



Computational Characterization of a Potential Energetic Compound: 1,3,5,7-Tetranitro-2,4,6,8-tetraazacubane

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Abstract: The high densities and (strain-induced) enthalpies of formation of cage-type molecules have drawn attention to their polynitro derivatives as potential energetic materials. Several such compounds have been synthesized, including octanitrocubane and hexanitrohexaazaisowurtzitane. One that has not yet been prepared but has evoked continuing interest is 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane. Some years ago, on the basis of a very high estimated density (about 2.19 g/cm³), it was predicted to have detonation properties greatly superior to those of HMX. We have now used computational procedures developed since that time to reassess the expected detonation performance of this compound. We find: density, 1.940 g/cm³; solid phase enthalpy of formation at 298 K, 757 cal/g; detonation velocity, 9.8 mm/μs; detonation pressure, 444 kbar; impact sensitivity, h₅₀ ~ 40 cm. These are all better than the corresponding values for HMX, but not by as much as had been estimated earlier.

Keywords: 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, energetic performance, density, impact sensitivity

Background

Among the properties sought in potential explosives are high detonation velocity D and detonation pressure P . These refer to the stable velocity of the shock front that characterizes detonation and the stable pressure that is developed behind the front [1-3].

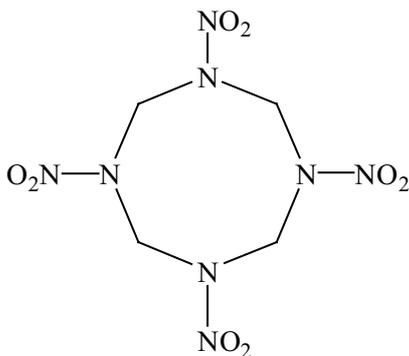
The detonation velocity and pressure can be estimated by means of eqs. (1) and (2) [4]:

$$D \text{ (mm/}\mu\text{s)} = 1.01N^{0.5}M_{\text{av}}^{0.25}Q^{0.25}(1 + 1.30\rho) \quad (1)$$

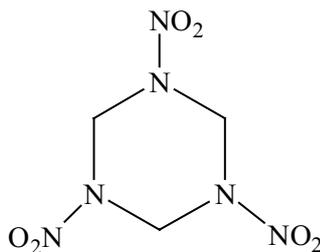
$$P \text{ (kbar)} = 15.58NM_{\text{av}}^{0.5}Q^{0.5}\rho^2 \quad (2)$$

where: N is the number of moles of gas produced per gram of explosive (or propellant), M_{av} is the average molecular mass of the gaseous products in g/mol, Q is $-\Delta H$ for the detonation reaction in cal/g, and ρ is the density of the explosive in g/cm³.

In eqs. (1) and (2), the density appears to a higher power than any of the other quantities, and thus plays a dominant role in determining D and P . Mader has described density as “the primary physical parameter in detonation performance” [5]. As he points out, the superior detonation performance of HMX, **1** ($D = 9.100$ mm/ μ s, $P = 393$ kbar) compared to RDX, **2** ($D = 8.754$ mm/ μ s, $P = 347$ kbar) [6] can be attributed to the higher density of the former (1.90 vs. 1.80 g/cm³), since N , M and Q are essentially the same for both compounds [4].



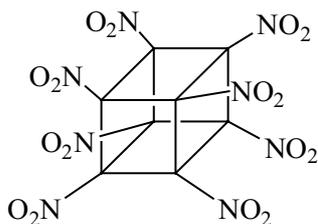
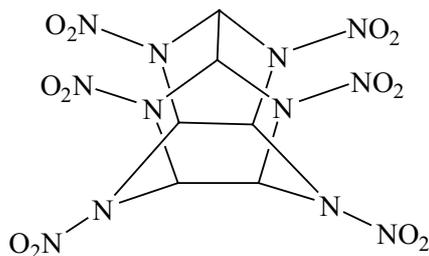
HMX, **1**



