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Some molecular/crystalline factors that affect the sensitivities of energetic materials: molecular surface electrostatic potentials, lattice free space and maximum heat of detonation per unit volume

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Abstract We discuss three molecular/crystalline properties that we believe to be among the factors that influence the impact/shock sensitivities of energetic materials (i.e., their vulnerabilities to unintended detonation due to impact or shock). These properties are (a) the anomalously strong positive electrostatic potentials in the central regions of their molecular surfaces, (b) the free space per molecule in their crystal lattices, and (c) their maximum heats of detonation per unit volume. Overall, sensitivity tends to become greater as these properties increase; however these are general trends, not correlations. Nitramines are exceptions in that their sensitivities show little or no variation with free space in the lattice and heat of detonation per unit volume. We outline some of the events involved in detonation initiation and show how the three properties are related to different ones of these events.

Keywords Detonation initiation · Electrostatic potentials · Energetic materials · Heat of detonation per unit volume · Lattice free space · Sensitivity

The problem of sensitivity

A key issue in the area of energetic materials is sensitivity, i.e., vulnerability to unintended detonation caused by an accidental

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external stimulus, such as impact or shock. The objective is to achieve low sensitivity in conjunction with a high level of detonation performance; the challenge is that sensitivity and detonation performance are frequently linked [1, 2]: The more powerful explosives tend to be more sensitive. A compromise must be sought. One promising approach is co-crystallization of a high-performing but sensitive compound with a lower-performing but less sensitive one [3–5].

Sensitivity depends upon a variety of factors: molecular, crystalline, and physical. The importance of physical factors — sizes and shapes of crystals, their hardness, their purity, the extents of lattice defects, atmospheric conditions, etc. [6–13] — means that measurements of sensitivities must be performed with as uniform sample preparation and testing procedures as possible. It is indeed well known that sensitivities determined at different laboratories can differ widely; see Table 1. However if each laboratory follows its procedure consistently and carefully, then the general trends should be similar, as is confirmed in Fig. 1.

Sensitivity is related to the ease of initiating detonation, a process that involves a series of events; some of them are summarized in Scheme 1. Experimental and computational (largely molecular dynamics) studies have provided considerable insight into these events [17–38]. A crystalline energetic material that is subjected to impact or shock undergoes compression, at a rate and to a degree that depend upon the strength of the external stimulus and the nature of the material. This produces crystal structural changes, among them being shear and slip, distortion, disorder, and alteration of existing lattice defects, e.g., collapse of voids. These structural effects result in local buildups of thermal energy in small portions of the lattice ("hot spots"). Some of this energy can be transferred to molecular vibrational modes that may initiate bond breaking and molecular rearrangements that eventually lead to self-sustaining exothermal chemical decomposition releasing energy and gaseous products. The consequence may be a high pressure, supersonic velocity shock wave

Table 1 Comparison of experimental impact sensitivities from different sources. Values are drop heights, h_{50} (cm), for a 2.5 kg mass. The smaller is h_{50}, the greater is the impact sensitivity. For this mass, a drop height of 100 cm corresponds to an impact energy of 24.5 J

| Compound	Source		
	Storm et al.[a]	Wilson et al.[b]	Meyer et al.[c]
Pentaerythritoltetranitrate (PETN)	12		12
Hexanitrobenzene	12	11	
Hexanitrohexaazaisowurtzitane (β-CL-20)	14[d]		16
Pentanitroaniline	15	22	
2,4,6-Trinitropyridine-N-oxide	20		9
1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)	26		31
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)	29		30
2,4,6-Trinitro-N-methyl-N-nitroaniline (Tetryl)	32	25	12
N,N'-Dinitro-1,2-diaminoethane	34		33
Hexanitrostilbene (HNS)	39		20
2,3,4,6-Tetranitroaniline	41	47	24
2,4,6-Trinitroresorcinol	43		30
Benzotrifuroxan	50	53	
Hexanitrobiphenyl	85	70	
2,4,6-Trinitrophenol (picric acid)	87	64	30
1,3,5-Trinitrobenzene (TNB)	100	71	30
2,4,6-Trinitrobenzoic acid	109		41
3,3'-Diaminohexanitrobiphenyl (DIPAM)	132	67	
2,4,6-Trinitrotoluene (TNT)	160	98	61
2,4,6-Trinitroaniline (picramide)	177	141	61
2,4,6-Trinitrocresol	191		49
2,4,6-Trinitroanisole	192		82

[a] Ref. [14] [b] Ref. [7] [c] Ref. [15]
[d] Ref. [16]

propagating through the system (detonation). Some of these events will be discussed in more detail in later sections.
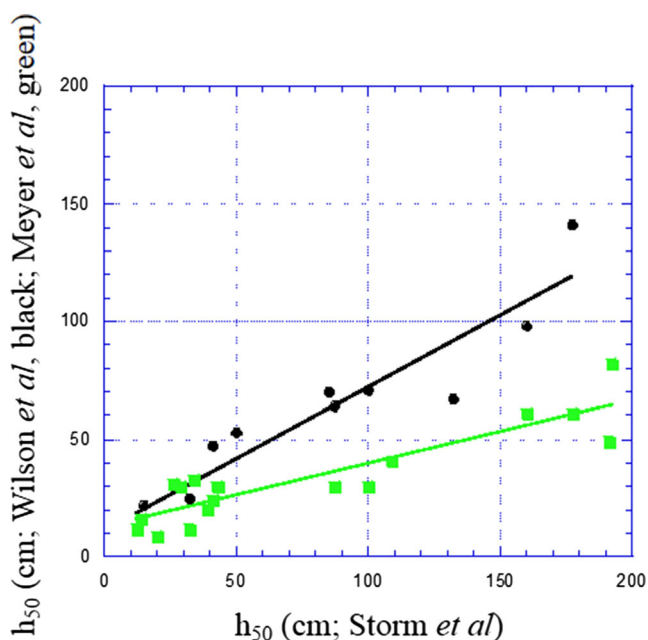
Fig. 1 Measured impact sensitivities, h_{50}, of Wilson et al. [7] (black circles) and Meyer et al. [15] (green squares) plotted against those of Storm et al. [14]. Data are from Table 1. The lines represent least squares fits

