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Sensitivity and the available free space per molecule in the unit cell

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Abstract Invoking the known link between impact sensitivity and compressibility, we have expanded upon an earlier preliminary study of the significance of the available free space per molecule in the unit cell, ΔV. We express ΔV as $V_{eff} - V_{int}$, where V_{eff} corresponds to zero free space, V_{eff}=molecular mass/density. V_{int} is the intrinsic gas phase molecular volume. We demonstrate that V_{int} can be appropriately defined as the volume enclosed by the 0.003 au contour of the molecule's electronic density; this produces packing coefficients that have the range and average value found crystallographically. Measured impact sensitivities show an overall tendency to increase as ΔV becomes larger. For nitramines, the dependence upon ΔV is rather weak; we interpret this as indicating that a single overriding factor dominates their initiation mechanism, e.g., $N-NO_2$ rupture. (An analogous situation appears to hold for many organic azides.) In addition to the conceptual significance of identifying ΔV as a factor in impact sensitivity, the present results allow rough estimates of relative sensitivities that are not known.

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Sensitivity

A prime concern in the area of energetic materials – e.g., explosives and propellants – is sensitivity. By this is meant the vulnerability of a compound to accidental detonation caused by an unintended stimulus. The latter might be impact, shock, heat [1–3], friction [3] or electric spark [4, 5]. In designing and evaluating proposed new energetic compounds, a high priority is given to minimizing sensitivity.

It is therefore important to have some means of estimating the likely sensitivities of compounds that have not yet been synthesized. Such a predictive capability might also provide some insight into the mechanisms by which detonation is initiated. However sensitivity depends upon a number of different factors: molecular and crystal properties, the physical state of the compound, environmental conditions, the nature of the stimulus, etc. [1, 2, 6–10]. Partly for these reasons, reproducibility of measured values is notoriously difficult [1–3, 7, 8, 10]. Given all this, it has sometimes been questioned whether meaningful predictions of sensitivity are possible. Kamlet and Adolph expressed a more positive view: if other factors, including the detailed measurement procedure, are kept as uniform as possible, then limited correlations of sensitivity with a single molecular (or crystal) property may be feasible [11, 12]. They demonstrated this with the various oxygen-balance relationships.

The fact is that, during the past 30 years, a large number of correlations have been established between different types of sensitivity and a remarkable array of individual molecular or crystal properties. These properties include the strengths or lengths of certain bonds, electronic energy levels, molecular electrostatic potentials, heats of fusion or sublimation, band gaps, NMR chemical shifts, the efficiencies of lattice-to-molecular vibrational energy transfer, atomic charges, electro-negativities, substituent constants, etc. Summaries can be found in several overviews [6, 8, 13, 14].

Some of these correlations are quite good, usually within a given group of compounds, such as nitroaromatics or nitramines. Nevertheless they are sometimes regarded skeptically [6, 9], in part because they seem to be trying to reduce the complexity of sensitivity to dependence upon a single property, and also because so many different properties have been invoked for this purpose.
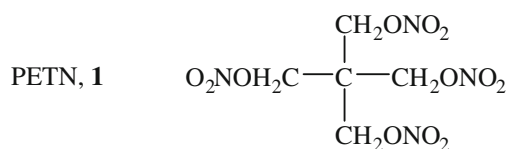
In this context, it is essential to keep in mind – as pointed out by Brill and James [6] and by Dlott [9] – that the existence of a correlation between sensitivity and some molecular or crystal property does not necessarily implicate the latter as a causative factor. It may simply be symptomatic of something else. For example, electrostatic potentials, NMR shifts, atomic charges, electronegativities and substit-uent constants all reflect the polarization of electronic charge density, which in turn affects bond strengths and lengths.

It is therefore necessary to be very cautious in describing any particular factor as "causative." A further important consideration is that mechanisms of detonation initiation can be quite different, even for compounds in the same chemical class, e.g., nitroaromatics. In some instances, evidence indicates that a key initiation step is the rupture of a specific type of bond, a "trigger linkage" [11, 12]. This appears to be the case for many nitramines; there is evidence that the N-NO_2 bonds – which are relatively weak [15] – often serve as trigger linkages [15–22]. In other chemical categories, C-NO_2, O-NO_2 or N-N_2 bonds may play this role, but a number of other mechanisms have also been implicated for some compounds containing these linkages: interactions of aromatic NO_2 groups with ortho substituents [6], N_2 release from 1,2,3-triazoles [23, 24], nitro/aci tautomerism [25], nitro/nitrite [26] and other intramolecular rearrangements [27], etc. For reviews, see Brill and James [6], Politzer and Murray [13], Zeman [14] and Shackelford [28].