RDX, **2**

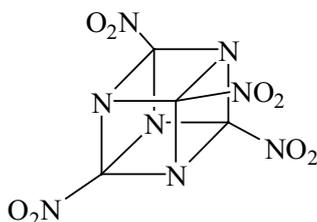
A high density is therefore a top priority in seeking to develop new explosives. Nielsen has listed some molecular structural features that are known to increase density [7]: high symmetry, quaternary and/or tertiary carbons, tertiary nitrogens and condensed rings. These requirements are met by polycyclic cage-like molecules, such as tetrahedrane, triprismane, cubane, adamantane, wurtzitanene, isowurtzitanene, etc., as well as the corresponding polyaza systems in which some carbons have been replaced by nitrogens. Another advantage of these molecules is that they tend to have significant degrees of strain. This

results in larger enthalpies of formation and thus greater heat release in the detonation reactions. There has accordingly been considerable attention focused upon polynitro derivatives of these molecules as potential high-performance explosives [7-9], and some have been synthesized, e.g. octanitrocubane, **3** [10] and hexanitrohexaazaisowurtzitane, **4** (HNIW, CL-20) [11]. They do indeed have high densities, 1.978 [12] and 2.044 g/cm³ [11, 13], respectively.

**3****4, HNIW, CL-20**

1,3,5,7-Tetranitro-2,4,6,8-tetraazacubane

A polynitropolyaza cage-like compound that has not yet been synthesized but in which there has been recurring interest [3, 8, 14-20] is 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, **5**. This molecule benefits from the stabilizing effect of the aza nitrogens [21, 22], which counteracts the weakening that NO₂ substituents introduce in some strained tertiary C-C bonds [23]. (For a detailed discussion, see Politzer and Murray [17]).

**5**

Early forecasts of the detonation properties of **5** were extremely favorable, indicating that both the velocity *D* and the pressure *P* would be greatly superior to those of HMX [8, 16]. However these values were based upon a very high

predicted density of about 2.19 g/cm³. There is good reason to question this. For example, octanitrocubane (**3**), which had not yet been prepared, was expected to have a density of 2.09 g/cm³ [8]; it was eventually found to be 1.978 g/cm³ [12]!

In view of the desirable structural features of **5**, and the continuing interest in it as a possible explosive and/or propellant, realistic estimates of its key properties are essential. Our objective in this work has accordingly been to revisit **5**, and to carry out a computational analysis of its potential as an energetic compound. We will apply techniques that have been developed since the earlier predictions were made.

Density

A very straightforward approach to estimating the densities of molecular crystals of energetic compounds has recently been utilized by Qiu *et al.* [24] and more extensively by Rice *et al.* [12]. They used the formula,

$$\text{density} = \frac{M}{V(0.001)} \quad (3)$$

in which M is the molecular mass, in g/molecule, and $V(0.001)$ is the volume of the isolated gas phase molecule, in cm³/molecule. This was taken to be the space encompassed by the 0.001 au (electrons/bohr³) contour of the molecule's electronic density, as proposed by Bader *et al.* [25].

This very simple approach is surprisingly successful, especially considering that no account is taken of lattice effects. For 180 C,H,N,O-containing compounds of different types (i.e. nitramines, nitroaromatics, nitrate esters, etc.), Rice *et al.* obtained an average absolute deviation from experimental values of 0.047 g/cm³ [12].

In some instances, however, there were rather large errors; for 11% of the compounds, the error is more than 0.10 g/cm³. Particularly relevant in the present context is the case of octanitrocubane (**3**) for which eq. (3) yields a density of 2.074 g/cm³ [12], considerably overestimating the actual 1.978 g/cm³. Such discrepancies suggested that eq. (3) needs to be corrected to better reflect the effects of intermolecular interactions within the crystal [26]. This was done in terms of the electrostatic potentials on the molecular surfaces.

The electrostatic potential $V(\mathbf{r})$ that the nuclei and electrons of a molecule create in the surrounding space is given by,

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (4)$$

where Z_A is the charge on nucleus A, located at \mathbf{R}_A , and $\rho(\mathbf{r})$ is the electronic density. $V(\mathbf{r})$ is a physical observable, which can be determined experimentally, by diffraction methods [27, 28], as well as computationally. Its sign in a given region depends upon whether the positive contribution of the nuclei or the negative one of the electrons is dominant there.