Sensitivity is determined, at least in part, by how readily these and related events take place — as well as by the physical features mentioned above. If one is dealing with a restricted group of compounds that behave similarly with respect to some of the events in Scheme 1, and if the physical features are fairly uniform, then it may be possible to relate the measured sensitivities reasonably well to a property that reflects just certain ones of the events. For instance, correlations that are perhaps surprisingly good, but limited in scope, have been obtained between sensitivity and properties of key bonds ("trigger linkages"); this focuses upon the bond-breaking step in Scheme 1. There are several overviews of such relationships [1, 39–41]. We emphasize, however, that Scheme 1 is
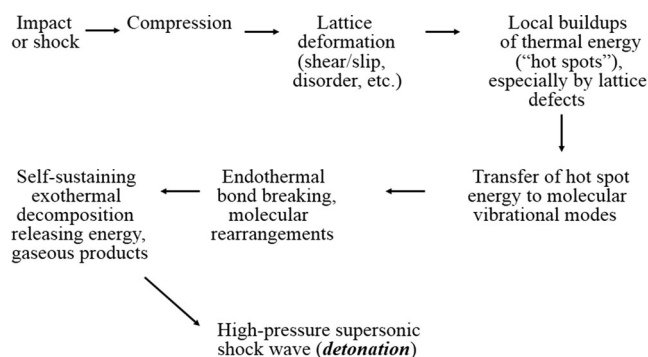
Scheme 1 Some of the events involved in initiation of detonation

simply a rough outline of some of the events involved in the initiation of detonation. There is certainly overlap between them, and the specific details and relative significance of each one vary with the nature of the energetic material, the physical conditions, and the external stimulus.

One of our objectives over a period of years has been to identify molecular and/or crystal factors that influence sensitivity. This could provide insight into how it might be controlled or diminished. Earlier, we have reported two such factors: (a) the electrostatic potential on the molecular surface of an energetic compound [42–45], and (b) the available free space per molecule in its crystal lattice [46–48]. We shall briefly review this past work to show how these relate to the series of events depicted in Scheme 1. We will then proceed to a third factor: the maximum possible heat of detonation per unit volume of the compound.

The electrostatic potential

The electrons and nuclei of any system create an electrostatic potential in the surrounding space. It directly reflects the charge distribution in the system, based upon Coulomb's law; the potential is negative or positive in any given region depending upon whether the effects of the electrons or the nuclei are dominant there. The electrostatic potential is a real and fundamentally significant physical property [49, 50], which can be determined both experimentally and computationally; it should not be confused with atomic charges, which are arbitrarily defined quantities with no rigorous physical basis [50, 51]. Our present interest will be in the electrostatic potentials computed on molecular surfaces (which are commonly taken to correspond to the 0.001 au contours of the molecules' electronic densities [52]).

The electrostatic potentials on the molecular surfaces of most energetic compounds differ quite markedly from those of typical organic molecules [1, 41, 42, 45, 49, 50, 53–55]. The latter frequently have quite prominent negative regions (reflecting primarily lone pairs and π electrons) that are often stronger than the positive ones. In contrast, the molecular surfaces of energetic compounds are normally dominated by strongly positive potentials in the central portions of the molecules and above C-NO$_2$ and N-NO$_2$ bonds, with weakly negative ones on the outsides of the molecules due to nitro and/or N-oxide oxygens and aza nitrogens. Rice and Hare display the surface potentials for a large number of molecules of energetic compounds [53].

Can the strongly positive central regions that characterize the molecular surface potentials of energetic compounds be linked to their sensitivities? Yes, within groups of compounds of a particular type, e.g., nitroaromatics or nitramines; the sensitivity generally increases as the central electrostatic potential becomes more positive. This is clearly evident in the results presented by Rice and Hare [53], and has also been demonstrated elsewhere [1, 41, 54, 55]. For compounds with similar molecular frameworks, this feature has been used to estimate their relative sensitivities, for instance by Klapötke et al. [56–59].

Particularly interesting in this context is a recent computational study by Li et al. of the 1:1 complex between TNT and CL-20 [5]. (The acronyms TNT and CL-20 are defined in Table 1.) They were modeling the interaction in the 1:1 TNT/CL-20 co-crystal that had recently been prepared by Bolton and Matzger [3], and shown to have an impact sensitivity significantly less than that of CL-20 itself. Li et al. found that the strongly positive electrostatic potential in the central region of an isolated CL-20 molecule was diminished in the complex with TNT, while that of the TNT was increased. This is fully consistent with the co-crystal being less sensitive than CL-20 alone but more than TNT alone.

