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Tricyclic Polyazine N-Oxides as Proposed Energetic Compounds

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Abstract: In designing proposed new explosives, we seek a balance between high detonation performance and low sensitivity. Accordingly we focus upon (1) planar molecules, for better packing efficiency and reduced shear strain upon impact/shock, (2) high nitrogen content, for greater density and enthalpy of formation, (3) N→O linkages rather than NO_2 or ONO_2 groups as sources of oxygen, and (4) presence of NH_2 groups, if possible, to increase density and diminish sensitivity. Here we report the results of a computational assessment of three tricyclic polyazine N-oxides that essentially satisfy these structural criteria. Their predicted crystal densities range from 1.96 to 2.03 g/cm^3. The calculated solid phase enthalpies of formation are between 135 and 314 kcal/mol. The computed detonation velocities and detonation pressures are similar to HMX for two of the compounds and significantly greater for the third, exceeding even CL-20. Impact sensitivities were estimated on the basis of (1) the free space available in the respective crystal lattices, and (2) the molecular surface electrostatic potentials. All three compounds are expected to be less impact sensitive than both HMX and CL-20. One of the three in particular is suggested to represent the best balance between detonation performance and sensitivity.

Keywords: tricyclic polyazine N-oxides, detonation performance, sensitivity, free space in crystal lattice, molecular electrostatic potentials

Design of New Explosive Compounds

Efforts to design new explosive compounds immediately encounter the difficulty of trying to reconcile two seemingly contradictory objectives: maximizing detonation performance but minimizing sensitivity (*i.e.* vulnerability

to unintended detonation due to accidental stimuli, such as impact, shock, *etc*.). Factors that promote one of these objectives often conflict with the other. The goal is therefore an optimum balance.

Detonation performance

Some indications of what affects detonation performance are provided by the empirical relationships, Eqs. (1) and (2), developed by Kamlet and Jacobs for estimating the detonation velocities D and the detonation pressures P of C,H,N,O-containing explosives [1]. D and P are, respectively, the stable velocity of the shock front that characterizes detonation and the stable pressure that is developed behind the front [2-4].

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

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

In Eqs. (1) and (2), 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. Q is the heat release of the detonation reaction in calories per gram of explosive; it equals the negative of the enthalpy change ΔH of the reaction. The quantity ρ is the loading density of the explosive in g/cm^3. In practice it is often less than the pure crystal density [1, 4], but the latter is generally used in predicting D and P for new compounds. The effectiveness of Eqs. (1) and (2) has been demonstrated on several occasions [1, 5, 6].

It is desirable that the detonation velocity and pressure be as high as is compatible with a low level of sensitivity; accordingly, large values of N, M_{ave}, Q and ρ are sought. However the issue of balance arises again, since N and M_{ave} vary inversely.

N, M_{ave} and Q depend upon the composition of the detonation products. While several schemes for predicting these have been proposed [7], comparisons with both experimental and computer-generated data have shown [1, 5] that good results are obtained by assuming that the products are N_2 (g), H_2O (g), CO_2 (g) and C(s), with oxygen being used to form H_2O before CO_2.

Since $Q = -\Delta H$, it can be found from the difference in the enthalpies of formation of the detonation products and the explosive compound. Q is therefore larger as the enthalpy of formation of the compound is more positive. This is one reason for the emphasis, in recent years, upon introducing nitrogens into the molecular frameworks of energetic compounds [8-16], even to the extent of linking several together (nitrogen catenation). The presence of nitrogens is known to increase the enthalpy of formation [9, 12, 16], presumably because of the

relative weakness of C-N and N-N bonds compared to the very strong one in N_2.

Nitrogens also serve to increase the crystal density ρ, the fourth quantity appearing in Eqs. (1) and (2) [9, 12, 13,16-18]. This can be explained, at least in part, in terms of the greater mass and smaller volume of a nitrogen atom compared to C-H [17].

