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Computational Characterization of Two Di-1,2,3,4-tetrazine Tetraoxides, DTTO and iso-DTTO, as Potential Energetic Compounds

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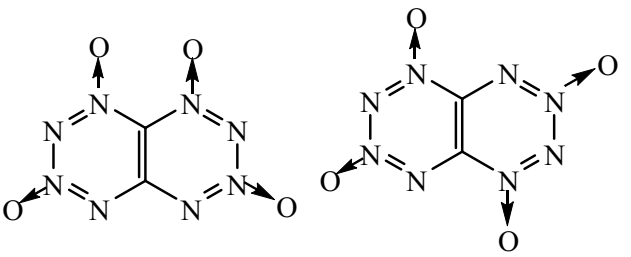
Abstract: The isomeric di-1,2,3,4-tetrazine tetraoxides DTTO and iso-DTTO have aroused considerable interest in recent years as potential energetic compounds, due to their predicted high densities and heats of formation and superior detonation properties. While neither has yet been synthesized, it has been suggested that the N→O linkages on alternate nitrogens will have a stabilizing effect. In the present study, we have reassessed the expected properties of DTTO and iso-DTTO. We find their anticipated detonation velocities and detonation pressures to be improved over HMX and similar to CL-20. The molecular surface electrostatic potentials of DTTO and iso-DTTO are consistent with the proposed stabilizing influence of the N→O bonds. Furthermore, estimates of the available free space in the crystal lattices indicate that DTTO and iso-DTTO may be significantly less sensitive to impact than either HMX or CL-20.

Keywords: DTTO, iso-DTTO, detonation properties, impact sensitivities

DTTO and iso-DTTO

The isomeric di-1,2,3,4-tetrazine tetraoxides DTTO (**1**) and iso-DTTO (**2**) have attracted considerable attention in recent years [1-6]. Much of this is due to the high densities, heats of formation and detonation properties that have

been predicted for them. For example, the calculated values of Song *et al.* [4] for iso-DTTO are compared in Table 1 with those obtained experimentally for HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and for CL-20 (hexanitrohexaazaisowurtzitane). From the data in Table 1, it would be anticipated that iso-DTTO should be superior as an energetic material to both HMX and CL-20, the current standards for high performance.



1, DTTO **2**, iso-DTTO

Table 1. Predicted properties of iso-DTTO (**2**) and experimental data for HMX and CL-20

Property	iso-DTTO[a]	HMX	CL-20
Density, g/cm^3	2.0-2.3	1.90[b]	2.04[c]
Heat of formation, kcal/mol	200 (s)	24.5[d]	90.2[d]
Detonation velocity, km/s	10.9	9.1[b]	9.38[c]
Detonation pressure, kbar	600	393[b]	---

[a]Reference 4; [b]Reference 7; [c]Reference 8; [d]Reference 9.

Neither DTTO nor iso-DTTO has yet been prepared. However there are reasons to believe that synthesis efforts may eventually be successful. It has been demonstrated that cyclic nitrogen catenation, such as is found in DTTO and iso-DTTO, is stabilized by involving the lone pairs of alternate nitrogens in coordinate covalent bonds to oxygens, N → O [10]. This presumably reduces the destabilizing repulsion between adjacent lone pairs. The effect of the oxygens has been described as producing alternating positive and negative charges on the ring nitrogens [1, 2, 10].

It was suggested that DTTO and iso-DTTO would be further stabilized because the positions of the oxygens would prevent both loss of N_2 and also destabilizing ring-chain tautomerism [2].

The exceptional predicted detonation properties of DTTO and iso-DTTO stem largely from their high estimated heats of formation and crystal densities,

especially the latter. To put into perspective the range of 2.0-2.3 g/cm^3 that Song *et al.* propose for iso-DTTO [4], consider that out of 229 C,H,N,O-containing energetic molecular solids (the compilation by Rice *et al.* [11] plus CL-20 [8]), only ten have experimental densities greater than 1.95 g/cm^3, the largest being 2.044 g/cm^3.

In view of the possibly superior performance levels of DTTO and iso-DTTO, and the consequent continued interest in them, it seemed reasonable to revisit these compounds from the standpoint of computational analyses of their potentials as energetic materials. We shall also examine the idea of alternating nitrogen charges that has been invoked as a stabilizing factor [1, 2, 10].