For compounds of a given type, e.g., nitramines, it has even been possible to establish quite satisfactory quantitative relationships between their sensitivities and certain features of their molecular surface electrostatic potentials that reflect the dominant positive central regions [42, 44, 45, 55]. A cautionary note: If a molecule has an extended three-dimensional framework, then its interior electrostatic potential may not be fully reflected on its surface. An example is PETN; the potential on its surface is not nearly as positive [53] as would be anticipated from its high sensitivity (Table 1).

Why might a strongly positive central region be linked to sensitivity? We will suggest two possible reasons (there may be others as well); one or both of these may be relevant in any particular case.

1. One of the consequences of the initial compression of an energetic compound is shear and slip in various directions within the crystal, i.e., lattice planes shifting past each other. The resistance to this is one avenue for producing the localized regions of thermal energy (hot spots) that facilitate endothermic processes, e.g., bond ruptures, that can lead to exothermal chemical decomposition and detonation (Scheme 1). The sensitivities of energetic compounds are known to be anisotropic, differing from one crystal direction to another [25, 60–63], and links have been found between directions of higher sensitivity and greater resistance to shear/slip [33, 35, 36, 64].

   Such resistance is likely to be significantly increased by repulsion between strongly positive surface regions on the molecules. More energy is then required to overcome this "friction," which promotes the formation of hot spots. Kuklja and Rashkeev have indeed shown that C-NO$_2$ bonds rupture more readily at shear interfaces [31, 34, 65]. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) lacks the strongly positive central potential that usually characterizes molecules of energetic compounds [53] and it is one of the most insensitive [14, 15]; it also shows relatively little shear resistance [29, 30, 34, 65].

2. The positive central regions are evidence of withdrawal of electronic charge — by the nitro groups, aza nitrogens, etc. — that diminishes C-NO$_2$ and N-NO$_2$ bond strengths. It has been shown that as the number of NO$_2$ groups increases, the surface potentials become more positive and C-NO$_2$ and N-NO$_2$ bonds become weaker [41, 43, 44, 55]. The positive potential is therefore symptomatic of the bond-breaking step in Scheme 1 being easier.

Free space per molecule in crystal lattice

Eckhardt and Gavezzotti have estimated the free space in C,H, N,O-containing energetic compounds to be roughly 15-30% of the unit cell volumes [66]. Free space facilitates the compression in the impact or shock direction that leads to structural effects (shear/slip, disorder, etc.) in various directions within the crystal, hot spot formation, etc. (Scheme 1).

Lattice defects that provide free space, such as voids and vacancies, increase compressibility [67], and can also produce hot spots. Molecules at void walls are less tightly held than those in the bulk solid [68] and can be ejected into the void by the energy introduced via compression, which is thereby transferred into spatially-localized molecular kinetic, vibrational, and rotational modes (hot spots) [17, 18, 20, 26].

It is furthermore relevant that C-NO$_2$ [69, 70] and N-NO$_2$ [71, 72] bonds are weaker and more easily broken when the molecule is at a crystal surface or by a lattice void (i.e., free space) than when it is in the bulk. Void-related rupture of N-NO$_2$ bonds in RDX was indeed observed in a molecular dynamics simulation by Nomura et al. [26].

The role of free space in promoting sensitivity is increasingly being recognized [26, 38, 46–48, 73, 74]. Quoting Baillou et al. [74], "Thus, there seems to be a correlation between shock sensitivity and magnitude of the internal porosity within the explosive grains." Kunz showed that PETN is more compressible in one of the directions in which it is more sensitive [75]. The very insensitive TATB has a very low compressibility [29].

We have investigated the link between sensitivity and free space in the crystal lattice in several studies [46–48]. We express the free space per molecule in the unit cell, ΔV, by the relationship:

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

In Eq. (1), V_{eff} is the hypothetical "effective" volume per molecule that would correspond to the unit cell being completely filled (i.e., the packing coefficient would be one and there would be no free space). V_{eff} can easily be determined:

$$V_{eff} = M/\rho, \tag{2}$$

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

V_{int} is the "intrinsic" volume of the molecule, for which there is no rigorous definition. After some experimentation, we settled upon $V_{int} = V(0.003)$ [47], where V(0.003) is the volume enclosed by the 0.003 au contour of the molecule's electronic density. This choice of V_{int} yields packing coefficients (given by V_{int}/V_{eff}) that are in good agreement with the range and average value of those determined by Eckhardt and Gavezzotti for energetic compounds [66].

Further support for this definition of V_{int} is the fact that it predicts, via Eq. (1), that the free space in the crystal lattice of defect-free RDX is about 22% of the volume [47], which is very similar to the degree of compression that can be achieved fairly readily [67]. Further compression is possible but requires a considerable increase in pressure.

