0.0295
1,2,4,5-tetrazine, <b>10</b>	1.48 (1.501) <sup>d</sup>	110.0	13.3	96.7	1.18	1.18	0.0366
1,2,4,5-tetrazine-1-oxide	1.60	96.7	14.8	82.0	0.836	1.43	0.0306
3-nitro-1,2,4,5-tetrazine	1.73	119.3	17.1	102.2	0.804	1.59	0.0295

<sup>a</sup>Ref. 44; <sup>b</sup>Ref. 9; <sup>c</sup>Ref. 35; <sup>d</sup>Ref. 22.

The trends are now quite different from those for  $\Delta H_{f,x}(s)$  in kcal/mole. In kcal/g,  $\Delta H_{f,x}(s)$  for the parent polyazine or polyazole is in every instance greater than for its derivatives, and the values for the N-oxides are almost always greater than for the nitro compounds. This reflects the very significant effect of dividing the  $\Delta H_{f,x}(s)$  by the molecular masses, which are larger for the N-oxides than for the unsubstituted molecules and yet much larger for the nitro derivatives.

## 5.5 Maximum heats of detonation

The  $Q_{max}$  show very distinct patterns. They are always considerably greater for the nitro and N-oxide derivatives than for the parent compounds (Tables 5 and 6). This shows the importance of having oxygens in the molecules, so as to form some H<sub>2</sub>O and possibly some CO<sub>2</sub>, both of which have negative heats of

**Table 6.** Calculated properties for polyazoles **11-16** and their mono-N-oxide and mono-nitro derivatives. Properties are gas phase heat of formation  $\Delta H_f(g)$ , heat of sublimation  $\Delta H_{sub}$ , solid phase heat of formation  $\Delta H_f(s)$  in both kcal/mol and kcal/g, maximum heat of detonation  $Q_{max}$  and number of moles of gaseous detonation products per gram of explosive  $N$ . Experimental values, when available, are in parentheses<sup>a</sup>

Compound	$\Delta H_f(g)$ , kcal/mol	$\Delta H_{sub}$ , kcal/mol	$\Delta H_f(s)$ , kcal/mol	$\Delta H_f(s)$ , kcal/g	$Q_{max}$ , kcal/g	$N$ , mol/g
pyrazole, <b>11</b>	42.4 (42.9)	17.7	24.7 (25.2)	0.363	0.36	0.0441
pyrazole-2-oxide	48.1	22.3	25.8	0.307	0.99	0.0357
4-nitropyrazole	41.1	21.2	19.9	0.176	1.15	0.0287
3-nitropyrazole	42.6	22.9	19.8	0.175	1.15	0.0287
5-nitropyrazole	42.1	17.7	24.4	0.216	1.19	0.0287
imidazole, <b>12</b>	32.5 (33.29)	21.0	11.5 (11.9)	0.169	0.17	0.0441
imidazole-3-oxide	40.9	27.2	13.6	0.162	0.85	0.0357
4-nitroimidazole	30.6	24.5	6.1	0.054	1.03	0.0287
2-nitroimidazole	31.5	21.9	9.7	0.086	1.06	0.0287
5-nitroimidazole	30.0	19.9	10.1	0.089	1.06	0.0287
1 <i>H</i> -1,2,3-triazole, <b>13</b>	60.9	21.6	39.4	0.570	0.57	0.0434
1 <i>H</i> -1,2,3-triazole-2-oxide	64.1	22.8	41.4	0.487	1.17	0.0353
1 <i>H</i> -1,2,3-triazole-3-oxide	64.1	25.3	38.7	0.455	1.13	0.0353
4-nitro-1 <i>H</i> -1,2,3-triazole	63.8	21.2	42.6	0.373	1.29	0.0307
5-nitro-1 <i>H</i> -1,2,3-triazole	64.8	17.7	47.1	0.413	1.33	0.0307
1 <i>H</i> -1,2,4-triazole, <b>14</b>	44.7 (46.1)	19.3	25.4 (25.98)	0.368	0.37	0.0434
1 <i>H</i> -1,2,4-triazole -2-oxide	53.1	22.0	31.1	0.366	1.05	0.0353
1 <i>H</i> -1,2,4-triazole -4-oxide	56.7	26.0	30.7	0.361	1.04	0.0353
3-nitro-1 <i>H</i> -1,2,4-triazole	50.0	21.9	28.0	0.245	1.16	0.0307
5-nitro-1 <i>H</i> -1,2,4-triazole	49.3	18.2	31.1	0.273	1.19	0.0307
2 <i>H</i> -1,2,3-triazole, <b>15</b>	56.7	16.1	40.6	0.588	0.59	0.0434
2 <i>H</i> -1,2,3-triazole-1-oxide	63.6	19.9	43.7	0.514	1.19	0.0353
4-nitro-2 <i>H</i> -1,2,3-triazole	60.4	19.4	41.0	0.359	1.28	0.0307
1 <i>H</i> -tetrazole, <b>16</b>	76.5 (76.6)	20.0 (20.3) <sup>b</sup>	56.5 (56.4)	0.807	0.81	0.0428
1 <i>H</i> -tetrazole-2-oxide	82.6	19.4	63.2	0.734	1.41	0.0349
1 <i>H</i> -tetrazole-3-oxide	77.8	23.1	54.7	0.636	1.31	0.0349
1 <i>H</i> -tetrazole-4-oxide	83.7	22.9	60.8	0.707	1.38	0.0349
5-nitro-1 <i>H</i> -tetrazole	86.0	17.6	68.4	0.595	1.46	0.0326

