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A possible crystal volume factor in the impact sensitivities of some energetic compounds

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Abstract We have investigated the possibility of a link between the impact sensitivities of energetic compounds and the space available to their molecules in their crystal lattices. As a measure of this space, we use $\Delta V = V_{eff} - V(0.002)$, where V_{eff} is the effective molecular volume obtained from the crystal density and V(0.002) is that enclosed by the 0.002 au contour of the molecule's gas phase electronic density, determined computationally. When experimental impact sensitivity was plotted against ΔV for a series of 20 compounds, the nitramines formed a separate group showing little dependence upon ΔV. Their impact sensitivities correlate well with an anomalous imbalance in the electrostatic potentials on their molecular surfaces, which is characteristic of energetic compounds in general. The imbalance is symptomatic of the weakness of the N–NO_2 bonds, caused by depletion of electronic charge. The impact sensitivities of non-nitramines, on the other hand, depend much more strongly upon ΔV, and can be quite effectively related to it if an electrostatically-based correction term is included.

Keywords Crystal volumes · Energetic compounds · Impact sensitivities · Molecular volumes · Electrostatic potentials

Background

A major and continuing objective in the area of energetic materials is reduced sensitivity to accidental detonations due to unintended stimuli. These can include impact, shock, heat [1–3], friction [3], electric spark [4, 5], etc. The challenge is to combine low sensitivity with a high level of detonation performance.

Sensitivity reflects the ease of initiating detonation, which in turn depends upon a complex interplay of a number of factors: molecular and crystal properties, physical conditions, the nature of the stimulus, etc. [1, 2, 6, 7]. One consequence of this is the notorious difficulty of reproducibly quantifying sensitivity. The type most often measured is impact sensitivity; this is usually done by dropping a given mass upon a sample of the compound and determining the height from which 50% of the drops produce evidence of reaction [1–3, 7]. Impact sensitivity is generally reported either as this height in cm, designated h_{50}, or as the corresponding impact energy in J; for a mass m, this is given by mgh_{50}, where g is the acceleration due to gravity. With a 2.5 kg mass, an h_{50} of 100 cm is equivalent to an impact energy of 24.5 J. The greater the value of h_{50} or the impact energy, the less is the sensitivity.

As is discussed in some detail elsewhere [1–3, 7], it is very difficult to obtain reproducible h_{50} values. They should accordingly be regarded as, at best, qualitative indicators of relative impact sensitivities. This, together

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with the variety of factors that can influence detonation initiation, has led some to conclude that meaningful correlations between impact sensitivity and specific molecular or crystal properties are unlikely to be achieved.

In designing and evaluating proposed new energetic compounds, however, it is very important to be able to make at least some estimates of their levels of sensitivity by molecular and/or crystal modeling techniques. This might also help to identify molecular or crystal properties that are involved in detonation initiation. Furthermore, as was discussed by Kamlet and Adolph [8, 9], a relationship of impact sensitivity to some particular molecular or crystal properties might be found if other factors that affect detonation initiation are kept as constant as possible.

There have accordingly been numerous attempts to correlate measured impact sensitivities (usually within a given class of compounds, e.g., nitroaromatics) and various molecular and crystal features; these have included the strengths of certain bonds, NMR chemical shifts, heats of fusion and sublimation, atomic charges, electronic energy levels, the efficiency of lattice-to-molecular vibrational energy transfer, molecular stoichiometry, etc. These efforts, which have often been quite successful, are summarized in more detail elsewhere [6, 7, 10, 11]. It is important to keep in mind, however, that the existence of a correlation does not necessarily indicate a causal relationship; it may simply be symptomatic of something else [6].

A concept that has received a great deal of attention is that the breaking of a certain type of bond, a "trigger linkage," is a key step in the decomposition process involved in the initiation of detonation [8, 9]. Some possible trigger linkages are $C-NO_2$ in nitroaromatics and nitroaliphatics, $N-NO_2$ in nitramines, $O-NO_2$ in nitrate esters and $N-N_2$ in organic azides. A considerable amount of work, reviewed on several occasions [6, 10–12], has focused upon potential trigger linkages, and there has been interest in factors, e.g., external electric fields, that could affect their properties [13–15].