The distances from the atomic nuclei to the 0.003 au contours are similar to the van der Waals radii of the atoms [48], which might suggest that the molecular surface could be
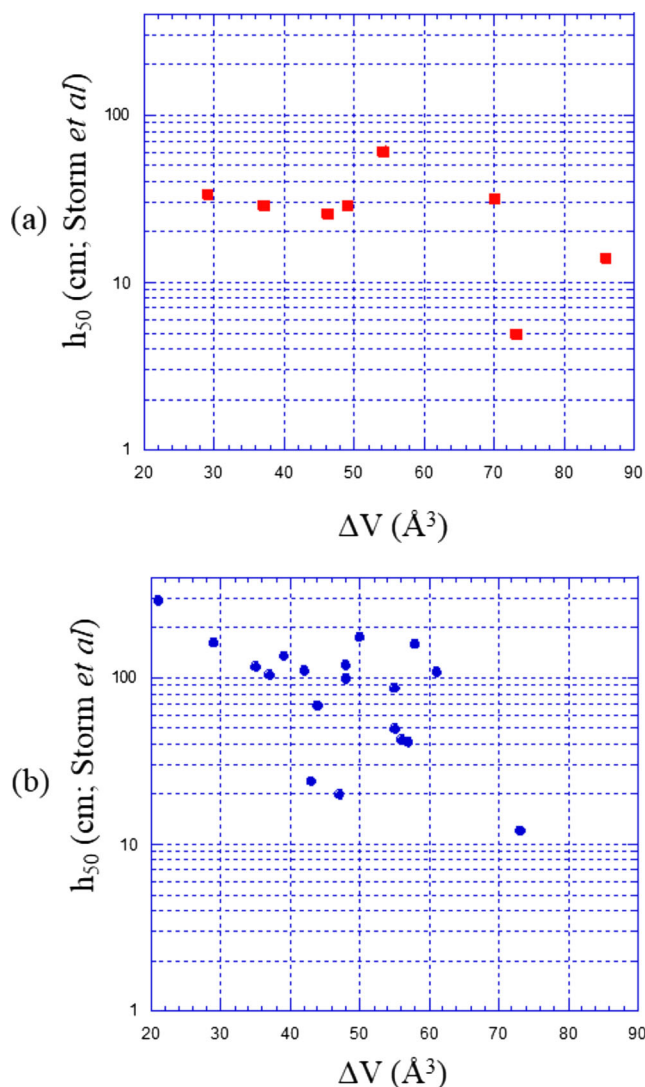
Fig. 2 Semi-logarithmic plots of measured impact sensitivities, h$_{50}$, of Storm et al. [14] vs. free space per molecule in the crystal lattice, ΔV, for (**a**) nitramines in Table 2, and (**b**) all other compounds in Table 2

defined in terms of overlapping atomic spheres with van der Waals radii. However contours of the electronic density, such as the 0.003 au and 0.001 au, have the advantage that they reflect features that are specific to each particular molecule, e.g., lone pairs, π electrons, and atomic anisotropy.

Our earlier studies showed a general tendency for impact sensitivity to increase as ΔV (the free space per molecule in the crystal lattice) becomes larger [46–48]. It is certainly not a correlation, but rather an overall trend. We observed, furthermore, that nitramines form a distinct subgroup. This can be seen again in Fig. 2, which is for a data-base (Table 2) that differs somewhat from those that we used previously, both in terms of the compounds included and also in that the h_{50} values are primarily from the extensive compilation by Storm et al. [14]. As recommended by Kamlet

[6], we now use log h_{50} rather than h_{50} as the measure of relative impact sensitivity.

For the nitramines, Fig. 2a shows h_{50} to vary only weakly with ΔV, decreasing very gradually as ΔV increases. Most nitramines are quite sensitive and have low h_{50} values regardless of the magnitudes of ΔV; 80% of those listed by Storm et al. have $h_{50} < 40$ cm [14]. One reason for this may be the relative weakness of N-NO_2 bonds [41, 55, 82, 83], but there are likely to also be other reasons, for example autocatalysis [6].

In Fig. 2b, the log h_{50} of the non-nitramines in Table 2 are plotted against the calculated ΔV. Given the well-known uncertainties in experimental h_{50} values [6, 7, 9, 11, 14, 53], as well as in some of the experimental crystal densities that are used to find ΔV, it is fair to say that Fig. 2b does show an overall trend (not a correlation), with a few outliers. The h_{50}

Table 2 Impact sensitivities h_{50} (cm), densities ρ (g/cm^3), molecular masses M (g mol^{-1}), and computed V_{eff}, V(0.003) and ΔV (all in Å^3). V_{eff} and ΔV were obtained with Eqs. (2) and (1), respectively. Acronyms used to identify some compounds are defined in Table 1

Compound	h_{50}[a]	ρ[b]	M	V_{eff}	V(0.003)	ΔV
Bis(2,2,2-trinitroethyl) nitramine	5	1.953	388.1	330.0	257.4	73
PETN	12	1.76[c]	316.1	298.2	225.2	73
β-CL-20	14[d]	1.985[d]	438.2	366.6	281.0	86
Trinitropyridine N-oxide	20	1.875[e]	230.1	203.8	157.2	47
1,4-Diamino-3,6-dinitropyrazolo [4,3-c]pyrazole (LLM-119)	24[f]	1.845[f]	228.1	205.3	162.2	43
RDX	26	1.806	222.1	204.2	158.6	46
HMX	29	1.894	296.2	259.7	210.5	49
1,3,3-Trinitroazetidine (TNAZ)	29[g]	1.84[h]	192.1	173.4	136.6	37
Tetryl	32	1.731	287.1	275.4	205.9	70
N,N'-Dinitro-1,2-diaminoethane	34	1.709	150.1	145.8	117.2	29
2,3,4,6-tetranitroaniline	41	1.861	273.1	243.7	187.2	57
2,4,6-Trinitroresorcinol	43	1.83[c]	245.1	222.4	166.6	56
Benzotrifuroxan	50	1.901	252.1	220.2	165.4	55
2,4,6-Trinitro-2,4,6,8-tetraazabicyclononane-3-one (HK-55)	61[f]	1.905[f]	263.1	229.3	175.6	54
2,4,5-Trinitroimidazole	68	1.88[j]	203.1	179.5	135.5	44
Picric acid	87	1.767[c]	229.1	215.3	160.2	55
TNB	100	1.76[c]	213.1	201.1	153.4	48
2,4-Dinitroimidazole	105	1.770	158.1	148.3	111.3	37
2,4,6-Trinitrobenzoic acid	109	1.786	257.1	239.0	177.9	61
2,2-Dinitro-1,3-propanediol	110	1.652	166.1	167.0	124.7	42
2,6-Diamino-3,5-dinitropyrazine 1-oxide (LLM-105)	117[i]	1.919[i]	216.1	187.0	152.0	35
3,5-Diamino-2,4,6-trinitrophenol	120	1.890	259.1	227.6	179.4	48
3,6-Dinitropyrazolo[4,3-c]pyrazole (DNPP)	136[f]	1.865[f]	198.1	176.4	137.4	39
TNT	160	1.654[c]	227.1	228.0	169.9	58
4-Amino-3,5-dinitropyrazole (LLM-116)	165[f]	1.90[f]	173.1	151.3	122.8	29
2,4,6-Trinitroaniline (picramide)	177	1.773	228.1	213.6	163.5	50
3-Nitro-1,2,4-triazole-5-one (NTO)	291	1.918	130.1	112.6	91.5	21

