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SOME CHEMICAL AND STRUCTURAL FACTORS RELATED TO THE
METASTABILITIES OF ENERGETIC COMPOUNDS

by

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13. ABSTRACT (Maximum 200 words) We have presented an overview of various attempts to relate the impact and shock sensitivities of energetic materials to their molecular structures. The objectives of such efforts are to better understand the chemical and structural determinants of these sensitivities, and to develop a predictive capability to facilitate the evaluation of new and proposed energetic compounds. Our particular emphasis in this discussion has been upon the relationship of impact sensitivities to the electrostatic potential patterns on the molecular surfaces. The current status of our analyses is represented by eqs. (7) - (9). While the success of these expressions is pleasing, we certainly do not claim that they are in final form. They reflect small data bases and measurements with a relatively high level of uncertainty. As more compounds are included, it may well be that the specific formulations given in eqs. (7) - (9) will be modified; i.e. other functions of $\bar{V}_S^-$ and $\bar{V}_S^+$ or σ_-^2 and σ_+^2 may turn out to be more effective. What is important at present, however, is the unifying concept that we have found to apply to all three of these classes of compounds, namely that their impact sensitivities can be related to the degree of imbalance between their typically stronger positive surface electrostatic potentials and weaker negative ones.					
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Some Chemical and Structural Factors Related to the Metastabilities of Energetic Compounds

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1. INTRODUCTION

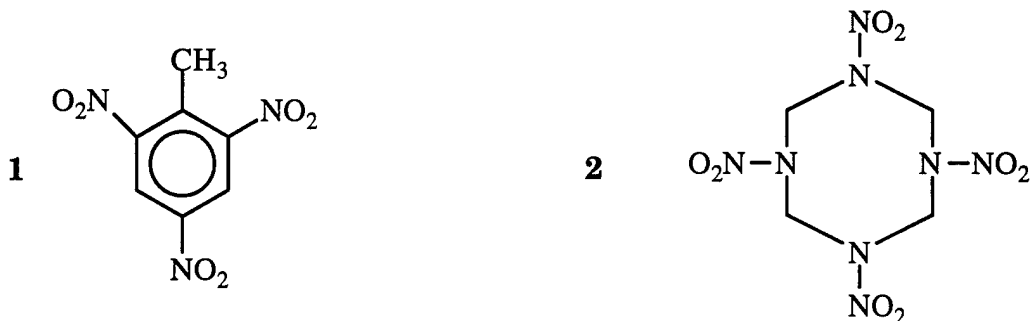
A continuing challenge in the design of new energetic materials (e.g. explosives and propellants) is to reconcile the necessary metastability with the desired insensitivity. Simply put, they should be sufficiently unstable to be capable of suddenly releasing a great deal of energy, but stable enough that this not happen before it is wanted! Since these two objectives are intrinsically somewhat contradictory, the realistic goal is an optimum compromise, which maximizes energetic performance while minimizing sensitivity to unintended stimuli.

Some of the data relevant to the first issue can now be predicted with generally satisfactory accuracy; this includes density [1-3], heat of formation [4-6], detonation pressure and velocity [7,8] and specific impulse [9]. These properties permit meaningful assessments of the potential level of energetic performance. The prediction of sensitivity, however, continues to be an area of considerable activity.

A key point, with regard to both issues, is the decomposition process of the compound: What are its energetics and how readily does it occur? Our emphasis in this chapter shall be upon factors that influence the ease with which decomposition can be initiated by unwanted external stimuli, i.e. sensitivity. These stimuli may be of various types, including impact, shock, friction, heat and electrostatic charge [8]. Relative vulnerabilities to these different effects need not be the same; for example, the onset temperatures for the thermal decomposition of TNT (1) and HMX (2) are quite similar, but the latter is much more likely to undergo detonation upon impact [8]. It has been shown, however, that there is a general correlation between impact and shock sensitivities [10], which are the ones upon which we will focus.

Impact and shock sensitivities depend upon a variety of factors: chemical, structural and physical. We shall limit our discussion to the effects of molecular structure (i.e. chemical composition and molecular geometry).

Thus we will not directly address, for example, the mechanisms of "hot spot" formation in the crystal [11-13], or the role of particle size [10,12,14].