$V(\mathbf{r})$ computed on an outer contour of a molecule's electronic density, for instance the 0.001 au, has proven to be an effective guide to noncovalent interactions [29]. This often involves characterizing the surface potential, labeled $V_S(\mathbf{r})$, in terms of certain statistical features [30]. Those that are relevant for our present purposes are the positive and negative variances, σ_+^2 and σ_-^2 :

$$\sigma_+^2 = \frac{1}{m} \sum_{i=1}^m [V_S^+(\mathbf{r}_i) - \bar{V}_S^+]^2 \quad (5)$$

$$\sigma_-^2 = \frac{1}{n} \sum_{j=1}^n [V_S^-(\mathbf{r}_j) - \bar{V}_S^-]^2 \quad (6)$$

In eqs. (5) and (6), 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 $V_S^-(\mathbf{r}_j)$. \bar{V}_S^+ and \bar{V}_S^- are the positive and negative averages. From σ_+^2 and σ_-^2 can be obtained the total variance, $\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2$, and the balance parameter v ,

$$v = \frac{\sigma_+^2 \sigma_-^2}{(\sigma_{\text{tot}}^2)^2} \quad (7)$$

The variance indicates the variability and range of $V_S(\mathbf{r})$, while v is a measure of the degree of balance between the positive and the negative surface potentials; when $\sigma_+^2 = \sigma_-^2$, v attains its maximum possible value of 0.25.

In extensive studies, summarized by Politzer and Murray [29], we have found that the product $v\sigma_{\text{tot}}^2$ is an excellent index of electrostatic interactive tendencies, particularly when the molecules are of the same kind (as in a molecular crystal). When σ_{tot}^2 is large and v is near 0.25, then *both* the positive and the negative potentials on the molecular surface are strong, maximizing the possibilities for attractive interactions.

It was accordingly proposed that the crystal density expression, eq. (3), be modified by the introduction of the interaction index $v\sigma_{\text{tot}}^2$ [26]:

$$\text{density} = \alpha \left(\frac{M}{V(0.001)} \right) + \beta (v\sigma_{\text{tot}}^2) + \gamma \quad (8)$$

The coefficients α , β and γ were obtained by means of a multiple regression procedure [31], utilizing a database of experimental densities for a diverse group of 36 energetic compounds. Molecular geometry optimizations and calculation of $V_S(\mathbf{r})$ were at the density functional B3PW91/6-31G(d,p) level.

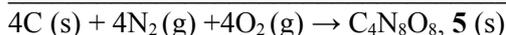
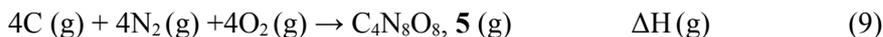
With eq. (8), the average absolute deviation from experimental densities for the 36 compounds was 0.036 g/cm³, and in only one instance was the error greater than 0.100 g/cm³. With eq. (8), the density of octanitrocubane (**3**) is predicted to be 1.982 g/cm³ [26], very close to the experimental 1.978 g/cm³.

We used eq. (8) to estimate the density of the proposed target compound **5**. Geometry optimization and calculation of $V(0.001)$, σ_{tot}^2 and v were with the B3PW91/6-31G(d,p) method. The density predicted for **5** is 1.940 g/cm³. This is 0.101 g/cm³ less than what is given by $M/V(0.001)$ alone, eq. (3). The correction via the interaction index lowers the estimated density, by roughly the same amount as for octanitrocubane.

A word of caution concerning eqs. (3) and (8) is in order. They are intended for C,H,N,O-containing energetic solids. These typically have higher densities than do other organic solids [32]. It is therefore to be expected (and we have confirmed [33]) that eqs. (3) and (8) will overestimate the densities of non-energetic organic crystals. The latter presumably require using a lower contour of the electronic density for the molecular volume.