[a] All h_{50} are measured values, from ref. [14] unless otherwise indicated

[b] All densities are experimental values, from ref. [76] unless otherwise indicated

[c] Ref. 15 [d] Ref. 16 [e] Ref. 77 [f] Ref. 78 [g] Ref. 79 [h] Ref. 80 [i] Ref. 81

[j] Computed, present work

tend to decrease (increasing sensitivity) as the ΔV become larger. Since Fig. 2b reflects only some of the series of events in Scheme 1 (e.g., lattice deformation, hot spot buildup and bond breaking), it would not be reasonable to expect more than a general trend, considering the different types of compounds that are included. However, Fig. 2 does support the concept, in agreement with other evidence cited earlier in this section, that the amount of free space per molecule in the

Table 3 Impact sensitivities h_{50} (cm), densities ρ (g/cm^3), solid phase ΔH_f (kcal mol^{-1}), molecular masses M (g mol^{-1}), calculated maximum heats of detonation Q_{max} (kcal/g), and products ρQ_{max} (kcal/cm^3). Q_{max} was obtained with Eq. (3). Acronyms used to identify some compounds are defined in Tables 1 and 2

Compound	h_{50} Storm et al.[a]	h_{50} Meyer et al.[b]	ρ[c]	$\Delta H_f(s)$[d]	M	Q_{max}	ρQ_{max}
Mannitol hexanitrate		3	1.604	−161.5	452.2	1.402	2.25
Bis(trinitroethyl)nitramine	5		1.953[e]	−6.69[f]	388.1	1.250	2.44
Heptanitropentane	8		1.908[e]	−36.7[f]	387.1	1.493	2.85
Nitroaminoguanidine		12	1.71	5.28	119.1	1.015	1.74
PETN	12	12	1.76	−128.8	316.1	1.514	2.66
Dipentaerythritol hexanitrate		16	1.63	−234	524.2	1.423	2.32
β-CL-20	14[g]	16	1.985[g]	103.0[g]	438.2	1.597	3.17
Trinitropyridine N-oxide	20	9	1.875[h]	24.40[i]	230.1	1.583	2.97
Ethyl tetryl		20	1.63	−4.31	301.2	1.360	2.22
Trinitropyridine		22	1.751[h]	8.20[i]	214.1	1.406	2.46
Dinitrodimethyl oxamide		24	1.523	−73.00	206.1	1.172	1.78
Dioxyethylnitramine dinitrate		24	1.488	−65.88	240.1	1.472	2.19
LLM-119	24[l]		1.845[l]	114[l]	228.1	1.419	2.62
RDX	26	31	1.806[e]	18.9[f]	222.1	1.501	2.71
TNAZ	29[j]		1.84[k]	8.70	192.1	1.626	2.99
HMX	29	30	1.894[e]	24.5[f]	296.2	1.498	2.84
Tetryl	32	12	1.731[e]	9.8[f]	287.1	1.438	2.49
Hexanitrodiphenylamine		31	1.64	9.88	439.2	1.369	2.24
Trinitrophenoxyethyl nitrate		32	1.68	−66.31	318.2	1.371	2.30
N,N′-Dinitro-1,2-diaminoethane	34	33	1.709[e]	−24.81	150.1	1.303	2.23
Hexanitrostilbene	39	20	1.74	16.2[f]	450.2	1.361	2.37
2,3,4,6-Tetranitroaniline	41	24	1.861[e]	−11.74[f]	273.1	1.394	2.59
2,4,6-Trinitroresorcinol	43	30	1.83	−111.7[f]	245.1	1.145	2.10
Benzotrifuroxan	50		1.901[e]	144.9[f]	252.1	1.694	3.22
3,6-Diamino-1,2,4,5-tetrazine 1,4-di-N-oxide (LAX-112)		51[m]	1.83[n]	48.02[m]	144.1	1.135	2.08
2,4,5-Trinitroimidazole	68		1.88[s]	15.5[s]	203.1	1.492	2.81
Hexanitrobiphenyl	85		1.69[o]	16.3[p]	424.2	1.419	2.40
Picric acid	87	30	1.767	−52.07[f]	229.1	1.280	2.26
TNB	100	30	1.76	−8.9[f]	213.1	1.358	2.39
2,4-Dinitroimidazole	105		1.770[e]	5.6[s]	158.1	1.293	2.29
2,4,6-Trinitrobenzoic acid	109	41	1.786[e]	−97.91[f]	257.1	1.145	2.05
LLM-105	117[q]		1.919[q]	−3.10[r]	216.1	1.173	2.25
DIPAM	132		1.79[o]	−6.8[p]	454.2	1.299	2.32
DNPP	136[l]		1.865[l]	65[l]	198.1	1.332	2.48
TNT	160	61	1.654	−15.1[f]	227.1	1.295	2.14
2,4,6-Trinitroaniline (picramide)	177	61	1.773[e]	−17.4[f]	228.1	1.255	2.23
Table 3 (continued). Compound	h_{50} Storm et al[a]	h_{50} Meyer et al[b]	ρ[c]	$\Delta H_f(s)$[d]	M	Q_{max}	ρQ_{max}
2,4,6-Trinitrocresol	191	49	1.68	−60.29	243.1	1.217	2.04
2,4,6-Trinitroanisole	192	82	1.61	−44.75[f]	243.1	1.281	2.06
Dinitrophenoxyethyl nitrate		82	1.60	−70.02	273.2	1.259	2.01
m-Dinitrobenzene		159	1.5	−6.51	168.1	1.208	1.81