A drawback of nitrogen catenation is that it frequently has a destabilizing effect [19, 20]. This may reflect such factors as repulsion between neighboring nitrogen lone pairs [21, 22], the weakness of any N-N single bonds and the possibility of decomposing through loss of the very stable N_2 [20]. It has been shown, however, that this destabilization can be reduced by involving some of the nitrogens in coordinate covalent $N^+ \rightarrow O^-$ bonds [11, 16, 21]. This can also result in a higher density and heat of formation [10, 23].

From the standpoint of detonation performance, all of the carbon should ideally be converted to CO_2 [5]. This avoids nonproductive solid carbon and gives a product (CO_2) with a relatively highly negative enthalpy of formation [24], thereby increasing Q.

Sensitivity

As mentioned earlier, a second major consideration in designing new explosive compounds – in addition to detonation performance – is achieving a low level of sensitivity (vulnerability to accidental stimuli). This is complicated by the number of factors that influence sensitivity: molecular, crystalline, the physical state of the compound and environmental conditions, *etc*. [2, 3, 25-29]. Our present focus will be upon certain molecular and crystalline features that have been related to sensitivity [29]:

(1) There is substantial evidence that sensitivity is directly linked to the compressibility of the solid compound [3, 30-33] and thus to the free space available in its crystal lattice [34, 35].

(2) If the lattice is composed of parallel planar layers, they can more readily slide past each other, thereby reducing the shear strain that results from shock or impact. This strain can create local buildups of the energy introduced by the shock or impact ('hot spots'), and thus facilitate the initiation of detonation [36, 37]. The likelihood of a layered crystal lattice (and diminished sensitivity) is enhanced by the molecules being planar and having the possibility of significant intermolecular attractive interactions within the layers.

(3) The presence of NH_2 groups often lessens sensitivity [10, 38]. This is probably due at least in part to hydrogen bonding, which (a) leads to closer packing, thus reducing the free space and also increasing the density, (b)

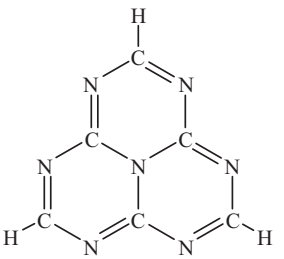
promotes a layered crystal lattice, and (c) may help to dissipate hot spot energy [39]. (Of course the stabilization induced by hydrogen bonding often comes at the price of a decrease in the enthalpy of formation.)

(4) Weak intramolecular bonds may make compounds more sensitive, since their rupture may be a key step in initiating detonation ('trigger linkages') [25-29].

Tricyclic Polyazines

Zheng *et al.* [40, 41] have drawn attention to tricyclic polyazines serving as possible molecular frameworks for energetic compounds. We will focus upon three such frameworks: Tri-*s*-triazine, **1**, and its two analogues **2** and **3** that correspond to replacing two or all three C-H units by nitrogen atoms.

Tri-*s*-triazine, **1**, has been known and studied for some time. It belongs to the polyazacycl[3.3.3]azine series, of which the first member is cycl[3.3.3] azine, **4**. While **4** is chemically quite reactive [42, 43], *e.g.* readily undergoing oxidation or addition, **1** is in contrast remarkably unreactive (except for rapidly decomposing in water) and appears to have very low basicity [44]. Only relatively recently have derivatives of **1** been reported, among them the triamine **5**, known as 'melem' [45].



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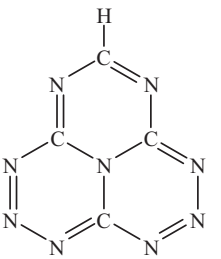

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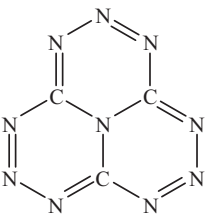

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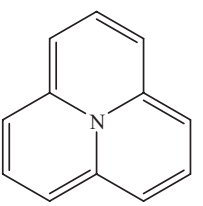