The problems associated with characterizing and measur-ing sensitivity suggest that seeking precise structure/activity correlations is unrealistic (except on a very limited scale). Accordingly our aim is to try to understand which factors and properties actually do influence sensitivity, as opposed to those that are symptomatic or only coincidentally related. On this basis, we hope to be able to make at least rough (but meaningful) predictions of relative sensitivities. The present paper extends two earlier ones with these objectives [15, 29].

Sensitivity and compressibility

The rapid compression of an energetic solid, e.g., due to shock or impact, generates local heating ("hot spots"), particularly in the vicinities of lattice defects [9, 30]. This localized energy can be used to initiate decomposition and detonation [9, 13, 31]. In this context, it is relevant to note the work of Dick, who subjected the explosive PETN (pentaerythritol tetranitrate, 1) to shock in different crystal-lographic directions [32]. He found distinctly different sensitivities. In particular, shock in the [001] direction produced detonation, but in the [100] it did not. Kunz subsequently showed that the compressibility of PETN is greater in the [001] direction than in the [100] [33].

$$PETN, \mathbf{1} \quad O_2NOH_2C \overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{\overset{|}{\underset{|}{C}}}} CH_2ONO_2$$

Energetic molecular solids tend to have higher densities than typical organic compounds. For example, the packing coefficients for the former average 0.77, compared to about 0.70 for the latter [34]. However there is still a significant amount of free space in the unit cells of energetic compounds, which affects their compressibilities and hence is linked to their sensitivities.

In a recent preliminary study [29], we demonstrated rough relationships between impact sensitivities and the estimated available free space per molecule in the unit cells of energetic solids. Our present objective is to establish a sounder basis for these relationships.

Available free space per molecule in unit cell

The free space per molecule in the unit cell, designated ΔV, can be represented as the difference between the effective volume per molecule that would be required to completely fill the unit cell, V_{eff}, and the intrinsic gas phase molecular volume, V_{int}:

$$\Delta V = V_{eff} - V_{int} \tag{1}$$

V_{eff} can be calculated exactly from the dimensions of the unit cell and the number of molecules that it encompasses, or alternatively by the formula,

$$V_{eff} = M/d \tag{2}$$

in which M is the molecular mass and d is the crystal density.

Assigning a value to V_{int} is less straightforward. Bader et al. suggested some time ago that molecular volumes could be defined by appropriate outer contours of the molecules' electronic densities [35]. This has the advantage of reflecting features specific to the molecule, such as lone pairs, π electrons, strained bonds, etc. In particular, the 0.001 au (electrons/bohr^3) contour has been very useful in the context of noncovalent interactions [36, 37]. It has also been found that the volume enclosed by the 0.001 au contour can be used to obtain generally reasonable estimates of the crystal densities of C,H,N,O-containing energetic compounds [38, 39],

$$d \approx M/V(0.001) \qquad (3)$$

(although these densities can sometimes be significantly improved by introducing an electrostatic interaction term into Eq. 3 [40]). The overall success of Eq. 3 means that V(0.001) is usually quite similar to V_{eff}, Eq. 2, and therefore cannot be used to approximate V_{int}.

It is evidently necessary to use a more inner contour of the electronic density to define V_{int}, so that $V_{int} < V_{eff}$. Some guidance is provided by Eckhardt and Gavezzotti's survey of the crystal structures of 38 energetic compounds [34]. They found that the packing coefficients vary between approximately 0.71 and 0.83, with an average of 0.77.

We have accordingly investigated which contour would best reproduce these observations. For the energetic compounds listed in Table 1, we tested the 0.002, 0.0025 and 0.003 au contours as possible determinants of V_{int}. (The 0.002 au contour was used in our preliminary study [29].) Geometry optimizations were carried out with Gaussian 09 [41] at the density functional B3PW91/6-31G(d,p) level. The Wave Function Analysis-Surface Analysis Suite was utilized to obtain the molecular surfaces and corresponding volumes [42]. V_{eff} was determined for each compound via Eq. 2 and its experimental crystal density [39], and the packing coefficient by means of Eq. 4:

$$\text{packing coefficient} = V_{int}/V_{eff} \qquad (4)$$

The results are in Table 2, which shows that the 0.003 au contour gives a range of packing coefficients and also an average value that are both very nearly the same as the crystallographic. Accordingly we will take the 0.003 au contour of the electronic density to define V_{int}.

The magnitudes of V_{int} corresponding to the 0.003 au contour are given for each compound in Table 1, along with their experimental impact sensitivities (h_{50}) and the values of V_{eff}. The available free space per molecule in the unit cell, ΔV, then follows from Eq. 1, and is listed for each compound.