Table 3 (continued)

Compound	h_{50} Storm et al.[a]	h_{50} Meyer et al.[b]	ρ[c]	$\Delta H_f(s)$[d]	M	Q_{max}	ρQ_{max}
NTO	291		1.918[e]	−24.09	130.1	0.9820	1.88
2,4,6-Triamino-1,3,5-trinitrobenzene (TATB)		204	1.937[e]	−33.40	258.1	1.089	2.11

[a] Measured h_{50} values, from ref. [14] unless otherwise indicated.

[b] Measured h_{50} values, from ref. [15] unless otherwise indicated.

[c] Experimental densities, from ref. [15] unless otherwise indicated.

[d] Experimental enthalpies of formation from ref. [15] unless otherwise indicated.

[e] Ref. [76]

[f] Ref. [99]

[g] Ref. [16]

[h] Ref. [77]

[i] Ref. [98]

[j] Ref. [79]

[k] Ref. [80]

[l] Ref. [78]

[m] Ref. [100]

[n] Ref. [101]

[o] Ref. [7]

[p] Ref. [89]

[q] Ref. [81]

[r] Computed, ref. [58]

[s] Computed, present work

crystal lattice is one of the factors that, for many compounds, affect sensitivity.

Maximum heat of detonation per unit volume of compound

The heat released in a detonation process depends upon several factors. Among these are the chemical composition of the explosive material, the nature of the final detonation products and physical conditions such as the loading density and the extent to which gaseous products are able to expand (expansion ratio) [84–86]. For an energetic compound X, the heat release Q per gram of X that comes from the chemical decomposition reactions (Scheme 1) is given by:

$$Q = -\Delta H / M, \tag{3}$$

where M is the molecular mass in g mol^{-1} and:

$$\Delta H = \sum_i n_i \Delta H_{f,i} - \Delta H_{f,X}. \tag{4}$$

$\Delta H_{f,i}$ and $\Delta H_{f,X}$ are the molar enthalpies of formation of final product i and compound X, and n_i is the number of moles of i. Since ΔH is negative for an exothermal decomposition, Q is positive.

The detonation reaction may involve a number of intermediates and equilibria, but the final products, for most C,H,N,O secondary explosives, are usually almost entirely some combination of $N_2(g)$, $H_2O(g)$, $CO(g)$, $CO_2(g)$, $H_2(g)$, and $C(s)$ [84, 87–90]. The proportions, which depend upon the loading density, temperature, pressure, etc., can be predicted by means of computer codes [87, 88, 91–93] or by one of several sets of proposed rules [87, 94–96].

Rice and Hare [53] and Zeman [39] observed, for groups of nitroaromatic compounds, a general tendency for impact sensitivity to increase (h_{50} smaller) as the detonation heat release per unit mass, Q, is larger (Q more positive).

A modified version of this was investigated by Pepekin et al. [97]. They considered the product ρQ_{max}, where ρ is the density and Q_{max} is the "maximum" heat release. They took Q_{max} to be the value obtained by using the Kamlet-Jacobs rules for predicting the detonation products [87], according to which these are $N_2(g)$, $H_2O(g)$, $CO_2(g)$, and $C(s)$, with oxygen going to $H_2O(g)$ prior to $CO_2(g)$. The formation of $CO_2(g)$ rather than $CO(g)$ generally produces a greater total heat release [96] since $\Delta H_{f,CO_2(g)}$ is much more negative than $\Delta H_{f,CO(g)}$, −94.05 vs. −26.417 kcal mol^{-1} [98].