Determination of Detonation Properties

For explosives, two key measures of performance are the detonation velocity D and the detonation pressure P. The first is the stable velocity of the shock front that characterizes detonation, the second is the stable pressure that is developed behind the front [12-14]. While high values of D and P are very desirable, this must be balanced with the need to minimize the sensitivity of the compound to detonation caused by accidental stimuli, such as impact, shock, friction, etc. [15-17].

An important contribution to gaining insight into the factors that govern detonation velocity and pressure was made by Kamlet and Jacobs [18]. They developed empirical relationships showing that D and P can be expressed quite well in terms of four quantities:

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

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

In Eqs. (1) and (2), N is the number of moles of gaseous detonation products per gram of the explosive, with M_{ave} being 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 for the reaction. Finally, ρ is the loading density of the explosive, in g/cm^3. For a pure compound, this is often less than its crystal density [14, 18], but the latter is generally used in computationally predicting D and P for proposed new compounds.

Several computer codes have been designed for predicting D and P, *e.g.* RUBY [19], TIGER [20], BKW [7], EXPLO5 [21] and CHEETAH [22]. Several other empirical formulations of detonation properties have also been proposed;

some of these, for detonation velocity, are summarized by Shekhar [23]. Kamlet and Jacobs showed that Eqs. (1) and (2) give results in good agreement with the RUBY code when N, M_{ave} and Q are taken from the RUBY output [18]. More recently, we have provided further support for Eqs. (1) and (2) in comparisons with experimental D and P, using our computed N, M_{ave}, Q and ρ [24]. Of the empirical procedures for estimating D, Shekhar concluded that the Kamlet-Jacobs is the most accurate [23]. In this work, we have used Eqs. (1) and (2) to obtain detonation velocities and pressures.

It is accordingly necessary to determine values for N, M_{ave}, Q and ρ. The first three of these depend upon the composition of the detonation products. Kamlet and Jacobs' analyses [18], results of the BKW computer code [7] and our comparisons with experimental D and P [24] all indicate that Eqs. (1) and (2) generally produce good results when the product composition is taken to be N_2 (g), H_2O (g), CO_2 (g) and C (s), with oxygen being used to form H_2O before CO_2.

For both DTTO and iso-DTTO, the detonation reactions are therefore taken to be,

$$C_2N_8O_4\,(s) \rightarrow 4N_2\,(g) + 2CO_2\,(g) \tag{3}$$

from which it follows that N = 0.02999 mol/g and M_{ave} = 33.35 g/mol. In order to find Q, we must first calculate the solid state heats of formation of DTTO and iso-DTTO.

Heats of Formation

The gas phase heats of formation $\Delta H_f^\circ(g)$ of DTTO and iso-DTTO were obtained by means of the atom equivalents procedure [9, 25, 26]:

$$\Delta H_f^\circ(g) = E(g) - \sum_i n_i x_i \tag{4}$$

In Eq. (4), E is the computed minimum energy of the molecule at 0 K, n_i is the number of atoms of element i and x_i is its atom equivalent energy. We have used the x_i determined by Rice and Byrd through a least-squares fitting of Eq. (4) to the experimental $\Delta H_f^\circ(g)$ of a series of C,H,N,O-containing energetic compounds [9], corresponding to E(g) at the density functional B3LYP/6-311++G(2df,2p) level. This gave:

DTTO: $\Delta H_f^\circ(g)$ = 223.3 kcal/mol

iso-DTTO: $\Delta H_f^\circ(g)$ = 223.5 kcal/mol

These values are in satisfactory agreement with the results of the correlation consistent Composite Approach, 232.2 and 231.1 kcal/mol for DTTO and iso-DTTO, respectively [6].

In order to calculate the detonation heat release Q for DTTO and iso-DTTO, it is necessary to have their solid state heats of formation. Liquid and solid ΔH_f° are related to the gas phase ΔH_f° by,

$$\Delta H_f^\circ(\text{liquid}) = \Delta H_f^\circ(\text{gas}) - \Delta H_{vap} \quad (5)$$

$$\Delta H_f^\circ(\text{solid}) = \Delta H_f^\circ(\text{gas}) - \Delta H_{sub} \quad (6)$$

in which ΔH_{vap} and ΔH_{sub} are the heats of vaporization and sublimation. We have shown some time ago that ΔH_{vap} and ΔH_{sub} can be expressed in terms of the electrostatic potential on the molecular surface [27], as shall now be briefly summarized.