Enthalpy of formation

A number of procedures for calculating enthalpies of formation, ΔH_f , have been proposed; some of these are discussed by Rice *et al.* [34] and by Politzer *et al.* [35]. A direct approach is to invoke the definition of ΔH_f : first compute ΔH for the gas phase formation of the compound from its elements, then combine this with the appropriate enthalpies of vaporization and/or sublimation so that the elements are in their standard states. For compound **5**, the sequence is,



$$\Delta H_f [C_4N_8O_8, \mathbf{5} (s)] = \Delta H (g) + 4\Delta H_{sub,C} - \Delta H_{sub,5} \quad (12)$$

$\Delta H_{sub,C}$ and $\Delta H_{sub,5}$ are the sublimation enthalpies of carbon and compound **5**, respectively.

Another approach is to use atom equivalents [34, 36, 37] to obtain the gas phase heat of formation:

$$\Delta H_f (g) = E(g) - \sum_i n_i x_i \quad (13)$$

In eq. (13), 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. Rice *et al.* determined the x_i through a least-squares fitting of eq. (13) to the experimental $\Delta H_f (g)$ of a series of C,H,N,O-containing energetic compounds [34, 37].

Eq. (13) gives the enthalpy of formation of gaseous **5**, as does the combination of $\Delta H (g) + 4\Delta H_{sub,C}$, eqs. (9) and (10). For practical purposes, however, we need the enthalpy of formation of solid **5**, $\Delta H_f [C_4N_8O_8, \mathbf{5} (s)]$. This requires subtracting the enthalpy of sublimation of **5**, eq. (11). It was observed some time ago by Politzer *et al.* [38] that enthalpies of sublimation correlate well with molecular surface area and the interaction index $v\sigma_{tot}^2$, which was already mentioned:

$$\Delta H_{sub} = a(\text{area})^2 + b(v\sigma_{tot}^2)^{0.5} + c \quad (14)$$

The coefficients a , b and c were determined specifically for an experimental database of C,H,N,O-containing energetic compounds by Rice *et al.* [34, 37].

We utilized three different procedures to first evaluate the enthalpy of formation of **5** in the gaseous state. Two of these involved computing (a) B3LYP/6-31G(d) and (b) B3LYP/6-311++G(2df,2p) values for $\Delta H (g)$ at 298 K, eq. (9), and then combining them with $4\Delta H_{sub,C}$; the experimental $\Delta H_{sub,C}$ was used (171.3 kcal/mol) [39]. The results were (a) 236 and (b) 246 kcal/mol. We also obtained $\Delta H_f [C_4N_8O_8, \mathbf{5} (g)]$ by means of eq. (13), with the B3LYP/6-31G(d) energy E and the corresponding atom equivalents from Rice *et al.* [34]. This gave 243 kcal/mol. Taking the average yields $\Delta H_f [C_4N_8O_8, \mathbf{5} (g)] = 242$ kcal/mol.

Finally, the enthalpy of sublimation of **5** was calculated with eq. (14) and the coefficients of Rice *et al.* at the B3LYP/6-31G(d) [34] and B3LYP/6-311++G(2df,2p) [37] levels. These yielded $\Delta H_{sub,5} = 25$ and 23 kcal/mol, respectively, an average of 24 kcal/mol. Subtracting this from $\Delta H_f [C_4N_8O_8, \mathbf{5} (g)]$ gives the desired solid phase enthalpy of formation of **5** at 298 K: $\Delta H_f [C_4N_8O_8, \mathbf{5} (s)] = 218$ kcal/mol. On a cal/g basis, this is 757 cal/g. For comparison, the enthalpy of formation of solid HMX is 60.5 cal/g [3].

Detonation performance

In order to calculate the detonation velocity and pressure of **5** via eqs. (1) and (2), we need to know ΔH for the detonation reaction, since $Q = -\Delta H$. For this purpose, we shall assume an idealized case: complete conversion of **5** into CO_2 and N_2 .



The actual process will certainly lead to small amounts of other gaseous products, but eq. (15) should be a reasonable approximation.