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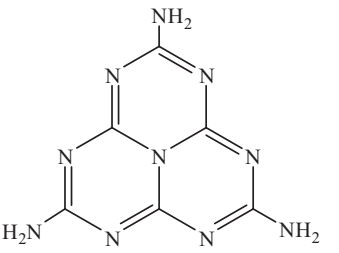

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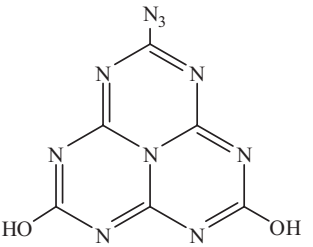

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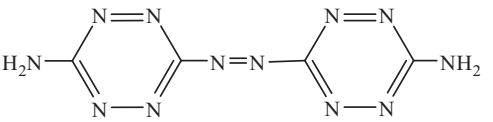
The molecular structure of tri-*s*-triazine as three fused *s*-triazine rings was correctly postulated by Pauling and Sturdivant [46]. It appears that Pauling retained his interest in this system; the azidodihydroxy derivative **6** was found, after his death in 1994, drawn on the chalkboard in his office [47]. There has been some speculation as to the reasons for this, and **6** has sometimes been labeled 'Pauling's mystery molecule'. In a reported interview in 1977, he suggested that compounds related to **6** might show anti-cancer activity [48].

The crystal density of tri-*s*-triazine, **1**, is quite high: 1.69 g/cm^3 [49]. As pointed out some time ago [18], this puts it among the most dense C,N,H compounds. The density of **1** exceeds those of all 20 C,N,H compounds in the compilation of experimental high-nitrogen crystal densities by Rice *et al.* [50], which average 1.51 g/cm^3. The highest C,N,H density of which we are aware is 1.78 g/cm^3 for the azobis(aminotetrazine) **7** [12].



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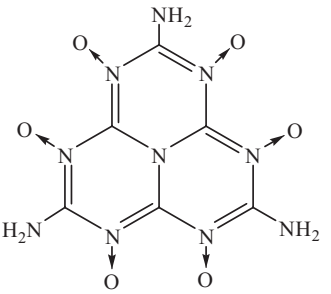
Proposed Compounds

In accordance with the preceding discussion, we selected **1** – **3** to be the molecular frameworks for our proposed energetic compounds. **1** is already known to be planar and to have a high crystal density [18, 49]. **2** and **3** can also be expected to be planar and to have even higher densities, since C-H units have been replaced by nitrogen atoms. The large proportions of nitrogens in **1** – **3** should also result in quite positive enthalpies of formation.

To promote hydrogen bonding, we plan to replace the hydrogens in **1** and **2** by NH_2 groups. Note that the triamine **5** has already been synthesized and characterized [45].

As sources of oxygens, we suggest forming N-oxides at some or all of the outer nitrogens. N-oxides of polyazines have aroused considerable interest as energetic materials [8-16, 23, 51]; in addition to providing oxygens, N-oxidation often increases the density and the enthalpy of formation [10, 12, 23, 51], and it can have a stabilizing effect when it involves catenated nitrogens [11, 16, 21].

Accordingly we propose compounds **8** – **10** for consideration as new explosives. We shall evaluate them from the standpoints of densities, detonation properties and sensitivities. Note that they contain no NO_2, ONO_2 or N_3 substituents.



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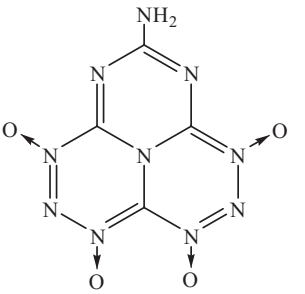

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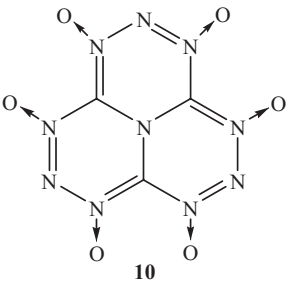