The electrostatic potential $V(\mathbf{r})$ that is produced in the space around a molecule by its nuclei and electrons is given by Eq. (7):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (7)$$

Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the molecule's electronic density. $V(\mathbf{r})$ is a physical observable, which can be obtained experimentally as well as computationally [28, 29]. We usually compute $V(\mathbf{r})$ on the molecular surface, taking this to be the 0.001 au (electrons/bohr^3) contour of the electronic density as suggested by Bader et al. [30]. $V(\mathbf{r})$ on this surface is labeled $V_S(\mathbf{r})$.

Certain statistical features of $V_S(\mathbf{r})$ have proven to be effective indicators of non-covalent interactions, and to correlate well with properties that depend upon such interactions; this is summarized by Politzer and Murray [31]. Among these features are the positive and negative variances, $\acute{o}_+^2$ and $\acute{o}_-^2$, and a balance parameter ν; they are defined by Eqs. (8) and (9):

$$\sigma_+^2 = \frac{1}{m}\sum_{i=1}^{m}\left[V_S^+(\mathbf{r}_i) - \overline{V}_S^+\right]^2 \quad \sigma_-^2 = \frac{1}{n}\sum_{j=1}^{n}\left[V_S^-(\mathbf{r}_j) - \overline{V}_S^-\right]^2 \quad (8)$$

$$\nu = \frac{\sigma_+^2\sigma_-^2}{(\sigma_{tot}^2)^2} \quad (9)$$

In Eqs. (8) and (9), the summations are over the m and n points at which $V_S(\mathbf{r})$ is 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, and $\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2$.

The variances reflect the variabilities and ranges of the positive and negative surface electrostatic potentials. The parameter ν is a measure of the balance between the positive and negative surface potentials; it attains a maximum of 0.25 when $\sigma_+^2 = \sigma_-^2$. The product $(\nu\sigma_{tot}^2)$ is an excellent index of electrostatic interactive tendencies, especially between molecules of the same kind (as in a molecular crystal) [31]. A large value of σ_{tot}^2 and ν near 0.25 implies that both the positive and the negative surface potentials are strong, maximizing the possibilities for attractive interactions.

Thus we were able to demonstrate that experimental heats of vaporization and heats of sublimation can be approximated well in terms of the molecular surface area and $(\nu\sigma_{tot}^2)$ [27, 31]:

$$\Delta H_{vap} = a_1(\text{area})^{1/2} + b_1(\nu\sigma_{tot}^2)^{1/2} + c_1 \quad (10)$$

$$\Delta H_{sub} = a_2(\text{area})^2 + b_2(\nu\sigma_{tot}^2)^{1/2} + c_2 \quad (11)$$

Byrd and Rice used a database of experimental ΔH_{vap} and ΔH_{sub} for C,H,N,O-containing energetic compounds to evaluate a_1, b_1 and c_1 and a_2, b_2 and c_2 [9], for B3LYP/6-311++G(2df,2p) computed areas and surface potentials.

Using Eqs. (10) and (11), the results for DTTO and iso-DTTO are:

DTTO: ΔH_{vap} = 14.2 kcal/mol ΔH_{sub} = 17.8 kcal/mol

iso-DTTO ΔH_{vap} = 14.4 kcal/mol ΔH_{sub} = 18.2 kcal/mol

It follows via Eqs. (5) and (6) that the liquid and solid state heats of formation are:

DTTO: ΔH_f°(liquid) = 223.3 – 14.2 = 209.1 kcal/mol

ΔH_f°(solid) = 223.3 – 17.8 = 205.5 kcal/mol

iso-DTTO: ΔH_f°(liquid) = 223.5 – 14.4 = 209.1 kcal/mol

ΔH_f°(solid) = 223.5 – 18.2 = 205.3 kcal/mol

All of the thermochemical data – ΔH_f°(g), ΔH_{vap}, ΔH_{sub}, ΔH_f°(liquid) and ΔH_f°(solid) – are predicted to be essentially identical for DTTO and iso-DTTO.