Impact sensitivity is taken to be inversely proportional to the height (h_{50}) from which a given weight falling upon the compound has a 50% probability of producing an explosion. Shock sensitivity is directly proportional to the maximum gap width through which a standard shock wave has a 50% probability of causing an explosion. It is important to recognize that both types of results are very dependent upon the specific physical conditions of the processes, and reproducibility can be a problem [8,12,15,16].

2. IMPACT/SHOCK SENSITIVITY AND MOLECULAR STRUCTURE: SOME BACKGROUND

2.1. Structure-Sensitivity Relationships

The effects of molecular structure upon impact/shock sensitivity have been analyzed and reviewed in some detail on a number of occasions [8,10,12,17]. Over the years, there have been frequent efforts to relate the experimental impact or shock sensitivities of groups of compounds of a given type (e.g. trinitroaromatics) to some molecular quantity or quantities. Molecular stoichiometry has proven to be remarkably effective in this context [10,15,16,18-20], most notably Kamlet's oxidant balance formula [15,16,18], which is essentially a measure of the oxygen that is present relative to what is needed to convert all hydrogens to H_2O and carbons to CO . In general, the larger is the oxidant balance, the greater is the impact sensitivity.

In his extensive and very significant analyses of the impact sensitivities of energetic compounds, Kamlet emphasized the roles of $C-NO_2$ and $N-NO_2$ bonds as "trigger linkages", the cleavage of which is often a key step in decomposition processes [15,18]. Considerable experimental evidence has accumulated in support of this view [21-35]. Kamlet also argued, with regard to $C-NO_2$ compounds, that rotation around the $C-NO_2$ bond has a desensitizing effect since it reduces the amount of externally-provided energy

that can go into a C-NO₂ stretching vibrational mode and promote bond-breaking [18]. Thus any steric hindrance of rotation can be expected to increase sensitivity. In this context, it is relevant to note recent studies indicating that nitro groups have an enhanced capacity for localizing transferred vibrational energy [36,37].

Reflecting this emphasis upon the C-NO₂ and N-NO₂ bonds, several studies have sought to correlate impact and shock sensitivities with properties of these bonds, particularly various measures of their stabilities. These have included the lengths of the bonds [38,39], the electrostatic potentials at their midpoints [38,40,41], and their polarities in excited states of the molecules [42]. Taking a different approach, Kohno *et al* have argued that the impact sensitivities of nitramines can be related to the differences between the N-NO₂ distances in the gas phase and in the crystal [43,44].

2.2. Some Specific Decomposition Pathways

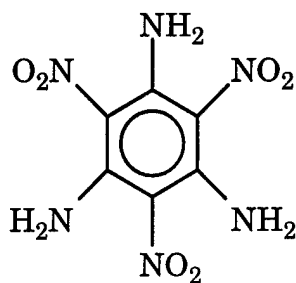
The various structure-sensitivity relationships mentioned above typically treat different classes of compounds separately. Nitramines, for example, are not expected to fit on the same correlations as nitroaromatics or nitroheterocycles. Even within a given class, however, a variety of decomposition mechanisms may be operative. Indeed, Kamlet and Adolph found it necessary to establish two oxidant balance correlations for nitroaromatics [16], one being only for molecules having a CH-containing substituent *alpha* to a nitro group, **3**:



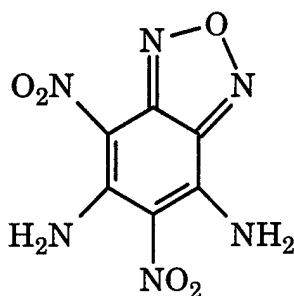
Evidently the α -H is likely to be involved in the early stages of the decomposition process [16], perhaps moving to an adjoining nitro group to form a nitronic acid tautomer, **4** [35,45,46]. These are known to be reactive and unstable [47]. The transfer or loss of a proton to yield a nitronic acid or a nitronate (*aci*) anion has also been invoked as the initial step in the decompositions of other energetic molecules, e.g. picric acid [35,48] and amine-sensitized nitromethane [49-51].

A particularly interesting compound is TATB, **5**, which shows a remarkable *lack* of sensitivity [10,16]. The decomposition of TATB proceeds, in its early stages, through furazan and furoxan intermediates [52,53], e.g. **6**, the

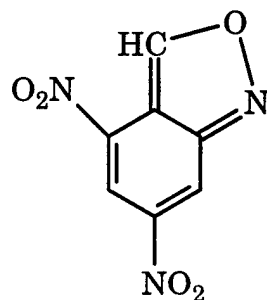
formation of which is believed not to involve any significant net release of energy [10,54,55]. This presumably means that the progression to detonation is less rapid than if these early steps were exothermic. This has been proposed as an explanation of the insensitivity of TATB [10,55]. As a contrast, TNT (1), which is much more sensitive than TATB, decomposes through the intermediate 7 (among others) [16,56,57], which is formed exothermically [54].