<sup>a</sup>Experimental values are from Ref. 9 except where otherwise indicated; <sup>b</sup>Ref. 35.

formation. Each N-oxide, with just a single oxygen, can only produce H<sub>2</sub>O, but a nitro derivative, with two oxygens, can also form some CO<sub>2</sub>, which has the more negative heat of formation. Accordingly the nitro derivatives in Tables 5 and 6 invariably have larger  $Q_{max}$  than do the N-oxides.

### 5.6 Numbers of moles of gaseous detonation products per gram of explosive

Here again, very clear patterns are apparent in Tables 5 and 6. The unsubstituted polyazines and polyazoles always have the largest  $N$  and the nitro derivatives always have the smallest. These trends follow from the molecular masses, since  $N$  is the number of moles of gaseous detonation products divided by the molecular mass of the explosive in g/mol. Even though the compositions of the detonation products are different for the parent compounds, the N-oxides and the nitro derivatives, the number of moles of gaseous products is quite similar for all of the compounds in Tables 5 and 6: it is 3 for the parent polyazines and polyazoles and their N-oxides, and it is between 3 and 4 for their nitro derivatives. The molecular masses, on the other hand, increase considerably from the parent compounds to the N-oxides and even more in going to the nitro derivatives. This accounts for the trends in the  $N$  values.

## 6 Discussion and Summary

Since it is the solid phases of explosives that concern us, we shall consider first the solid phase heats of formation, and on a gram basis, which is what is relevant for detonation performance via Equations 2 and 3. The trends are quite consistent: on a gram basis,  $\Delta H_{f,x}(s)$  is almost always larger for the N-oxide than for the nitro derivative – but both are less than that of the respective polyazole or polyazine. The effect of molecular mass is responsible for this! Thus  $\Delta H_{f,x}(s)$  of the compound BTATz, **4**, is correctly described as “exceptionally large” on a molar basis [34], at 211 kcal/mole, but this corresponds to only 0.85 kcal/g, which is relatively low (see Section 2). It is less than the unsubstituted polyazines **7**, **9** and **10** in Table 5.

Despite the N-oxides having the larger  $\Delta H_{f,x}(s)$  per gram, the nitro derivatives always have the greater maximum heats of detonation  $Q_{max}$  because their detonation products include some CO<sub>2</sub> as well as H<sub>2</sub>O. The effect of the very negative  $\Delta H_f(g)$  of CO<sub>2</sub> dominates over that of  $\Delta H_{f,x}(s)$ . The importance of the explosive compound’s heat of formation should not be exaggerated.

While a large  $Q_{max}$  is good from the standpoint of detonation performance,



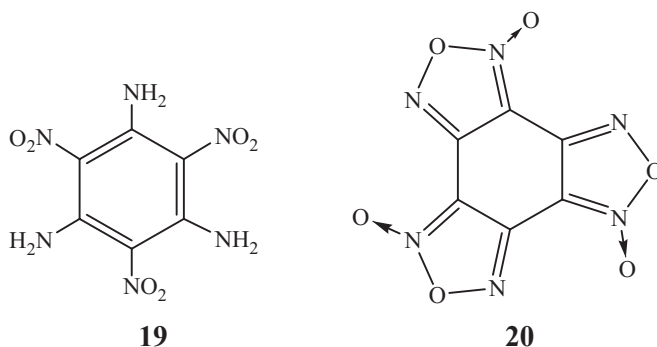
Equations 2 and 3, it has the problem of generally being associated with high sensitivity [38, 40-43, 49], as was discussed earlier.  $Q_{max}$  needs to be limited to a moderate value – which does not preclude having high detonation velocity and detonation pressure [38, 49]!

RDX (**5**) and HMX (**6**) both have relatively large calculated  $Q_{max}$  of 1.50 kcal/g [38, 49], and both are quite sensitive; their measured impact drop heights  $h_{50}$  for a 2.5 kg mass are 24 cm and 26 cm, respectively [71]. Four of the polyazines in Table 5 – two N-oxides and two nitro derivatives – have higher  $Q_{max}$  and thus might be even more sensitive than RDX and HMX. In contrast, insensitive TATB (**19**), which has  $h_{50} > 320$  cm [71], has  $Q_{max} = 1.09$  kcal/g [43]. It should be noted, however, that  $Q_{max}$  is not the only determinant of sensitivity. For example, the amount of free space per molecule in the crystal lattice, the molecular surface electrostatic potential and a variety of physical factors are also known to play significant roles [43, 49].