In the case of nitramines in particular, there is compelling evidence of the significance of $N-NO_2$ rupture in the early stages of detonation initiation [16–23], the weakness of the $N-NO_2$ bond being consistent with this idea [24]. For example, Kohno et al. have pointed out that the crystallographic $N-NO_2$ distances in several nitramines are significantly shorter, by 0.05–0.08 A, than the computed gas phase values [20–22]. This was not observed for C–N or N–O bonds. They suggested that this $N-NO_2$ bond compression introduces strain and thus is destabilizing. A rough correlation was found between the extent of bond shortening and sensitivity.

While the trigger linkage concept may be widely applicable in the case of nitramines, and sometimes for other types of compounds as well, a number of other mechanisms have also been implicated in detonation initiation. Among these are interactions of aromatic NO_2 groups with *ortho* substituents [6], N_2 release from 1,2,3-triazoles [25, 26], nitro-nitrite [27], nitro/*aci* tautomerism [28] and other intramolecular rearrangements [29], etc.

In earlier work [24, 30–33], we have demonstrated that there is a characteristic anomalous imbalance in the molecular surface electrostatic potentials of energetic compounds, and that it can be related quantitatively – albeit perhaps symptomatically – to the impact sensitivities within groups of nitroaromatics, nitramines and nitroheterocycles. In the most recent study [24], we began to explore in greater depth the apparent connection between surface potential imbalance and sensitivity, focusing upon the bond energies of possible trigger linkages. We continue this exploration now, examining the roles of crystal and molecular volumes in conjunction with molecular surface electrostatic potentials.

In doing so, we recognize the limitations that are imposed by the number of factors that can affect impact sensitivity and by the uncertainty in its measurement. Our goal, therefore, is not a precise structure/activity correlation, but rather to continue to try to understand which factors and properties actually do influence sensitivity, as opposed to relationships that are symptomatic (which can also be useful) or even coincidental.

Molecular electrostatic potentials of energetic compounds

The electrostatic potential $V(\mathbf{r})$ that is created at any point $\mathbf{r}$ by the nuclei and electrons of a molecule is,

$$V(\mathbf{r}) = \sum_{A} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (1)$$

in which 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, and can be obtained experimentally by diffraction techniques [34, 35] as well as computationally. The sign of $V(\mathbf{r})$ in any given region depends upon whether the positive contribution of the nuclei or the negative one of the electrons dominates there.

While the electrostatic potential has considerable fundamental significance [36], it has also been found to be very effective for analyzing and predicting noncovalent interactions [37–39]. For this purpose, $V(\mathbf{r})$ is commonly computed on the molecular surface defined, as proposed by Bader et al. [40], by the 0.001 au (electrons/bohr^3) contour of the electronic density. The resulting surface potential, labeled $V_S(\mathbf{r})$, can be characterized by means of several statistically-defined quantities [37–39], including its positive, negative and total variances (σ_+^2, σ_-^2 and σ_{tot}^2) and an electrostatic balance parameter ν. These are given by Eqs. 2–4:

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

$$\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2 \tag{3}$$

$$\nu = \frac{\sigma_+^2\sigma_-^2}{\left(\sigma_+^2 + \sigma_-^2\right)^2} \tag{4}$$

In Eq. 2, m and n are the numbers of surface points at which $V_S(\mathbf{r})$ is positive, $V_S^+(\mathbf{r})$, and negative, $V_S^-(\mathbf{r})$, respectively. $\overline{V}_S^+$ and $\overline{V}_S^-$ are the averages of the positive and negative surface potentials.

The quantities σ_+^2, σ_-^2 and σ_{tot}^2 are indicators of the strengths and variabilities of the positive, negative and total surface potentials. Since the terms in Eq. 2 are squared, the effects of the positive and negative extrema are emphasized. The degree of balance between the positive and negative surface potentials is measured by ν, which reaches a maximum of 0.250 when $\sigma_+^2 = \sigma_-^2$.