10

Densities

It has been demonstrated that the densities of C,H,N,O energetic molecular solids can be predicted with reasonable accuracy by means of Eq. (3) [52]:

$$\text{density} = \alpha\left(\frac{M}{V(0.001)}\right) + \beta\left(\nu\sigma_{tot}^2\right) + \gamma \qquad (3)$$

M is the molecular mass in g/molecule, V(0.001) is the volume in cm^3/molecule that is enclosed by the 0.001 au contour of the molecule's electronic density, and $\nu\sigma^2_{tot}$ is an 'electrostatic interaction index'. This index is defined in terms of the electrostatic potential $V_S(\mathbf{r})$ that the nuclei and electrons of the molecule create on the surface defined by the 0.001 au contour. σ^2_{tot} is the sum of the positive and negative variances of $V_S(\mathbf{r})$, $\sigma^2_{tot} = \sigma^2_+ + \sigma^2_-$, and ν is a balance parameter:

$$\sigma^2_+ = \frac{1}{m}\sum_{i=1}^{m}\left[V_S^+(\mathbf{r}_i) - \overline{V}_S^+\right]^2 \qquad \sigma^2_- = \frac{1}{n}\sum_{j=1}^{n}\left[V_S^-(\mathbf{r}_j) - \overline{V}_S^-\right]^2 \tag{4}$$

$$\nu = \frac{\sigma^2_+\sigma^2_-}{(\sigma^2_{tot})^2} \tag{5}$$

In Eq. (4), the summations are over the *m* and *n* points at which $V_S(\mathbf{r})$ is respectively positive and negative, $V_S^+(\mathbf{r}_i)$ and $V_S^-(\mathbf{r}_j)$. $\overline{V}_S^+$ and $\overline{V}_S^-$ are the positive and negative averages.

The quantities σ^2_+ and σ^2_- reflect the strengths and the variabilities of the positive and negative surface electrostatic potentials and ν is a measure of the degree of balance between them; it attains a maximum of 0.25 when $\sigma^2_+ = \sigma^2_-$. The product $\nu\sigma^2_{tot}$ has been found to be an excellent index of electrostatic interactive tendencies, especially between molecules of the same kind [53]. A large value of σ^2_{tot} and ν near 0.25 indicates that both the positive and the negative surface potentials are strong, maximizing the possibilities for attractive interactions.

The coefficients α, β and γ were assigned by fitting Eq. (3) to the experimentally-determined densities of 36 energetic C,H,N,O compounds of different types [52]. The calculations of V(0.001) and $V_S(\mathbf{r})$ were at the B3PW91/6-31G(d,p) level.

Eq. (3) is an extended and improved version of an earlier procedure which approximated the density as simply M/V(0.001) [50, 54]. This was sometimes quite effective, but since it reflects just a single isolated molecule and completely neglects crystal factors, it could also produce sizable errors. In a group of 180 C,H,N,O energetic compounds, using just M/V(0.001) resulted in more than 10% having errors greater than 0.10 g/cm^3 [50]; the average absolute deviation from experiment was 0.047 g/cm^3. In contrast, Eq. (3) gave an average absolute deviation of 0.036 g/cm^3 and for only one of the 36 compounds was the error greater than 0.10 g/cm^3.

A word of caution however: Eq. (3) was parametrized specifically for C,H,N,O energetic compounds, which tend to have higher densities than

organic molecular solids in general [55]. It should not be assumed that the same parameters and the 0.001 au volume will necessarily be appropriate for the latter.

Using Eq. (3), the estimated densities of the three proposed compounds are:
8: 2.03 g/cm^3 **9**: 1.96 g/cm^3 **10**: 1.99 g/cm^3

These values are listed in Table 1.