ΔH for reaction (15) can be obtained as the sum of the enthalpies of formation of the products minus that of the reactant. Taking the former from Lias *et al.* [39], $\Delta H = -594$ kcal/mol. Then $Q = -\Delta H = 2062$ cal/g.

For reaction (15), $N = 0.02777$ moles/g and $M_{\text{av}} = 36.01$ g/mol. Inserting these values into eqs. (1) and (2), along with $\rho = 1.940$ g/cm³ and $Q = 2062$ cal/g gives $D = 9.8$ mm/ μs and $P = 444$ kbar for compound **5**. These are significantly higher than the experimental D and P for HMX, $D = 9.100$ mm/ μs and $P = 393$ kbar [6], although not as much as was predicted earlier [8, 15].

Sensitivity

C-NO₂ bond strength

For an energetic material, the term sensitivity refers to its vulnerability to accidental detonation caused by unintended stimuli such as impact, shock, friction, etc. Since this vulnerability is highly undesirable, there have been extensive efforts to (a) achieve a better understanding of the initiation of detonation, and (b) develop methods for predicting the sensitivities of proposed target compounds [1, 40-43]. For some compounds, a key initiating step appears to be the rupture of a particular bond, a “trigger linkage”. There is evidence that this is the case for many nitramines, the trigger linkage being an N-NO₂ bond [44-47]. On the other hand, breaking a C-NO₂ bond may or may not be involved in detonation initiation in those compounds that possess this linkage; other pathways may be followed in specific instances [40, 41, 47, 48].

In order to assess the likelihood of a C-NO₂ bond in **5** being a trigger linkage, we have computed ΔH at 298 K for the process of breaking one of the C-NO₂ bonds in **5**. Three different computational approaches gave similar results for this bond dissociation enthalpy: B3LYP/6-31G(d): 49.0 kcal/mol; B3PW91/6-

31G(d,p): 50.3 kcal/mole; B3LYP/6-311++G(2df,2p): 46.6 kcal/mol.

With a dissociation enthalpy of about 49 kcal/mol, the C-NO₂ bond in **5** is relatively weak; for example, computed values for nitromethane, 1,3,5-trinitrobenzene and 2,4-dinitroimidazole are 57, 64 and 68 kcal/mol [47]. It is accordingly conceivable that rupture of a C-NO₂ bond could be an initiating step in the detonation of **5**.

It might be thought that the relatively low C-NO₂ bond dissociation enthalpy can be attributed to relaxation of the molecular framework after splitting off NO₂. However the computed bond lengths do not support this interpretation. For example, the B3LYP/6-311++G(2df,2p) C-N_{aza} and C-N_{nitro} distances are 1.498-1.503 and 1.495-1.497 Å in **5** and 1.492-1.509 and 1.497 Å after loss of an NO₂ group; they are virtually unaffected.

Estimated sensitivity

We have recently proposed that one of the factors that determines impact sensitivity is the free space ΔV that is available to the molecule in its crystal lattice [49]. ΔV was defined as,

$$\Delta V = V_{\text{eff}} - V(0.002) \quad (16)$$

V_{eff} is the effective volume of the molecule corresponding to 100% packing of the unit cell: $V_{\text{eff}} = M/\text{density}$. $V(0.002)$ is the space enclosed by the 0.002 au contour of the molecule's electronic density. We were able to demonstrate a rough correlation between ΔV and the impact sensitivity h_{50} (2.5 kg drop mass); the larger is ΔV , the greater is the impact sensitivity.

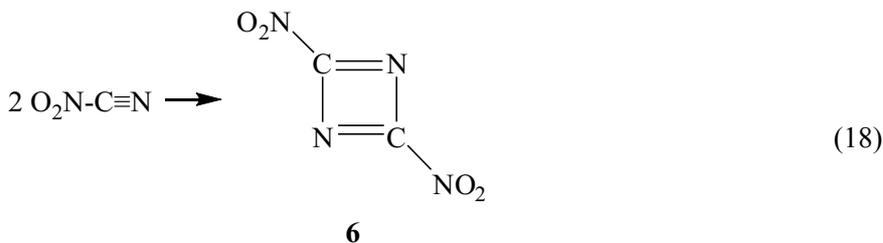
Using our predicted density for **5**, 1.940 g/cm³, and computing $V(0.002)$ at the B3PW91/6-31G(d,p) level for consistency with our earlier work, we estimate the impact sensitivity h_{50} to be about 40 cm (an impact energy of roughly 9.8 J). This would make **5** slightly less sensitive than HMX ($h_{50} = 29$ cm [50], impact energy = 7.1 J).