On the surfaces of most organic molecules, the most positive electrostatic potentials are usually associated with hydrogens and sometimes with the σ-holes of Group IV–VII atoms [41], while negative potentials are most often due to lone pairs and π electrons. The positive regions may be more extensive than the negative, but they tend to be weaker, so that in general, $\sigma_-^2 > \sigma_+^2$ [33, 37, 39].

Molecules of energetic compounds are different. They frequently feature several highly electron-attracting components, e.g., NO_2, ONO_2 or N_3 groups and/or aza nitrogens. As a result, the surface potential above the central portion of the molecule is likely to be strongly positive, with negative regions mainly limited to the periphery, reflecting the lone pairs of the NO_2 oxygens, any aza nitrogens, etc. For example, whereas the π electrons of benzene produce $V_S(\mathbf{r})$ that reach −18 kcal mol^{-1} above/below the ring, these negative regions are completely gone in 1,3,5-trinitrobenzene, which instead has maximum $V_S(\mathbf{r})$ of +29 kcal mol^{-1} above/below the ring [24].

The electrostatic potentials on the molecular surfaces of energetic compounds are therefore characterized by an anomalous imbalance; the positive regions are typically stronger and more variable than the negative, so that $\sigma_+^2 > \sigma_-^2$ [24, 30–33], in contrast to the majority of organic molecules. This is depicted graphically by Murray et al. [24, 30] and very extensively by Rice and Hare [7].

Molecular electrostatic potentials and sensitivity

We have shown in the past that there is a link – not necessarily a causal relationship – between the anomalous imbalance in the molecular surface electrostatic potentials of energetic compounds and their impact sensitivities [24, 30–33]. Using various measures of this imbalance (some involving σ_+^2, σ_-^2 and ν), very good correlations with experimental impact sensitivities have been obtained for nitroaromatics, nitramines and nitroheterocycles, treated separately. The unifying concept, as has been pointed out [7, 24, 33], is that the most sensitive molecules have high levels of the imbalance between the strong positive and weaker negative surface potentials.

Among the most positive portions of energetic molecular surfaces are those related to C-NO_2 and N-NO_2 bonds [24, 31, 32]. These regions become more positive as the number of NO_2 groups, aza nitrogens, etc., increases and further depletes the electronic charge in the central part of the molecule. What is particularly significant is that the C-NO_2 and N-NO_2 bonds concomitantly become weaker; this was demonstrated computationally at the density functional B3PW91/6-31++G(3d,2p) level [24]. Thus, to the extent that C-NO_2 and N-NO_2 bonds are trigger linkages in some energetic compounds, the link between the imbalance in their molecular surface potentials and impact sensitivity may be that the former reflects the electronic charge depletion that facilitates the breaking of these bonds.

The N-NO_2 bonds in nitramines are quite weak, with bond energies of 37 to 46 kcal mol^{-1} [24], and nitramines tend to be very sensitive; 80% of those listed by Storm et al. have h_{50}<40 cm [2]. These observations, together with the evidence cited earlier [16–23], support the trigger linkage concept in nitramine detonation initiation. Indeed, the impact sensitivities of a group of eight nitramines correlate fairly well (correlation coefficient R=0.93) with just σ_+^2 and ν [24].

In contrast to the N-NO_2 bonds in nitramines, the C-NO_2 bonds in nitroaromatics and nitroheterocycles are normally considerably stronger, with bond energies greater than 60 kcal mol^{-1}. Thus other mechanisms may be competitive with C-NO_2 bond rupture, or sometimes dominant, in the decomposition and detonation initiation process. For example, Kamlet and Adolph concluded, in developing their oxygen balance correlations with impact sensitivity [9], that nitroaromatics with an *ortho* substituent having a C-H bond must be treated separately from the others. Accordingly, for classes of energetic compounds other than those having particularly weak trigger linkages (e.g., N-NO_2, N-N_2), some additional factor(s), besides the surface potential imbalance, may need to be taken into account in establishing correlations with sensitivity.