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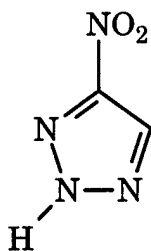


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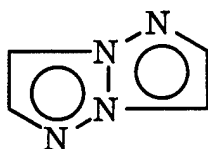


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A structural feature that is frequently associated with instability is the presence of several linked nitrogens [58]. Depending upon the molecular environment, this can provide a relatively facile decomposition pathway through the loss of N_2 . Storm *et al* used this reasoning to interpret the observed sensitivities of some picryl triazoles [59], and we have shown computationally that the high sensitivity of the triazole 8 can be explained in an analogous manner [60]. On the other hand, some derivatives of the tetraazapentalenes 9 and 10 have shown a surprising degree of stability [58,61,62]; we have speculated that this is related to the relatively positive character of the two triply-coordinated nitrogens [63].



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It should be apparent from even this very brief discussion that impact and shock sensitivities can depend upon a variety of chemical and structural factors. Any generalizations should be made cautiously, and are likely to be subject to qualifications and limitations.

3. RELATIONSHIPS BETWEEN IMPACT SENSITIVITIES AND MOLECULAR SURFACE ELECTROSTATIC POTENTIALS

3.1. Analysis and Characterization of Surface Potentials

We have shown in earlier work that it is possible to quantitatively relate a variety of liquid, solid and solution phase properties to the electrostatic potential patterns on the surfaces of the individual molecules [64-66]. Among these properties are pK_a , boiling points and critical constants, enthalpies of fusion, vaporization and sublimation, solubilities, partition coefficients, diffusion constants and viscosities. For these purposes, we take the molecular surface to be the 0.001 au contour of the molecular electronic density $\rho(\mathbf{r})$, following the suggestion of Bader *et al* [67].

The electrostatic potential that is produced at any point $\mathbf{r}$ in the space around a molecule by its nuclei and electrons is given by eq (1):

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

Z_A is the charge on nucleus A, located at $\mathbf{R}_A$. The sign and magnitude of $V(\mathbf{r})$ are the net result of the positive and negative contributions of the nuclei and electrons, respectively, at the point $\mathbf{r}$. For $V(\mathbf{r})$ computed on the molecular surface, we determine the local maxima and minima (i.e. the most positive and negative values, $V_{S,\max}$ and $V_{S,\min}$), the average deviation Π and the total variance σ_{tot}^2 . The latter two are defined by eqs. (2) and (3):

$$\Pi = \frac{1}{n} \sum_{i=1}^n |V(\mathbf{r}_i) - \bar{V}_S| \quad (2)$$

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m [V^+(\mathbf{r}_i) - \bar{V}_S^+]^2 + \frac{1}{n} \sum_{j=1}^n [V^-(\mathbf{r}_j) - \bar{V}_S^-]^2 \quad (3)$$

$\bar{V}_S$ is the average potential over the entire surface: $\bar{V}_S = \frac{1}{n} \sum_{i=1}^n V(\mathbf{r}_i)$. $V^+(\mathbf{r}_i)$

and $V^-(\mathbf{r}_j)$ are the positive and negative values of $V(\mathbf{r})$ on the surface, and $\bar{V}_S^+$

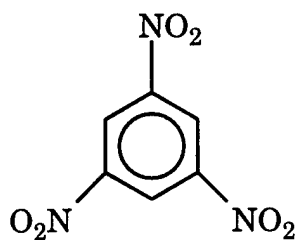
and $\bar{V}_S^-$ are their averages: $\bar{V}_S^+ = \frac{1}{m} \sum_{i=1}^m V^+(\mathbf{r}_i)$ and $\bar{V}_S^- = \frac{1}{n} \sum_{j=1}^n V^-(\mathbf{r}_j)$.