Table 1 Experimental and computed data[a,b]

Compound[c]	h_{50}[d]	V_{eff}[e]	V(0.003)	ΔV
bis(2,2,2-trinitroethyl)nitramine	5	330.05	257.36	72.69
PETN	14	306.12	225.15	80.97
Tetryl	25	275.38	205.95	69.43
RDX	26	204.23	158.62	45.61
HMX	29	259.69	210.49	49.20
TNAZ	30[f]	171.41	136.19	35.22
N,N'-dinitro-1,2-diaminoethane	34	145.83	117.25	28.58
2,3,4,6-tetranitroaniline	47	243.74	187.23	56.51
benzotrifuroxan	53	220.16	165.34	54.82
1,4-dinitroimidazole	55	145.84	111.89	33.95
picric acid	64	215.22	160.25	54.97
1,3,5-trinitrobenzene	71	211.11	153.36	57.75
2,4,6-trinitrotoluene	98	227.95	169.88	58.07
7-amino-4,6-dinitrobenzofuroxan	100	209.60	167.98	41.62
2,4-dinitro-1H-imidazole	105	148.29	111.29	37.00
2,4,6-trinitrobenzoic acid	109	239.08	177.93	61.15
2,2-dinitro-1,3-propanediol	110[g]	166.95	124.71	42.24
3,5-diamino-2,4,6-trinitrophenol	120[g]	227.62	179.43	48.19
FOX-7	126	130.58	107.41	23.17
2,4,6-trinitroaniline	141	213.61	163.53	50.08
NTO	291	112.57	91.49	21.08

[a] Computational level: B3PW91/6-31G(d,p)

[b] Units: h_{50} is in cm; V_{eff}, V(0.003) and ΔV are in Å^3

[c] Acronyms: PETN: pentaerythritol tetranitrate; Tetryl: 2,4,6-trinitro-N-methyl-N-nitroaniline; RDX: 1,3,5-trinitro-1,3,5-triazacyclohexane; HMX: 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane; TNAZ: 1,3,3-trinitroazetidine; FOX-7: 1,1-diamino-2,2-dinitroethene; NTO: 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one

[d] All h_{50} are from ref. 8 unless otherwise indicated

[e] Ref. [39]

[f] Ref. [43]

[g] Ref. [2]

Table 2 Ranges and averages of packing coefficients for different electronic density contours, for compounds in Table 1
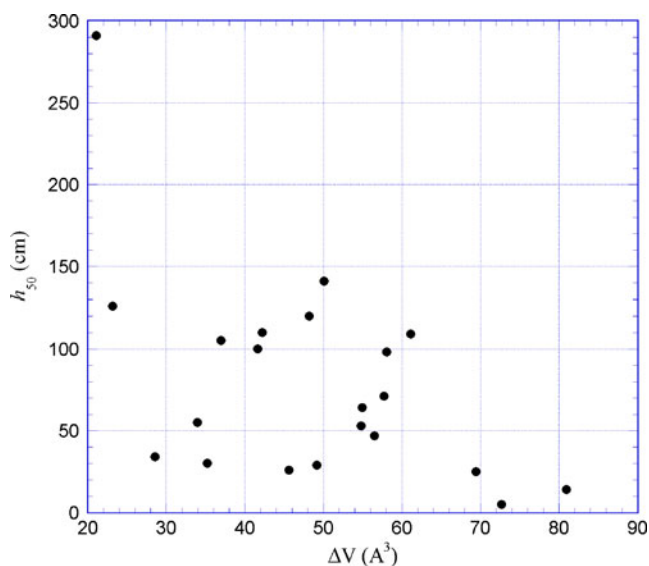
Contour of electronic density (au)	Range of packing coefficients	Average
0.002	0.81 – 0.92	0.86
0.0025	0.76 – 0.86	0.81
0.003	0.73 – 0.82	0.77
Crystallographic[a]	0.71 – 0.83	0.77

[a] Reference [34]