A crystal volume/electrostatic potential relationship with sensitivity

The preceding discussion has focused upon molecular properties in relation to sensitivity. Now we would like to also include an aspect of crystal structure. We have investigated the possibility that one of the factors involved in determining impact sensitivity is the space available to a molecule of the compound in its crystal lattice. How can a measure of this available space be obtained? If the crystal density d is known, then an effective volume per molecule is given by,

$$V_{eff} = M/d \qquad (5)$$

where M is the molecular mass. Alternatively, V_{eff} can be calculated from the unit cell dimensions and the number of molecules per unit cell. V_{eff} simply apportions the total volume of the unit cell among these molecules; it corresponds to a hypothetical 100% packing efficiency. Thus if V_{eff} could be compared to a more realistic measure of the volume of the molecule, the difference would be indicative of the "free space" available to it.

The volume enclosed by the 0.001 au surface, V(0.001), is not suitable for this purpose, since it has been found to be very similar to V_{eff} for many C,H,N,O energetic compounds [42–44]. In fact, Eq. 5 in conjunction with V(0.001) often yields quite satisfactory estimates of C,H,N,O crystal densities; for a group of 180 compounds, 41% of the predicted densities were within 0.030 g cm^{-3} of the experimental values [43]. In some instances, however, V(0.001) differs significantly from V_{eff}, and the predicted densities can then be too high or too low by as much as 0.100 g cm^{-3} or more. It has been demonstrated that the overall results can be improved, and the number of rather bad predictions (error >0.100 g cm^{-3}) considerably decreased by introducing the term $\nu\sigma^2_{tot}$ into Eq. 5 [44]. We will return to this later.

Since V(0.001) is not appropriate for our needs, we have used instead the volume defined by the 0.002 au contour of $\rho(\mathbf{r})$, i.e., V(0.002). All computed results to be presented were obtained with the density functional B3PW91/6-31G (d,p) procedure, and pertain to the 0.002 au surfaces.

In Table 1 are listed 20 energetic compounds of different chemical types: nitroaromatics, nitramines, nitroheterocycles, benzofuroxans, a nitrate ester, a nitroalkane, and a nitroalkene. They are listed in order of decreasing sensitivity, bis(2,2,2-trinitroethyl)nitramine being the most sensitive. The h_{50} values are taken primarily from Rice and Hare [7], with a few from Storm et al. [2]. The V_{eff} in Table 1 were calculated from the experimental densities [43], using Eq. 5, and the V(0.002) were obtained computationally, as were σ^2_+, σ^2_-, and $\nu\sigma^2_{tot}$. Note that in every instance is seen the characteristic anomalous imbalance, $\sigma^2_+ > \sigma^2_-$, which is sometimes considerable.

Table 1 Experimental and computed data[a,b]