Table 1. Computed and experimental properties relevant to detonation

Property	**8**[a]	**9**[a]	**10**[a]	HMX	CL-20
Density, g/cm^3	2.03	1.96	1.99	1.90[b]	2.04[c]
Enthalpies of formation					
Gas phase, kcal/mol	171	236	337	---	---
Solid phase, kcal/mol	135	209	314	24.5[d]	90.2[d]
Detonation heat					
release, Q, cal/g	1430	1604	2192	1498[e]	1567[e]
Detonation velocity, D, km/s					
Experimental	---	---	---	9.1[b]	9.38[c]
Calculated, Eq. (1)	9.0	9.1	10.3	9.2[e]	9.6[e]
Detonation pressure, P, kbar					
Experimental	---	---	---	393[b]	---
Calculated, Eq. (2)	385	387	494	383[e]	441[e]

[a]Present work. [b]Ref. 56. [c]Ref. 60. [d]Ref. 58. [e]Ref. 5.

Enthalpies of Formation

The atom equivalent procedure [57, 58], Eq. (6), was utilized to find the gas phase enthalpies of formation $\Delta H_f^\circ(g)$ of **8** – **10**:

$$\Delta H_f^\circ(g) = E(g) - \sum_i n_i \varepsilon_i \tag{6}$$

In Eq. (6), E(g) is the computed minimum molecular energy at 0 K, n_i is the number of atoms of element i in the molecule and ε_i is its atom equivalent energy (to be determined).

Since it is actually the solid phase enthalpies of formation of **8** – **10** that will be needed, it is necessary to convert each $\Delta H_f^\circ(g)$ to $\Delta H_f^\circ(s)$, via Eq. (7),

$$\Delta H_f^\circ(s) = \Delta H_f^\circ(gas) - \Delta H_{sub} \tag{7}$$

in which ΔH_{sub} is the enthalpy of sublimation. We have shown some time ago that ΔH_{sub} can also be estimated from the electrostatic interaction index, in conjunction with the area of the 0.001 au molecular surface [59]:

$$\Delta H_{sub} = a(\text{area})^2 + b(\nu\sigma^2_{tot})^{1/2} + c \quad (8)$$

The atom equivalents ε_i in Eq. (6) and the coefficients a, b and c in Eq. (8) were taken from Byrd and Rice [58], who obtained them by fitting Eqs. (6) and (8) to experimental $\Delta H^\circ_f(g)$ and ΔH_{sub} for databases of C,H,N,O energetic compounds. They computed the molecular energies $E(g)$, the surface areas and the electrostatic potentials with the B3LYP/6-311++G(2df,2p)//B3LYP/6-31G(d) procedure.

We have used Eqs. (6) – (8) to calculate $\Delta H^\circ_f(g)$, ΔH_{sub} and $\Delta H^\circ_f(s)$ for compounds **8** – **10**. The results are in Table 1.

Detonation Properties

In accordance with earlier analyses [1, 5], the detonation products of **8** – **10** will be taken to be $N_2(g)$, $H_2O(g)$, $CO_2(g)$ and solid carbon, with H_2O forming before CO_2. The detonation reactions are therefore,

Compound **8**: $C_6H_6N_{10}O_6$ (s) → 5 $N_2(g)$ + 3 $H_2O(g)$ + 3/2 $CO_2(g)$ + 9/2 C(s) (9)
Compound **9**: $C_4H_2N_{10}O_4$ (s) → 5 $N_2(g)$ + $H_2O(g)$ + 3/2 $CO_2(g)$ + 5/2 C(s) (10)
Compound **10**: $C_3N_{10}O_6$ (s) → 5 $N_2(g)$ + 3 $CO_2(g)$ (11)

The enthalpies of detonation, ΔH_{det}, can be determined from the experimental enthalpies of formation of the products [24] and the solid state enthalpies of formation of the compounds **8** – **10** (Table 1). The detonation heat release Q for each compound is then $Q = -\Delta H_{det}$. Our predicted Q for **8** – **10** are in Table 1.

With Q and the density ρ now available for each of the proposed compounds, the remaining quantities needed to estimate their detonation velocities and pressures by means of Eqs. (1) and (2) are the respective N (the number of moles of gaseous detonation products per gram of explosive) and M_{ave} (their average molecular mass). These can readily be evaluated from the reactions in Eqs. (9) – (11).