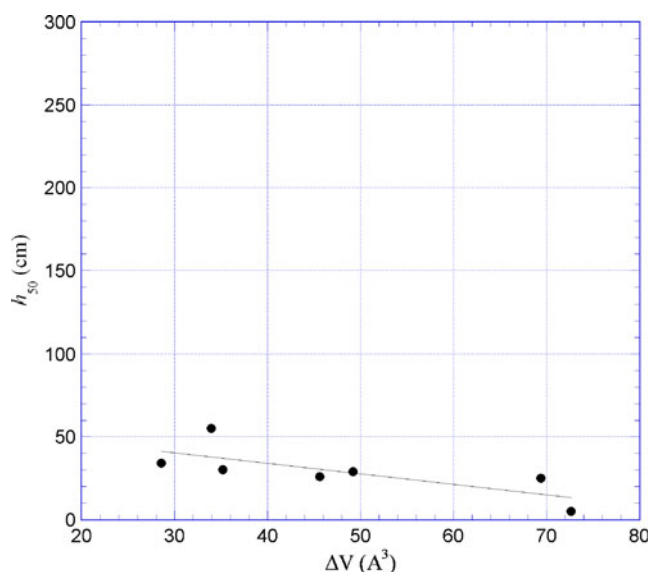## Sensitivity and the available free space per molecule in the unit cell

We are considering specifically impact sensitivity. This is commonly measured by dropping a given mass upon a sample of the compound and noting the height from which 50% of the drops produce evidence of reaction [1–3, 7, 8, 10]. The impact sensitivity is then reported as this height in centimeters, designated h_{50}, or as the resulting impact energy in Joules. (For a 2.5 kg mass m, $h_{50} =$ 100 cm corresponds to an impact energy of $mgh_{50} = 24.5$ J, where g is the acceleration due to gravity.) The greater h_{50} is, or the impact energy, the less sensitive is the compound.

The measured impact sensitivities of the compounds in Table 1 are plotted against their ΔV in Fig. 1. Despite the uncertainties associated with h_{50} measurements, there does nevertheless appear to be a general tendency for h_{50} to decrease (increasing sensitivity) as ΔV becomes larger. However there can also be discerned a structural factor that should be taken into account.

There are seven nitramines in Table 1: bis(2,2,2-trinitroethyl)nitramine, Tetryl, RDX, HMX, TNAZ, N, N'-dinitro-1,2-diaminoethane and 1,4-dinitroimidazole. Except for the last, they are all quite sensitive, with $h_{50} \leq$ 34 cm. This is indeed typical of nitramines; 80% of those in the extensive compilation by Storm et al. have $h_{50} <$ 40 cm [2]. In Fig. 2, which shows only the seven nitramines, it can be seen that their impact sensitivities decrease nearly linearly with ΔV, but that the dependence upon ΔV is relatively weak. It is much stronger for the non-nitramine compounds in Table 1 (Fig. 3). This suggests that the nitramines should be viewed separately, as is demonstrated by Figs. 2 and 3.

A plausible interpretation [15, 29] is that the detonation initiation of nitramines has the unifying feature of being dominated by a single factor, which may be the ease of N-NO$_2$ rupture [15–22]. ΔV plays only a relatively minor role. For other classes of compounds, the situation is less straightforward; combinations of different factors may be involved even for members of the same chemical family (e.g., nitroaromatics). Figure 3 indicates that one of these is ΔV.

Fig. 1 Impact sensitivities, h_{50}, plotted against available free space per molecule in the unit cell, ΔV, for the 21 energetic compounds in Table 1

Fig. 2 Impact sensitivities, h_{50}, plotted against available free space per molecule in the unit cell, ΔV, for the seven nitramines in Table 1

The organic azides (not included in Table 1) are another group of energetic compounds that, in many instances, appear to follow a common dominant initiation mechanism – the facile loss of N_2 [44]. Does it follow that, like the nitramines,

the azide h_{50} have little dependence upon ΔV? Indeed, many azides, such as **2 – 4**, have extremely high impact sensitivities, corresponding to $h_{50} < 4$ cm [45], regardless of the magnitude of ΔV (which varies from 24 to 40 $Å^3$ for **2 – 4**).
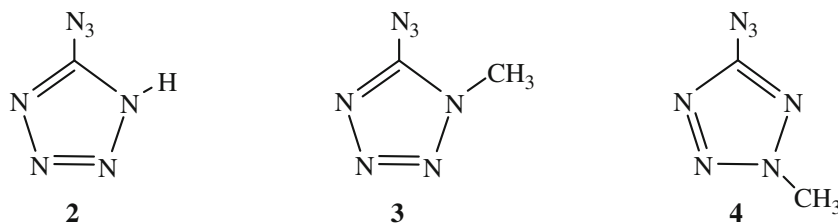
In order to further explore the implications of Figs. 1-3, we insert Eq. 2 into Eq. 1, to give,

$$\Delta V = (M/d) - V_{int}. \tag{5}$$

Thus if M and V_{int} are held constant, then $\Delta V \sim 1/d$. These conditions are met by polymorphic forms of a solid; M and V_{int} (the intrinsic gas phase molecular volume) are the same for all of the polymorphs. Then to the extent that h_{50} does decrease as ΔV increases (Figs. 1-3), it should follow that $h_{50} \sim d$; the impact sensitivities of polymorphs should diminish as their densities become greater. For the four polymorphs of HMX, at least, this prediction is borne out. The order of increasing density is $\delta < \gamma < \alpha < \beta$ [21, 46], while sensitivity decreases as $\delta > \gamma \geq \alpha > \beta$ [21, 47].