Compound[c]	h_{50}[d]	V_{eff}[e]	V(0.002)	ΔV	σ^2_+	σ^2_-	$\nu\sigma^2_{tot}$
bis(2,2,2-trinitroethyl)nitramine	5	330.05	281.40	48.65	355.61	17.65	16.82
PETN	14	306.12	249.24	56.88	160.82	17.95	16.15
Tetryl	25	275.38	227.43	47.95	151.44	39.44	31.29
RDX	26	204.23	175.33	28.90	188.54	46.49	37.29
HMX	29	259.69	231.60	28.09	235.04	43.20	36.49
TNAZ	30[f]	171.41	151.09	20.32	206.15	35.23	30.09
N,N'-dinitro-1,2-diaminoethane	34	145.83	130.51	15.32	243.69	67.08	52.60
2,3,4,6-tetranitroaniline	47	243.74	206.51	37.23	175.54	37.68	31.02
benzotrifuroxan	53	220.16	183.49	36.67	171.59	25.68	22.34
1,4-dinitroimidazole	55	145.84	124.94	20.90	170.87	102.88	64.22
picric acid	64	215.22	177.44	37.78	137.38	44.38	33.55
1,3,5-trinitrobenzene	71	211.11	170.36	40.75	111.34	33.44	25.72
2,4,6-trinitrotoluene	98	227.95	188.36	39.59	88.18	35.17	25.14
7-amino-4,6-dinitrobenzofuroxan	100	209.60	185.77	23.83	188.83	86.12	59.15
2,4-dinitro-1H-imidazole	105	148.29	124.26	24.03	344.11	75.38	61.83
2,2-dinitro-1,3-propanediol	110[g]	166.95	138.12	28.83	168.01	48.39	37.57
3,5-diamino-2,4,6-trinitrophenol	120[g]	227.62	198.30	29.32	108.69	64.13	40.33
FOX-7	126	130.58	120.07	10.51	444.52	115.83	91.89
2,4,6-trinitroaniline	141	213.61	181.02	32.59	113.62	47.62	33.56
NTO	291	112.57	102.27	10.30	300.47	71.13	57.51

[a] Computational level: B3PW91/6-31G(d,p). [b] Units: h_{50} is in cm; V_{eff}, V(0.002) and ΔV are in Å^3; σ^2_+, σ^2_- and $\nu\sigma^2_{tot}$ are in (kcal mol^{-1})^2. [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. [7] unless otherwise indicated.

[e] Ref. [43]. [f] Ref. [46]. [g] Ref. [2].

The first point of interest concerns the differences between the V_{eff} and the V(0.002), i.e., $\Delta V = V_{eff} - V(0.002)$. Is there evidence of any relationship whatsoever between h_{50} and ΔV?

Figure 1 shows that there are in fact two rough experimental relationships, one for the six nitramines (Group A) and the other for the remaining 14 compounds (Group B). The correlation coefficients R are, respectively, 0.69 and 0.80. The general trends are that the compounds become more sensitive (lower h_{50}) as ΔV increases.

For Group A, however, h_{50} is seen in Fig. 1 to depend only marginally upon ΔV. This reinforces the idea, already discussed, that the key to nitramine decomposition and detonation initiation is breaking the N-NO_2 bond, the ease of which is promoted by the electronic charge depletion that is reflected in the anomalous surface potential imbalance. Thus we found in a previous study that the h_{50} of a series of eight nitramines can be expressed in terms of just σ_+^2 and ν [24]. Similarly, when multivariable regression analysis [45] is applied to fit the h_{50} of the six nitramines in Table 1 to,

$$h_{50} = \alpha\sigma_+^2 + \beta\nu + \gamma \qquad (6)$$

R=0.96, with an average absolute deviation from experiment of 3 cm and a root-mean-square deviation of 6 cm. (The coefficients α, β and γ are given in Table 2.) The database that was used is of course very small, but these results do provide further evidence that the weakness of the N-NO_2 trigger linkage, of which the surface potential imbalance is a symptom, is likely to be the critical factor in nitramine sensitivity.

Table 2 Data pertaining to Eqs. 6 and 7

Property	Eq. 6	Eq. 7
α	−0.0064	−234.83
β	241.42	−3.197
γ	−3.43	962.0
R	0.96	0.93
Average absolute deviation from experiment	3 cm	19 cm
Root-mean-square deviation from experiment	6 cm	27 cm

Figure 1 suggests that ΔV is significantly more important for group B than for group A, although it certainly does not suffice for the former, as can be seen from the example of FOX-7. Its ΔV of 10.5 Å^3 would give an h_{50} of about 240 cm, rather than the actual 126 cm. Thus, while Fig. 1 does imply a relationship with ΔV for Group B, some additional correction term is needed.