Heat Releases in Detonation

Once the solid state heats of formation of DTTO and iso-DTTO are available, the respective enthalpy changes ΔH_{det} for the detonation reactions, Eq. (3), can readily be evaluated:

ΔH_{det}(DTTO or iso-DTTO) = $4\Delta H_f^\circ(N_2,g) + 2\Delta H_f^\circ(CO_2,g) - \Delta H_f^\circ$(DTTO or iso-DTTO,s) (12)

$\Delta H_f^\circ(N_2,g)$ is zero by definition, and the experimental $\Delta H_f^\circ(CO_2,g)$ is -94.05 kcal/mol [32]. Then using our $\Delta H_f^\circ(s)$ for DTTO and iso-DTTO gives,

DTTO: ΔH_{det} = -393.6 kcal/mol Q = 1967 cal/g

Iso-DTTO: ΔH_{det} = -393.4 kcal/mol Q = 1966 cal/g

Densities

The remaining quantities that are needed in order to predict the detonation velocities and pressures of DTTO and iso-DTTO by means of Eqs. (1) and (2) are their densities. Qiu *et al.* [33] and more extensively Rice *et al.* [34] have shown that the densities of energetic molecular solids can be estimated with reasonable accuracy with the simple formula,

$$\text{density} = \frac{M}{V(0.001)} \tag{13}$$

where M is the molecular mass in g/molecule and V(0.001) is the volume, in cm^3/molecule, that is encompassed by the 0.001 au contour of the molecule's electronic density.

Eq. (13) is surprisingly successful, considering that it reflects just a single isolated molecule and completely neglects crystal factors; for 180 C,H,N,O-containing compounds (nitramines, nitroaromatics, nitrate esters, etc.), Rice *et al.* had an average absolute deviation from experimental densities of 0.047 g/cm^3 [34]. For more than 10% of the compounds, however, the error was greater than 0.100 g/cm^3.

These occasional large discrepancies stimulated the development of an improved version of Eq. (13), in which intermolecular interactions within the crystal are taken into account via the electrostatic potentials on the molecular surfaces [35]. This is done by introducing the electrostatic interaction index ($\nu\sigma_{tot}^2$), defined by Eqs. (8) and (9); it was utilized earlier to determine the heats of vaporization and sublimation. Eq. (13) then becomes,

$$\text{density} = \alpha\left(\frac{M}{V(0.001)}\right) + \beta\left(\nu\sigma_{tot}^2\right) + \gamma \tag{14}$$

The coefficients α, β and γ were assigned by fitting Eq. (14) to the experimental densities of a diverse group of 36 energetic compounds [35]; the necessary calculations were at the B3PW91/6-31G(d,p) level.

Eq. (14) has an average absolute deviation from experiment of 0.036 g/cm^3 and in only one instance was the error greater than 0.100 g/cm^3. Eq. (14) was therefore used to obtain the densities of DTTO and iso-DTTO:

DTTO: density = 1.899 g/cm^3 iso-DTTO: density = 1.897 g/cm^3

These are essentially the same as the experimental density of HMX, 1.90 g/cm^3 (Table 1).

It should be noted that Eqs. (13) and (14) pertain specifically to C,H,N,O-containing energetic compounds, which typically have higher densities than organic molecular solids in general [36]. Accordingly Eqs. (13) and (14) can be expected to overestimate the densities of non-energetic organic crystals.

Computed Detonation Properties

Inserting the N, M_{ave}, Q and ρ that have been obtained in this work into Eqs. (1) and (2) gives,

DTTO: D = 9.71 km/s P = 432 kbar

iso-DTTO: D = 9.70 km/s P = 431 kbar

Both D and P are better for DTTO and iso-DTTO than the experimental values for HMX and CL-20, as shown in Table 2. However a more meaningful comparison may be to the D and P calculated for HMX and CL-20 with Eqs. (1) and (2), using their experimental Q and ρ. These are also in Table 2, along with all of the Q and ρ. The predicted D and P of DTTO and iso-DTTO are higher than those produced by Eqs. (1) and (2) for HMX but about the same as those for CL-20.

The data is Table 2 demonstrate again, as was emphasized earlier [24], that on a relative basis, the density is not as dominant in determining the detonation velocity and pressure as might be inferred from Eqs. (1) and (2), in which it appears to higher powers than any other quantity. The D and P of DTTO and iso-DTTO exceed those of HMX even though the densities are the same, and are similar to those of CL-20 despite the latter having a significantly higher density!

According to Eqs. (1) and (2), D and P depend upon Q and the product $NM_{ave}^{0.5}$ as well as upon ρ. The magnitude of $NM_{ave}^{0.5}$ for DTTO and iso-DTTO (0.173) is very similar to those for HMX (0.176) and for CL-20 (0.172). Thus the fact that the detonation velocities and pressures of DTTO and iso-DTTO are higher, relative to HMX and CL-20, than would be anticipated from the densities can

be attributed primarily to the much greater detonation heat releases of DTTO and iso-DTTO (Table 2).