Our predicted detonation velocities D and detonation pressures P for compounds **8** – **10**, obtained with Eqs. (1) and (2) and the values of ρ, N, M_{ave} and Q that were found in this work, are:

Compound **8**: D = 9.0 km/s P = 385 kbar
Compound **9**: D = 9.1 km/s P = 387 kbar
Compound **10**: D = 10.3 km/s P = 494 kbar

All of our computed properties relevant to the detonation behavior of **8** – **10** are presented in Table 1, where they are compared to those of HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and CL-20 (hexanitrohexaazaisowurtzitane), the current standards for high detonation performance. For HMX and CL-20 are given both the experimental D and P and also the D and P calculated for them with Eqs. (1) and (2), using their experimental Q and ρ. The two sets of D and P are in quite good agreement for both HMX and CL-20, attesting to the effectiveness of Eqs. (1) and (2).

Table 1 shows again [5, 15] that density is not as dominant in determining relative detonation properties as might be anticipated from Eqs. (1) and (2), in which it appears to higher powers than the other quantities. For example, compounds **8** and **9** are both predicted to have higher densities than HMX, especially **8**, but quite similar D and P. The estimated density of **8** is nearly the same as that of CL-20, but its D and P are significantly less. On the other hand, **10** has a lower density than CL-20, but considerably higher D and P.

All of this simply illustrates the fact that the detonation properties depend upon N, M_{ave} and Q as well as ρ. Thus the product $NM_{ave}^{1/2}$ is 0.158 for **8**, well below the 0.176 for HMX; this counteracts the greater density of **8**, and the D and P of **8** and HMX differ very litte.

The high detonation velocity and detonation pressure predicted for **10**, superior to those of HMX and CL-20, can be attributed primarily to the heat release Q of **10**, which markedly exceeds any other in Table 1. This in turn follows from its large enthalpy of formation plus the fact that all of the carbon forms CO_2(g) (which has quite a negative enthalpy of formation [24]) rather than solid carbon, which contributes nothing to Q.

It should be noted that the enthalpy of formation predicted for **10** would not be the highest known for an energetic compound. Huynh *et al.* reported experimental values of 519 and 419 kcal/mol for two compounds involving hydrazo- and azo-linked tetraazido-*s*-triazines [61].

Sensitivity

We have designed the proposed compounds **8** – **10** to incorporate structural features that have been associated with reduced sensitivity, as discussed earlier. Thus the molecules are planar, and two of the three have NH_2 groups. We have

avoided introducing bonds that tend to be weak, *e.g*. C-NO, O-NO, O-NO_2, N-NO, N-NO_2 and N-N_2 [62].

Any attempt to predict sensitivity should be made with extreme caution. As already pointed out, sensitivity depends upon a number of factors [2, 3, 25-29] and it is not clear which one(s) may be dominant in any particular case.

Sensitivity and free space in crystal lattice

There is evidence indicating that one of the factors related to sensitivity is the compressibility of the solid compound [3, 30-33], and that sensitivity increases with the amount of free space available in the crystal lattice [34, 35]. We have suggested that this free space ΔV can be formulated as [34],

$$\Delta V = V_{eff} - V(0.003) \quad (12)$$

In Eq. (12), V_{eff} is the effective volume of the molecule that would correspond to 100% packing of the unit cell; it is given by,

$$V_{eff} = M/density \quad (13)$$

V(0.003) is the space encompassed by the 0.003 au contour of the molecule's electronic density; this is viewed as being the intrinsic volume of the molecule. The 0.003 au contour was selected because we found that the ratio $V(0.003)/V_{eff}$ reproduces very well the actual packing coefficients of energetic compounds [55].