We view Π as an indicator of the internal charge separation, or local polarity, that is present even in molecules with zero dipole moments. It has been shown to correlate with dielectric constants [68] and with an experimentally-based measure of polarity [65]. The total variance, σ_{tot}^2 , which is the sum of the positive and negative variances, reflects the spread, or range of values, of the surface electrostatic potential. It is particularly sensitive to the positive and negative extremes, because of the terms being squared. We have found σ_{tot}^2 to be effective as a measure of a molecule's tendency for noncovalent interactions; for example, it enters into our expressions for boiling point [69], enthalpy of vaporization [64], solubilities [70,71], etc.

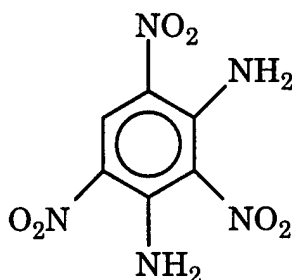
3.2. Unsaturated C-Nitro Derivatives: Nitroaromatics and Nitroheterocycles

The electrostatic potential of a ground state atom is positive everywhere [72]; the nuclear term in eq. (1) dominates over that of the dispersed electrons. When atoms combine to form a molecule, some negative region or regions normally develop; these are often due to lone pairs on the more electronegative atoms, e.g. nitrogen, oxygen, the halogens, etc., but they may also reflect other factors, such as unsaturated or strained C-C bonds [73,74]. The introduction of the strongly electron-withdrawing nitro group into an unsaturated molecule generally has the effect of eliminating the regions of negative electrostatic potential due to the π electrons. For example, whereas benzene and aniline have extensive negative potentials above the ring, nitrobenzene is positive everywhere except near the oxygens [75]. Analogous statements apply to the regions above the triple bonds of acetylene and nitroacetylene [76].

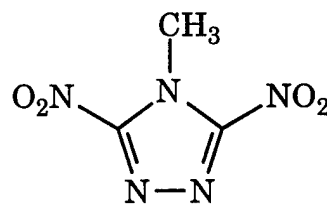
Two classes of unsaturated compounds that are of interest in the present context, as energetic materials, are trinitroaromatics and nitroheterocycles, e.g. imidazoles and triazoles. The electrostatic potential on the molecular surface of 1,3,5-trinitrobenzene, **11**, which is the parent molecule for the trinitroaromatics that we shall consider, has local maxima above the ring and near each of the C-NO₂ bonds [77]. This pattern is modified somewhat when other substituents are introduced, but its basic features remain even under the influence of electron-donating groups, e.g. in 2,4-diamino-1,3,5-trinitrobenzene **12**, although the maxima are now less positive [76]. The



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nitroheterocycles, such as 1-methyl-1,4-dinitro-1,3,4-triazole, **13**, have surface potential maxima near the C–NO₂ bonds [77]. The only negative surface regions shown by any of these three molecules, **11** - **13**, are associated with the nitro oxygens.

The surface potential maxima near the C–NO₂ bonds are a particularly interesting feature of this linkage. Buildups of positive electrostatic potential above C–NO₂ bond regions have been observed in a variety of types of molecules [75-84], and it has been demonstrated that they can serve as channels for nucleophilic attack [78,84].

In a recent study of the computed electrostatic potentials and related quantities on the molecular surfaces of 13 trinitroaromatic derivatives [77], we noted two rough trends; both the local polarity Π and the surface potential maximum above the ring, $V_{S,max}$, tend to increase as the impact sensitivity increases. Accordingly we used a statistical analysis program [85] to investigate whether an acceptable quantitative relationship could be developed. We found that the sensitivity h_{50} could indeed be represented in terms of Π and $V_{S,max}(\text{ring})$; our best expression was [77],

$$h_{50} = \alpha [\Pi^2 V_{S,max}(\text{ring})]^{-1} + \beta \Pi^2 + \gamma \quad (4)$$

In eq. (4), $\alpha > 0$, $\beta > 0$ and $\gamma > 0$. The linear correlation coefficient is 0.989 and the standard deviation is 14 cm, for experimental impact sensitivities that range from 36 cm to 320 cm. In view of the uncertainties associated with the measured values, we were pleased to obtain as good a correlation as this.