For this role, we tested the same quantity, $\nu\sigma_{tot}^2$, that was found to produce improved crystal densities [44]. This quantity is a well-established index of electrostatic interactive tendencies, particularly between molecules of the same kind (as in molecular crystals); it is a key term in analytical representations of a variety of liquid and solid phase properties that depend upon noncovalent interactions, e.g., heats of phase transitions, boiling points and critical constants [37–39]. Since $\nu\sigma_{tot}^2$ is effective in correcting crystal densities based upon poor estimates of V_{eff} [44], it seems reasonable to ask if it might in an analogous manner benefit ΔV.

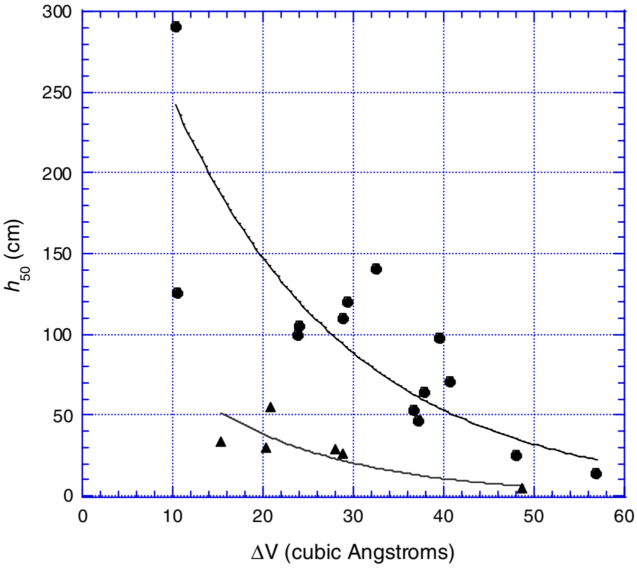

Fig. 1 Measured impact sensitivities (h_{50}) plotted against computed ΔV for the compounds in Table 1. Triangles correspond to nitramines, circles to all others

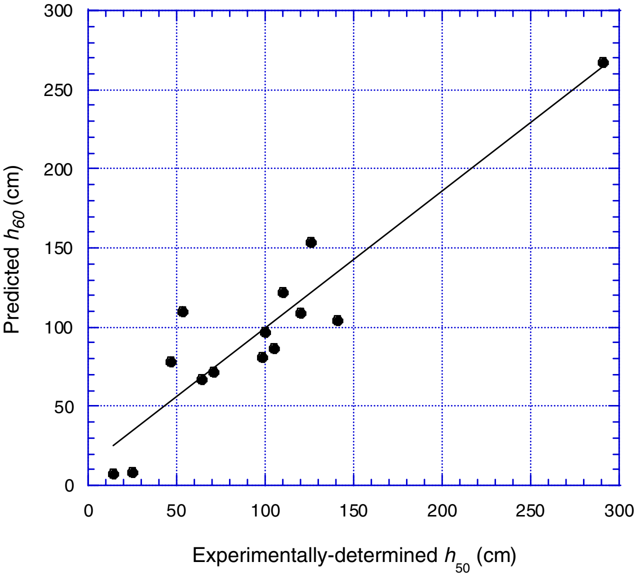

Fig. 2 Comparison of impact sensitivities predicted by Eq. 7 with experimental values, for non-nitramines in Table 1

Fitting the experimental h_{50} of group B to

$$h_{50} = \alpha(\Delta V)^{1/3} + \beta\nu\sigma^2_{\rm tot} + \gamma \tag{7}$$

yielded R=0.93, an average absolute deviation of 19 cm and a root-mean-square deviation of 27 cm. (We found the fit to be statistically better in terms of $(\Delta V)^{1/3}$ rather than ΔV. The coefficients α, β and γ are in Table 2.) These results are quite satisfactory, given the uncertainty in measuring impact sensitivity. The h_{50} predicted by Eq. 7 are compared to the experimental in Fig. 2.

It might be argued that Eq. 7 can be applied only to existing compounds, since ΔV requires a knowledge of $V_{\rm eff}$, which is obtained from the crystal density or lattice dimensions. However we have demonstrated that the density can be predicted computationally with an average absolute error of 0.036 g cm^{-3} [44]. This should allow Eq. 7 to be applied, with reasonable reliability, to proposed compounds and others for which the density is not known.