The quantity ρQ_{max} is accordingly the maximum available heat of detonation per unit volume of the compound. Pepekin et al. view this as indicating the "limiting capability" of the compound to convert chemical energy into detonation
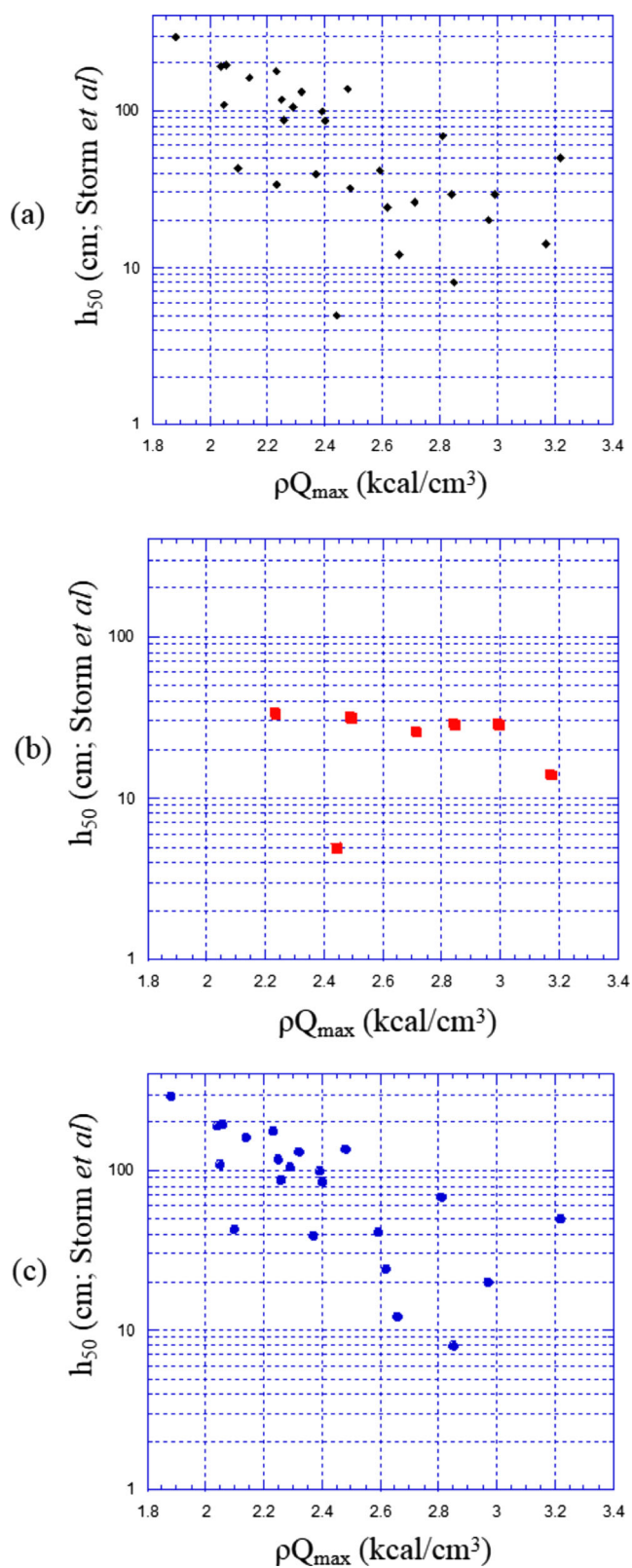
Fig. 3 Semi-logarithmic plots of measured impact sensitivities, h_{50}, of Storm et al. [14] vs. maximum heat of detonation per unit volume, ρQ_{max}, for (**a**) all available compounds in Table 3, (**b**) available nitramines in Table 3, and (**c**) all available non-nitramines in Table 3
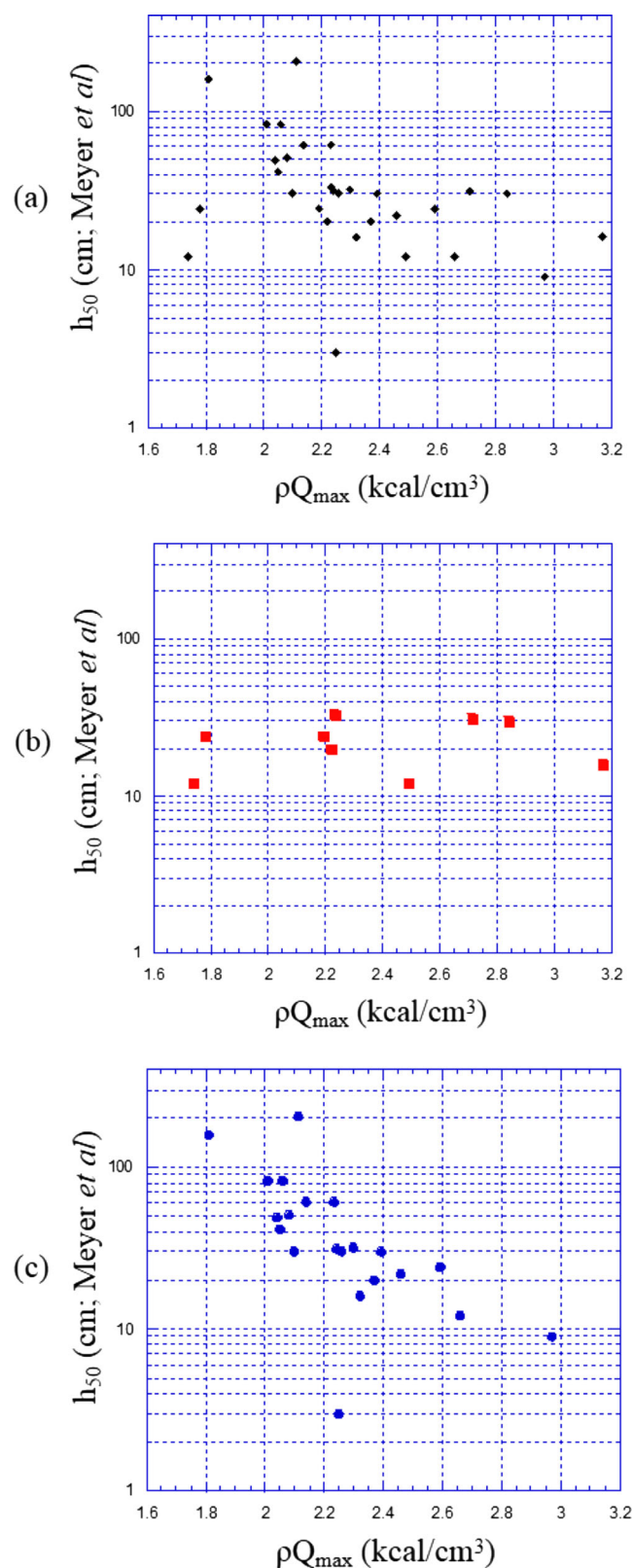
Fig. 4 Semi-logarithmic plots of measured impact sensitivities, h_{50}, of Meyer et al. [15] vs. maximum heat of detonation per unit volume, ρQ_{max}, for (**a**) all available compounds in Table 3, (**b**) available nitramines in Table 3, and (**c**) all available non-nitramines in Table 3