Table 2. Computed and experimental properties relevant to detonation

Property	DTTO[a]	iso-DTTO[a]	HMX	CL-20
Density, g/cm^3	1.899	1.897	1.90[b]	2.04[c]
Detonation heat release, Q, cal/g	1967	1966	1498[d]	1567[d]
Detonation velocity, km/s				
Experimental	---	---	9.1[b]	9.38[c]
Calculated, Eq. (1)	9.71	9.70	9.15[d]	9.62[d]
Detonation pressure, kbar				
Experimental	---	---	393[b]	---
Calculated, Eq. (2)	432	431	383[d]	441[d]

[a] Calculated in present work; [b] Reference 7; [c] Reference 8; [d] Reference 24.

Sensitivities

A very important consideration in designing and evaluating energetic materials is sensitivity, *i.e.* vulnerability to accidental detonation caused by unintended stimuli, such as impact, shock, etc. A primary objective, and a very challenging one, is to minimize sensitivity while maximizing detonation performance.

Sensitivity depends upon a number of molecular, crystalline and physical factors [12, 13, 15-17, 37, 38]. We have recently presented evidence suggesting that one of these factors is the free space ΔV that is available to the molecule in its crystal lattice [39],

$$\Delta V = V_{eff} - V(0.003) \quad (15)$$

In Eq. (15), V_{eff} is the effective volume of the molecule corresponding to 100% packing of the unit cell. It is given by,

$$V_{eff} = M/\text{density} \quad (16)$$

V(0.003) is the space enclosed by the 0.003 au contour of the molecule's electronic density. V(0.003) was selected for this purpose because the ratio $V(0.003)/V_{eff}$ was found to reproduce very well the actual packing coefficients of energetic compounds. We showed that there exists a rough correlation between ΔV and impact sensitivity: the greater is ΔV, the available free space in the lattice,

the more sensitive is the compound [39]. (A relevant analysis has recently been carried out by Zhang [40].)

We used our calculated densities for DTTO (1.899 g/cm^3) and iso-DTTO (1.897 g/cm^3), and computed V(0.003) with the B3PW91/6-31G(d,p) procedure (for consistency with the work that established the ΔV – sensitivity correlation [39]). The estimated impact sensitivities h_{50} of both DTTO and iso-DTTO, in terms of the 2.5 kg drop mass scale, are about 110 cm (impact energies roughly 27 J). This would make DTTO and iso-DTTO significantly less sensitive than both CL-20 and HMX. (The impact sensitivity of CL-20 has variously been reported as h_{50} = 12-21 cm, impact energy = 3-5 J [41] and as h_{50} = 48-51 cm, impact energy = 12 J [42, 43], given here in terms of a 2.5 kg drop mass, while for HMX the values are h_{50} = 26-32 cm, impact energy = 6-8 J [41].) A word of caution: The free space available in the lattice is only one of the factors that influence sensitivity [12, 13, 15-17, 37, 38], and its role in any given case may be overshadowed by some other one. Estimates based upon ΔV should be regarded as suggestive, certainly not conclusive.

Charge Distributions and Molecular Surface Electrostatic Potentials

In order to investigate the proposed alternation of charges on the nitrogens of DTTO and iso-DTTO [1, 2], we have computed the electrostatic potentials on their 0.001 au surfaces. The electrostatic potential is a real property, accessible experimentally [28, 29], and therefore gives more meaningful insight into charge distributions than do atomic charges, which are defined quantities with no rigorous physical basis [44].

The surface potentials $V_S(\mathbf{r})$ of DTTO and iso-DTTO are presented in Figures 1 and 2. They were calculated at the B3PW91/6-31G(d,p) level with the WFA code [45]. They are strongly positive above and below the central portions of the molecules, as is characteristic of energetic compounds [41, 46], and negative around the peripheries. These negative $V_S(\mathbf{r})$ are due to the oxygens and the unsubstituted ring nitrogens. $V_S(\mathbf{r})$ is positive above and below all of the nitrogens, but more so the ones bearing oxygens.