The coefficients α, β and γ in Eqs. 6 and 7 will change somewhat with the development of larger databases. We are encouraged to believe, however, that these or similar relationships will provide a capacity for qualitatively ranking, with reasonable reliability, the relative impact sensitivities of many energetic compounds.

Discussion and summary

There is need for caution in drawing inferences concerning factors determining impact sensitivity. Different mechanisms may be involved even within a given class of energetic compounds, e.g., nitroaromatics [6, 9]. One consideration must certainly be the ease or difficulty of breaking possible trigger linkages, such as C-NO_2 and N-NO_2. These become weaker as more NO_2 groups and aza nitrogens are introduced into the molecule and withdraw electronic charge [24]. This gives rise to the anomalous imbalance in the molecular surface electrostatic potentials that is characteristic of energetic compounds. Thus, in those cases in which trigger linkage rupture is a key step in detonation initiation, the surface potential imbalance can be symptomatic of sensitivity. Our present and recent [24] analyses indicate that such is often the case for nitramines; this is also consistent with a great deal of earlier work [16–23, 33].

Our current study also draws attention to the possible significance of ΔV with respect to impact sensitivity. Why might this be a factor? Perhaps the availability of more space enhances the molecule's ability to absorb and localize, vibrationally or translationally, the external energy coming from the impact.

An interesting aspect of ΔV is suggested by Fig. 1, in which it separates the six nitramines from the other compounds. Perhaps a relatively low dependence of h_{50} upon ΔV is a characteristic of compounds in which trigger linkage rupture is a dominant factor in determining sensitivity. In any case, the role of the surface potential in Eq. 7 is that of a correction term.

In this context, it is relevant to point out that there are three compounds in Table 1 – Tetryl, TNAZ and 1,4-dinitroimidazole – that have both C-NO_2 and N-NO_2 bonds. Purely structurally, therefore, it is not obvious whether each of them should or should not be viewed as a nitramine. Figure 1 clearly puts TNAZ and 1,4-dinitroimidazole with the nitramines, and this is confirmed by Eq. 6, which predicts their h_{50} to be 25 and 52 cm, respectively, very close to the experimental 30 and 55 cm (Table 1). In contrast, Eq. 7 would assign them h_{50} of 225 and 110 cm.

The case of Tetryl is more ambiguous. In Fig. 1, it could be with either group of compounds. We have treated it as a non-nitramine [24], but Eqs. 6 and 7 both give reasonable predictions for it, 35 and 9 cm respectively, compared to the experimental h_{50} of 25 cm. The decomposition of Tetryl warrants further investigation.

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References

1. Iyer S, Slagg N (1988) In: Liebman JF, Greenberg A (eds) Structure and reactivity. VCH , New York ch 7
2. Storm CB, Stine JR, Kramer JF (1990) In: Bulusu SN (ed) Chemistry and physics of energetic materials. Kluwer, Dordrecht (The Netherlands) ch 27
3. Meyer R, Köhler J, Hornburg A (2007) Explosives, 6th edn. Wiley-VCH, Weinheim
4. Zeman S, Friedl Z, Koci J, Pelikan V, Majzlik J (2006) Centr Europ J Energ Mater 3(3):27–44
5. Zeman S, Friedl Z, Koci J (2007) Centr Europ J Energ Mater 4 (4):23–31
6. Brill TB, James K (1993) Chem Rev 93:2667–2692
7. Rice BM, Hare JJ (2002) J Phys Chem A 106:1770–1783
8. Kamlet MJ (1976) Proc 6th Symp (Internat) Deton, Report No ACR 221, Office of Naval Research, p 312
9. Kamlet MJ, Adolph HG (1979) Propellants Explos 4:30–34
10. Politzer P, Murray JS (2003) In: Politzer P, Murray JS (eds) Energetic materials, part 2. Detonation, combustion. Elsevier, Amsterdam ch 1
11. Zeman S (2007) Struct Bond 125:195–271
12. Shackelford SA (2008) Centr Europ J Energ Mater 5(1):75–101
13. Politzer P, Murray JS, Concha MC, Lane P (2007) Centr Europ J Energ Mater 4(4):3–21
14. Politzer P, Murray JS (2009) Int J Quantum Chem 109:3–7