Figures 2 and 3 can be used to roughly estimate and qualitatively rank the h_{50} of compounds for which

experimental measurements are not available. For example, it has been pointed out that heptanitrocubane (**5**) has some attractive features with respect to energetic performance [48], including a high crystal density of 2.028 g/cm^3. To our knowledge, however, its impact sensitivity has not been determined experimentally. Using the known density to obtain V_{eff} and computing V_{int}, we find $\Delta V = 73$ $Å^3$, which implies (Fig. 3) an h_{50} in the neighborhood of 40 cm. Thus, heptanitrocubane can be anticipated to be slightly less sensitive to impact than RDX and HMX (Table 1).
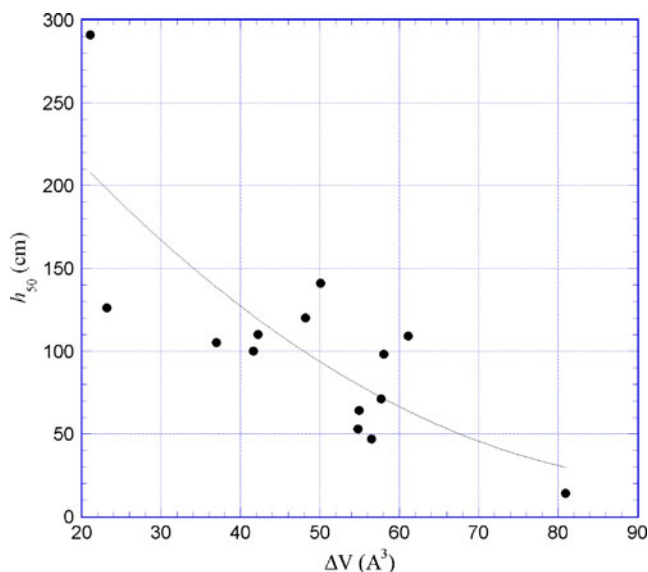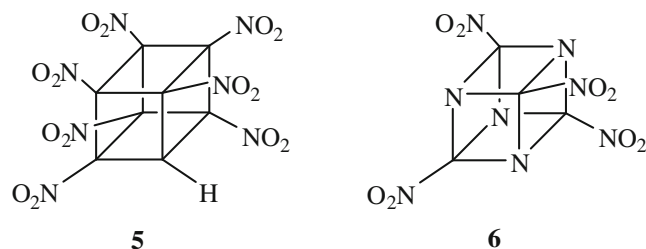

Such predictions can be made even if a compound of interest has not been synthesized and its crystal density is accordingly not known experimentally. The density can be determined quite readily computationally, with an average absolute error of less than 0.04 g/cm^3, with the procedure mentioned earlier [40]. This has been done recently in evaluating the energetic potential of 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane (**6**) [49], which has not yet been prepared.

Fig. 3 Impact sensitivities, h_{50}, plotted against available free space per molecule in the unit cell, ΔV, for the 14 non-nitramines in Table 1

Summary

The sensitivity of an energetic compound to impact depends, in general, upon a combination of factors. We propose, on the basis of Figs. 1-3, that one of these is ΔV, the available free space per molecule in the unit cell. This is

consistent with the well-established link between sensitivity and compressibility.

In order to determine ΔV for a compound, it is necessary to establish a basis for evaluating V_{int}, the intrinsic gas phase molecular volume. We have demonstrated that V_{int} can be suitably defined by the 0.003 au contour of the molecule's electronic density; for energetic compounds, this leads to packing coefficients that have essentially the same range and average value as is observed crystallographically.

The members of some groups of compounds may have in common a specific mechanistic step – such as the breaking of a particular trigger linkage – that is the overriding factor in their detonation initiation. The dependence upon ΔV may then be rather minor (nitramines) or essentially negligible (many organic azides).

While Figs. 2 and 3 can be used to obtain at least rough estimates of relative impact sensitivities, our continuing objective, as in other recent studies [15, 29], has been to identify factors that help to determine sensitivity. Our focus so far has been upon a molecular property, trigger linkages, and a crystalline one, ΔV. It is interesting that investigating the latter may reveal, in some cases, a dominant role of the former (Figs. 1-3).

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