The parent polyazoles and polyazines, having no oxygens and therefore unable to form either H<sub>2</sub>O or CO<sub>2</sub> as detonation products, have the lowest  $Q_{max}$  in Tables 5 and 6, although the tetrazines **9** and **10** do reach values of 1.29 kcal/g and 1.18 kcal/g, respectively. These latter could be viewed as being in the moderate range.

Overall, Tables 5 and 6 show the polyazines and their derivatives to be better sources of energy than the polyazole systems. The former have higher heats of formation – gas phase and solid phase – and larger maximum detonation heat releases.

The effect upon detonation performance of the number of moles of gaseous detonation products per gram of explosive should not be overlooked. Consider benzotrifuroxan, **20**. Its density, 1.901 g/cm<sup>3</sup>, is essentially the same as the 1.894 g/cm<sup>3</sup> of HMX (**6**) [22] and it has a greater  $Q_{max}$ , 1.69 vs. 1.50 kcal/g [38, 49]. Yet its detonation velocity and detonation pressure by Equations 2 and 3,  $D = 8.50$  km/s and  $P = 331$  kbar, are markedly less than those of HMX,  $D = 9.13$  km/s and  $P = 381$  kbar [38, 49]. This is because the value of  $N$  is very low for benzotrifuroxan, 0.0238 mol/g, compared to 0.0338 mol/g for HMX. The problem is that **20** contains no hydrogens, and therefore forms only the two heaviest gaseous detonation products, N<sub>2</sub> and CO<sub>2</sub>. For  $N$  it is only the *number* of moles of gaseous products that is important, not the sizes of the molecules, and **20** is not efficient in converting its molecular mass into numbers of gaseous molecules. In contrast, HMX can form the lighter H<sub>2</sub>O as well as N<sub>2</sub> and CO<sub>2</sub>, and hence produces more moles of gaseous products per gram of explosive (*i.e.* has a larger  $N$ ).



While the nitro derivatives in Tables 5 and 6 do release slightly more moles of gaseous products than the N-oxides, this is outweighed by the much larger increase in molecular mass that is incurred by introducing an  $\text{NO}_2$  group compared to an oxygen atom. The unsubstituted polyazines and polyazoles have the smallest molecular masses and the largest  $N$ .

To summarize, the key properties upon which the detonation velocity and detonation pressure depend, by Equations 2 and 3, are  $\rho$ ,  $Q_{max}$  and  $N$ . The unsubstituted parent compounds in Tables 5 and 6 have the best  $N$  and sometimes could have acceptable  $Q_{max}$ . However they have relatively low densities (Table 5). We are not aware of any C,H,N compound that has a crystal density as high as the  $1.80 \text{ g/cm}^3$  that has been proposed as “essential” for advanced energetic materials [39]. One of the highest C,H,N densities known is the  $1.76 \text{ g/cm}^3$  of BTATz, 4 [31].

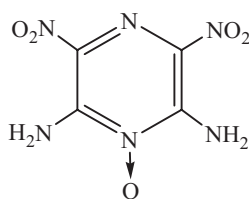
With respect to comparing the effects of a single  $\text{NO}_2$  group vs. a single  $\text{N}^+ \rightarrow \text{O}^-$  linkage, which is our primary purpose in this work, the data in Tables 5 and 6 show the following:

- (1) Both an  $\text{NO}_2$  group and an  $\text{N}^+ \rightarrow \text{O}^-$  linkage result in greater crystal densities and  $Q_{max}$  but lower  $N$  than for the parent polyazines and polyazoles.
- (2) The densities and the  $Q_{max}$  of the nitro derivatives exceed those of the N-oxides (despite the N-oxides having larger solid phase heats of formation on a gram basis). However the advantage of the nitro compounds in terms of  $Q_{max}$  must be balanced against the general tendency for sensitivity to increase with the magnitude of  $Q_{max}$ .
- (3) The N-oxides have larger  $N$  than the nitro derivatives.

An advantage of N-oxides that should be noted is that the  $\text{N}^+ \rightarrow \text{O}^-$  linkage somewhat mitigates the destabilization associated with nitrogen catenation [15, 16, 50, 51].

N-oxides can offer a useful compromise between C,H,N compounds and

nitro derivatives, especially if efforts are made to increase crystal densities (for example by focusing upon small, planar or near-planar molecules [20, 49]). An alternative is to use  $N^+ \rightarrow O^-$  linkages and  $NO_2$  groups in the same molecule, thereby requiring fewer of the latter. An example that has stimulated considerable interest is LLM-105, **21** [32, 57]. It has a very good density of  $1.919 \text{ g/cm}^3$  and a relatively low sensitivity,  $h_{50} = 117 \text{ cm}$  [72]. In terms of calculated detonation performance, LLM-105 ( $D = 8.28 \text{ km/s}$  and  $P = 316 \text{ kbar}$ ) is somewhat below RDX ( $D = 8.83 \text{ km/s}$  and  $P = 347 \text{ kbar}$ ) [38, 49], but its much lesser sensitivity ( $h_{50} = 24 \text{ cm}$  for RDX [71]) is attractive.



**21**, LLM-105

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