15. Politzer P, Murray JS, Lane P (2009) Int J Quantum Chem 109:534–539
16. Brill TB, Oyumi Y (1986) J Phys Chem 90:2679–2682
17. Oyumi Y, Brill TB (1988) Propellants Explos Pyrotech 13:69–73
18. Stewart PH, Jeffries JM, Zellweger JM, McMillen DF, Golden DM (1989) J Phys Chem 93:3557–3563
19. Politzer P, Murray JS, Lane P, Sjoberg P, Adolph HG (1991) Chem Phys Lett 181:78–82
20. Kohno Y, Maekawa K, Tsuchioka T, Hashizume T, Imamura A (1993) Chem Phys Lett 214:603–608
21. Kohno Y, Maekawa K, Tsuchioka T, Hashizume T, Imamura A (1994) Combust Flame 96:343–350
22. Kohno Y, Ueda K, Imamura A (1996) J Phys Chem 100:4701–4712
23. Oxley JC (2003) In: Politzer P, Murray JS (eds) Energetic materials, part 1. Decomposition, crystal and molecular properties. Elsevier, Amsterdam, ch 1
24. Murray JS, Concha MC, Politzer P (2009) Mol Phys 107:89–97
25. Storm CB, Ryan RR, Ritchie JP, Hall JH, Bachrach SM (1989) J Phys Chem 93:1000–1007
26. Politzer P, Grice ME, Seminario JM (1997) Int J Quantum Chem 61:389–392
27. Gindulyte A, Massa A, Huang L, Karle J (1999) J Phys Chem A 103:11045–11051
28. Murray JS, Lane P, Göbel M, Klapötke TM, Politzer P (2009) Theor Chem Acc, doi:10.1007/s00214-009-0620-2
29. Liu W-G, Zybin SV, Dasgupta S, Klapötke TM, Goddard WA III (2009) J Am Chem Soc 131:7490–7491
30. Murray JM, Lane P, Politzer P (1995) Mol Phys 85:1–8
31. Politzer P, Murray JS (1995) Mol Phys 86:251–255
32. Politzer P, Murray JS (1996) J Mol Struct 376:419–424
33. Murray JS, Lane P, Politzer P (1998) Mol Phys 93:187–194
34. Stewart RF (1979) Chem Phys Lett 65:335–342
35. Politzer P, Truhlar DG (eds) (1981) Chemical applications of atomic and molecular electrostatic potentials. Plenum, New York
36. Politzer P, Murray JS (2002) Theor Chem Acc 108:134–142
37. Politzer P, Murray JS (1998) Theochem 425:107–114
38. Politzer P, Murray JS (1999) Trends Chem Phys 7:157–165
39. Politzer P, Murray JS (2001) Fluid Phase Equilib 185:129–137
40. Bader RFW, Carroll MT, Cheeseman JR, Chang C (1987) J Am Chem Soc 109:7968–7979
41. Murray JS, Lane P, Politzer P (2009) J Mol Model 15:723–729
42. Qiu L, Xiao H, Gong X, Ju X, Zhu W (2007) J Hazard Mater 141:280–288
43. Rice BM, Hare JJ, Byrd EFC (2007) J Phys Chem A 111:10874–10879
44. Politzer P, Martinez J, Murray JS, Concha MC, Toro-Labbé A (2009) Mol Phys, doi:10.1080/00268970903156306
45. Hintze J (2006) NCSS, Kaysville, UT, www.ncss.com
46. Zhang C, Shu Y, Huang Y, Zhao X, Dong H (2005) J Phys Chem B 109:8978–8982