(Scheme 1) [86, 97]. They looked for a link between ρQ_{max} and the "critical pressure" of an energetic compound; the latter is the minimum applied pressure that will initiate detonation, and is accordingly expected to be related to the sensitivity of the compound. Pepekin *et al.* found that the critical pressures of a group of 18 energetic compounds of different types decrease roughly linearly (i.e., the compounds become more sensitive) as ρQ_{max} increases [97]; they did have some outliers.

We have now investigated the significance of ρQ_{max} with respect to sensitivity for a much larger database, given in Table 3. It contains 42 energetic compounds: nitroaromatics, nitramines, nitroheterocycles, nitrate esters, and N-oxides. As measures of sensitivity were taken two sets of experimental h_{50} values, those reported by Storm *et al.* [14] and those of Meyer *et al.* [15]. For some of the compounds, h_{50} is available from only one of the two sources. We plotted each set of log h_{50} separately against the calculated ρQ_{max}, in order to allow comparisons.

The two sets of sensitivities produce qualitatively very similar results. Figures 3a and 4a show that the overall tendency is for sensitivity to increase (h_{50} smaller) as the maximum heat of detonation per unit volume ρQ_{max} becomes greater. However, just as was found for free space in the crystal lattice (Free space per molecule in crystal lattice), the nitramines again constitute a special subgroup; their sensitivities exhibit little or no variation with ρQ_{max}, Figs. 3b and 4b. For the remaining compounds, Figs. 3c and 4c show a clear trend for h_{50} to decrease (increasing sensitivity) as ρQ_{max} becomes larger.

It is reassuring that the h_{50} values from Storm *et al.* [14] and those from Meyer *et al.* [15], while sometimes differing considerably in magnitude (Table 3), are in qualitative agreement concerning log h_{50} *vs.* ρQ_{max} relationships, Figs. 3 and 4. The general trends are the same, which is consistent with Fig. 1.

Discussion and Summary

We have discussed three molecular/crystalline properties that appear to be among the factors (certainly not the only ones) that influence the sensitivities of energetic compounds: (a) the anomalously strong positive electrostatic potentials on the central portions of their molecular surfaces, (b) the free space per molecule in their crystal lattices, and (c) their maximum heats of detonation per unit volume. These properties affect different combinations of the events outlined in Scheme 1.

In general, sensitivity increases as each of these properties becomes more positive or larger. However these are not correlations but rather overall trends. The relative importance of each factor varies from one compound to another (as is demonstrated by the nitramines in Figs. 2 and 4). This helps

to account for the outliers in Figs. 2 and 4, which also undoubtedly reflect the uncertainties in some of the experimental data, particularly the h_{50} values and the enthalpies of formation of the energetic compounds.

The nitramines present an interesting situation. Most nitramines are quite sensitive [14, 15], including all those in Table 3, and Figs. 2a, 3b, and 4b show that changes in ΔV or ρQ_{max} have little or no effect upon these nitramines' sensitivities. This may indicate that some other overriding factor is involved; the typical weakness of the $N-NO_2$ bond comes to mind [41, 55, 82, 83], or the autocatalysis mentioned by Kamlet [6]. It should be noted that nitrate esters are generally also very sensitive [14, 15] and $O-NO_2$ bonds tend to be as weak as $N-NO_2$ [83]. However the nitrate esters in Table 3 fit quite well the trends exhibited by the other non-nitramine compounds, Figs. 3c and 4c. Why do the nitramines behave differently? This remains to be clarified.

By computing ΔV and/or ρQ_{max} for a compound, Figs. 2 and 4 can be used to roughly estimate a range of h_{50} values for it, relative to those of either Storm *et al.* [14] or Meyer *et al.* [15]. For a recent example using ΔV, see Zhang and Gong [102]. However since ΔV and ρQ_{max} reflect different molecular and crystalline features and are related to different events in Scheme 1, the estimates based upon ΔV and ρQ_{max} may not agree. Which one should then be viewed as more meaningful? Caution would dictate accepting the estimate that indicates greater sensitivity. This is another issue that needs to be clarified.

Finally, we observe that Figs. 3c and 4c illustrate the statement in the section The problem of sensitivity that sensitivity and detonation performance are often linked (except for nitramines). Large values of ρQ_{max} usually increase detonation velocity and detonation pressure [1–37, 41, 87, 90, 94], but they also tend to be associated with higher sensitivity. This is a general trend, not a close correlation, but it needs to be considered in designing and synthesizing new energetic compounds. Pepekin *et al.* have also addressed this point [97, 103].

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