We have shown that there is a rough relationship between ΔV and the experimental impact sensitivity [34]: the sensitivity tends to increase as ΔV, the available free space in the lattice, becomes larger. We have applied this relationship to estimating the impact sensitivities of **8** – **10**. The V_{eff} were calculated using our predicted densities and Eq. (13); the respective V(0.003) were computed with the B3PW91/6-31G(d,p) procedure. The results will be given both as drop heights h_{50} (2.5 kg drop mass) and as impact energies:

Compound **8**: ΔV = 42 Å^3 h_{50} ~ 115 cm impact energy ~ 28 J
Compound **9**: ΔV = 45 Å^3 h_{50} ~ 105 cm impact energy ~ 26 J
Compound **10**: ΔV = 55 Å^3 h_{50} ~ 75 cm impact energy ~ 18 J

The larger are h_{50} and the impact energy, the lower is the impact sensitivity. For comparison, experimental impact sensitivities of HMX are in the ranges h_{50} = 26-32 cm, impact energy = 6-8 J [63], while for CL-20 they have variously been reported as h_{50} = 12-21 cm, impact energy = 3-5 J [63] and as h_{50} = 48-51 cm, impact energy = 12 J [64, 65], for a 2.5 kg drop mass.

We want to stress again that our results are only rough estimates which are

based upon a single factor, the available free space in the crystal lattice. This does not necessarily play the dominant role in determining the impact sensitivities of **8** – **10**.

Sensitivity and the molecular electrostatic potential

We shall also address sensitivity from another standpoint: the electrostatic potential $V_S(\mathbf{r})$ on the molecule's 0.001 au surface, which was mentioned earlier. It should be noted that the electrostatic potential is a real physical property, an observable, which is accessible experimentally [66, 67] as well as computationally. It rigorously reflects the charge distribution in a molecule. (For reviews of its fundamental significance and practical applications, see Politzer and Murray [68, 69].)

For typical organic molecules, the regions of negative potential $V_S(\mathbf{r})$ on their surfaces – due primarily to lone pairs and π electrons – are usually stronger than the positive [68-70], although the latter may cover larger areas. In energetic molecules, the situation is quite different. They commonly have highly electron-withdrawing components on their peripheries – NO_2 groups, aza nitrogens, *etc*. These deplete the electronic densities in the central portions of the molecules, leaving them strongly positive, with weaker negative regions on the outsides near the lone pairs of the NO_2 oxygens, aza nitrogens, *etc*. Overall, the positive potentials tend to be strongly dominant in energetic molecules, as has been shown on numerous occasions [26, 28, 29, 63, 71]. This can be quantified by comparing the positive and negative variances, σ_+^2 and σ_-^2, Eq. (4). For typical organic molecules, $\sigma_-^2 > \sigma_+^2$; for typical energetic, $\sigma_+^2 >> \sigma_-^2$ [70].

There is considerable empirical evidence that this anomalous potential imbalance that characterizes many energetic molecules is linked, at least symptomatically, to sensitivity [26, 28, 29, 63, 70-74]. This has been discussed at length by Murray *et al.* [28, 29].

In Figure 1 are presented the electrostatic potentials on the 0.001 au surfaces of **8** – **10**, computed with the WFA-SAS code [75] at the B3PW91/6-31G(d,p) level. For each molecule, the potential above the entire tricyclic polyazine framework is positive, particularly in the central portion. Negative regions are only on the peripheries of the molecules, associated with the oxygen and aza nitrogen lone pairs. There are no negative regions reflecting π electrons of the rings.

In order to quantify the relative strengths of the positive and negative potentials on the surfaces of **8** – **10**, we give the positive and negative variances:

Molecule **8**: $\sigma_+^2 = 147$ (kcal/mol)^2 $\sigma_-^2 = 183$ (kcal/mol)^2
Molecule **9**: $\sigma_+^2 = 264$ (kcal/mol)^2 $\sigma_-^2 = 65$ (kcal/mol)^2
Molecule **10**: $\sigma_+^2 = 281$ (kcal/mol)^2 $\sigma_-^2 = 20$ (kcal/mol)^2

The positive potential is clearly increasingly dominant in going from **8** to **10**, which suggests (but does not guarantee) that the sensitivities are likely to increase in that order. This is in agreement with the predictions based upon the available free space in the respective crystal lattices.