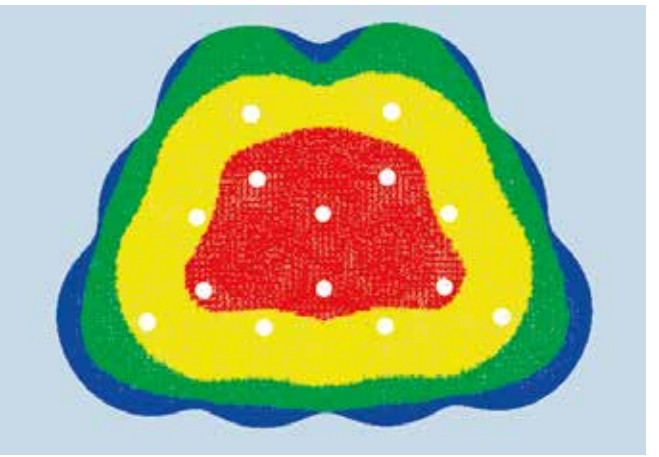


Figure 1. Computed electrostatic potential on the 0.001 au molecular surface of DTTO (**1**). Positions of nuclei are indicated by white circles. Color ranges, in kcal/mole, are: red, greater than 30; yellow, between 0 and 30; green, between -10 and 0; blue, more negative than -10.

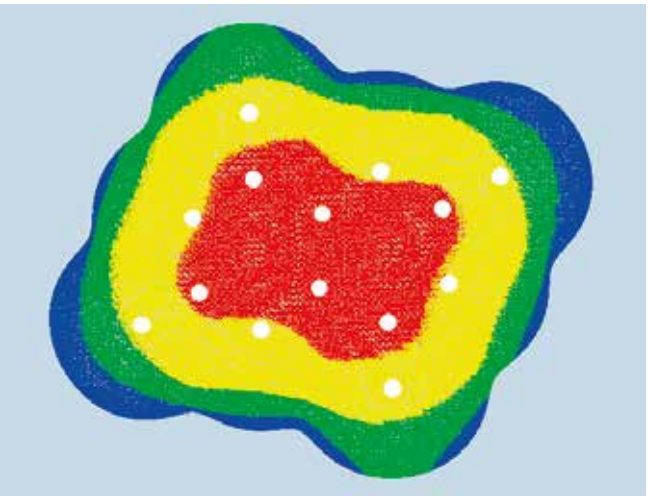


Figure 2. Computed electrostatic potential on the 0.001 au molecular surface of iso-DTTO (**2**). Positions of nuclei are indicated by white circles. Color ranges, in kcal/mole, are: red, greater than 30; yellow, between 0 and 30; green, between -10 and 0; blue, more negative than -10.

Thus the unsubstituted nitrogens appear to have regions of both positive and negative surface potentials, which is not unusual for covalently-bonded atoms and illustrates the fallacy of trying to assign single atomic charges [47, 48]. It

is fair to say that the unsubstituted nitrogens are more negative (or less positive) than the substituted ones, and that structures **1A** and **2A** can be regarded as making some contributions.

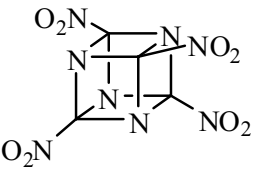
Summary

In Table 3 are listed the properties of DTTO and iso-DTTO that have been computed/estimated in this work. The properties considered are virtually identical for the two compounds. In detonation velocity and detonation pressure, DTTO and iso-DTTO are expected to be better than HMX and about the same as CL-20 (Table 2). In terms of impact sensitivity, DTTO and iso-DTTO may have a significant advantage over both HMX and CL-20.

Finally, we want to mention our recent computational characterization of another proposed energetic compound in which there has long been interest, 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, **3** [49]. Our predicted density, solid phase heat of formation, detonation velocity and detonation pressure for **3** are quite similar to those found for DTTO and iso-DTTO, but **3** is expected to be much more sensitive: h_{50} ~40 cm, impact energy ~9.8 J.

Table 3. Summary of computed properties

Property	DTTO	iso-DTTO
Density, g/cm^3	1.90	1.90
Heat of formation, gas phase, kcal/mol	223	223
Heat of vaporization, kcal/mol	14	14
Heat of sublimation, kcal/mol	18	18
Heat of formation, liquid, kcal/mol	209	209
Heat of formation, solid, kcal/mol	206	205
Heat release in detonation, Q, cal/g	1967	1966
Detonation velocity, km/s	9.71	9.70
Detonation pressure, kbar	432	431
Impact sensitivity		
h_{50}, cm	~110	~110
impact energy, Joules	~27	~27



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Acknowledgments

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