Synthesis

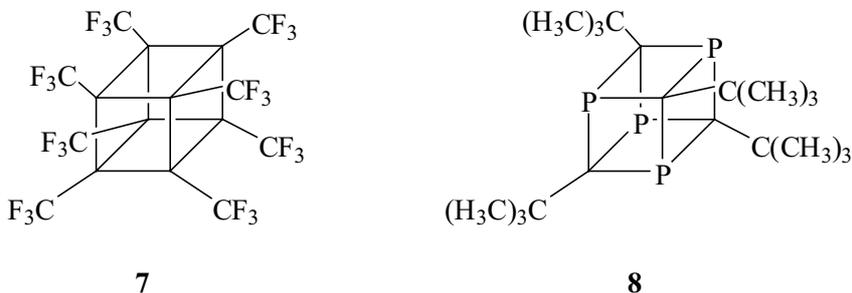
A possible synthetic route to **5** that has been considered in the past is the cyclic tetramerization of nitril cyanide [18, 20]:



This could conceivably proceed through the intermediate **6**:



Some encouragement is provided by the successful conversions of $\text{F}_3\text{C}-\text{C}\equiv\text{C}-\text{CF}_3$ and $(\text{H}_3\text{C})_3\text{C}-\text{C}\equiv\text{P}$ (in series of steps) to **7** [51] and **8** [52], respectively.



We have investigated reactions (17) and (18) computationally, in the gaseous phase, with the B3P86/6-31G(d,p) procedure [18]. At 298 K, the dimerization to form **6**, reaction (18), was found to have an activation enthalpy of 45 kcal/mol, and overall ΔH and ΔG of 27 and 38 kcal/mol. The tetramerization to **5**, reaction (17), was also predicted to be endothermic: $\Delta\text{H}(298 \text{ K}) = 19 \text{ kcal/mol}$, $\Delta\text{G}(298 \text{ K}) = 59 \text{ kcal/mol}$. These results suggest that reactions (17) and (18) may be a questionable pathway to **5**.

Summary

This study was motivated by the continuing interest in 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, **5**, as a possible energetic compound, and the need for more reliable data in terms of which to evaluate its potential. Table 1 summarizes our computed properties for **5**, and compares them to the experimental values for HMX, **1**. In order to give a more complete picture of **5** as an energetic compound,

we have also included in the table an estimate of its relative specific impulse I_s . This is a measure of the thrust, or recoil force, developed by a propellant [3, 53]. The relative value given for **5** in Table 1 is an estimate from some time ago, but we believe that it is still meaningful.

From Table 1, **5** is expected to be somewhat better than HMX in detonation and propellant performance. Whether the margin of superiority is sufficient to stimulate interest in the synthesis of **5** remains to be seen.

Table 1. Comparison of predicted properties of 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, **5**, and HMX, **1**

Property	5	HMX
Density, g/cm ³	1.940	1.90 ^a
Enthalpy of formation, 298 K, solid phase		
kcal/mol	218	17.9 ^b
cal/g	757	60.5 ^b
Detonation velocity, mm/ μ s	9.8	9.100 ^a
Detonation pressure, kbar	444	393 ^a
C-NO ₂ dissociation enthalpy, kcal/mol	49	---
Impact sensitivity		
h ₅₀ (cm)	40	29 ^c
impact energy (Joules)	9.8	7.1 ^c
Specific impulse relative to HMX	1.12 ^d	1.00

^a Reference 6; ^b reference 3; ^c reference 50; ^d reference 53.

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