However the magnitudes of the variances reveal an interesting anomaly. While $\sigma_+^2 >> \sigma_-^2$ for **9** and **10**, as expected for energetic molecules, this is not the case for **8**; instead $\sigma_+^2 > \sigma_-^2$. This confirms what can be inferred from Figure 1, that the positive potentials are not dominant in **8**, as they are in **9** and **10**. It is unusual for an energetic molecule to have approximately similar σ_+^2 and σ_-^2, but not unknown; it is often associated with lower sensitivity [63, 70].

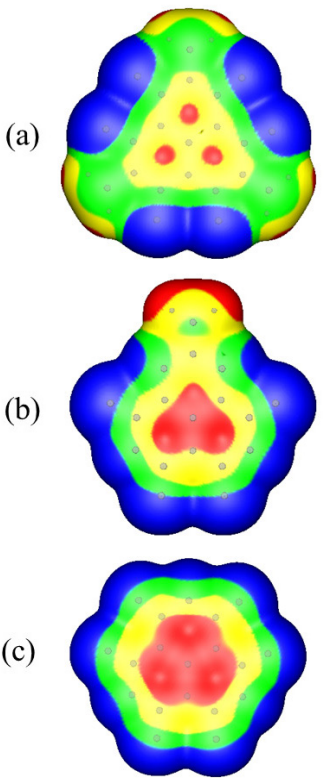


Figure 1. Calculated electrostatic potentials on the 0.001 au molecular surfaces of (a) molecule **8**, (b) molecule **9** and (c) molecule **10**. Color ranges, in kcal/mol, are: red, greater than 40; yellow, between 20 and 40; green, between 0 and 20; blue, less than 0 (negative). Positions of atoms are shown as gray circles.

Discussion and Summary

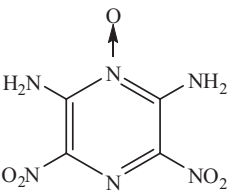
Our analyses predict **8** and **9** to be comparable to HMX in detonation properties, and **10** to exceed HMX and even CL-20 (Table 1). Compounds **8** – **10** are also expected to be less impact sensitive than both HMX and CL-20, especially **8** and **9**.

The fact that $\sigma_-^2 > \sigma_+^2$ for **8**, which is atypical for an energetic molecule, can be attributed to delocalization of electronic charge from the amino nitrogens into the rings, **11**. This somewhat diminishes analogous delocalization from the oxygens, **12** [16].

11 **12**

It follows that there should be increasing N-O double bond character in going from **8** to **9** to **10**, which is borne out by the respective computed N-O distances: 1.29 Å, 1.24 Å and 1.23 Å, with the B3PW91/6-31G(d,p) procedure. For comparison, the experimental gas phase N-O bond length in pyridine N-oxide is 1.278 Å [76]; our computed value is 1.266 Å [16].

Are the N-O bonds in **8** therefore relatively weak, so that they might serve as trigger linkages facilitating the initiation of detonation, making **8** undesirably sensitive? Reassurance on this point is provided by the compound LLM-105, **13**, which has been prepared and characterized [10]. It has an NH_2 on both sides of the N→O linkage, and our computed N-O distance in **13** is 1.29 Å, just as in **8**. However the experimental impact sensitivity of **13** is a quite acceptable h_{50} = 117 cm (29 J) [51], very similar to what we predict for **8** and **9** on the basis of the available free space in the crystal lattices, 115 cm (28 J) and 105 cm (26 J), respectively. If the density of **13** is obtained by Eq. (3) and used to determine the free volume in the lattice, the estimated impact sensitivity is h_{50} = 120 cm (29 J).



13

While **8** – **10** should all be of interest as possible energetic compounds, it appears that **8** may represent the best balance between high detonation performance and low sensitivity. With respect to its synthesis, it is encouraging that the triamine **5**, a possible precursor, is known and characterized [45].

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