Our success with the trinitroaromatics prompted us to try the same approach with five nitroheterocycles (2 nitroimidazoles and 3 nitrotriazoles) [77]. These molecules do not have surface potential maxima above the rings, so we used for each one the most positive of the maxima near its C–NO₂ bonds, $V_{S,max}(\text{C–NO}_2)$. These tend to increase as the impact sensitivity increases, just as was observed for the $V_{S,max}(\text{ring})$ values of the trinitroaromatics. While Π does not show a parallel trend for these nitroheterocycles, nevertheless a satisfactory representation of h_{50} was obtained involving both $V_{S,max}(\text{C–NO}_2)$ and Π [77]:

$$h_{50} = \alpha [\Pi^2 V_{S,max}(\text{C–NO}_2)]^{-1} + \beta \quad (5)$$

In eq. (5), $\alpha > 0$ and $\beta > 0$. The linear correlation coefficient is 0.986 and the standard deviation is 19 cm, for experimental sensitivities between 35 cm and 291 cm. There is a notable similarity between the first terms on the right sides of eqs. (4) and (5).

A possible explanation for the role of $V_{S,\max}(\text{C-NO}_2)$ in eq. (5) is provided by our finding that it shows a fair correlation with the computed dissociation energy of the C-NO₂ bond, for a total of eight such bonds in a group of five nitroheterocycles [86]. When we sought to generalize this observation to a series of eleven nitroalkanes, we did find a relationship between the calculated C-NO₂ dissociation energy and $V_{S,\max}(\text{C-NO}_2)$, which now also includes the molecular surface area [87]. (The fact that the latter was not needed for the nitroheterocycles may mean simply that those five molecules have similar areas.) Thus it may be that $V_{S,\max}(\text{C-NO}_2)$ in eq. (5) is an indirect measure of the strengths of the C-NO₂ bonds in the nitroheterocycles; this would be consistent with the widespread emphasis upon C-NO₂ and N-NO₂ bonds as trigger linkages, mentioned earlier. For the nitroaromatics, it may be that the potential maximum above the ring reflects all three C-NO₂ bonds, due to their symmetrical distribution.

Understanding the function of Π in eqs. (4) and (5) poses a greater challenge. Eq. (5) and the very rough correlation between Π and sensitivity among the nitroaromatics seem to suggest that the latter increases with internal charge separation, which presumably counteracts the stabilizing effect of electronic delocalization in these unsaturated molecules. We have advanced this argument in the past [77,87]. For the nitroheterocycles, however, even though Π does appear in eq. (5), its values do not correlate in any obvious manner with sensitivity [77]. The form of eq. (4) also raises a question: The contributions of the two variable terms on the right side are both positive and of the same order of magnitude [77]; yet Π appears in the numerator of one and the denominator of the other. This ambiguity concerning the role of Π led us to reexamine the relationship of impact sensitivity to the molecular surface electrostatic potential.

3.3. Impact Sensitivity and Surface Potential Imbalance

The negative portions of a molecular surface are generally the smaller part of the total area, but they are frequently relatively strong; thus the average negative surface potential, $\bar{V}_S^-$, is typically larger in magnitude than its positive counterpart, $\bar{V}_S^+$, and the negative variance σ_-^2 is greater than the positive, σ_+^2 . This can be seen, for a representative group of molecules, in Table 1. The exceptions tend to be those having several strongly electron-attracting constituents, such as CF₄ and *p*-dinitrobenzene. It is instructive to compare the last of these to nitrobenzene; the second nitro group actually decreases the magnitudes of both $\bar{V}_S^-$ and σ_-^2 , because the polarizable electronic charge must now be shared between two electron-withdrawing substituents. We have encountered analogous situations on a number of previous occasions [76,81,88]. One consequence is that the value of Π tends to level off as the number of strongly electron-attracting constituents increases

Table 1.
Some computed molecular surface quantities.^a

Molecule	Π	$\bar{V}_S^+$	$\bar{V}_S^-$	σ_+^2	σ_-^2
cyclohexane	2.2	2.7	-1.6	2.5	0.7
C ₆ H ₅ CH ₃	4.6	4.2	-5.2	6.8	11.1
benzene	4.9	4.8	-5.0	7.1	9.2
(H ₅ C ₂) ₂ O	6.7	5.9	-9.4	8.0	129.8
(H ₃ C) ₃ COH	7.7	6.2	-12.3	31.1	182.7
CF ₄	8.3	11.5	-4.6	66.9	2.9
pyridine	8.5	6.8	-13.0	18.5	212.3
C ₆ H ₅ OH	8.6	8.7	-8.5	63.8	73.7
CH ₃ COCH ₃	9.4	7.7	-18.8	15.9	159.8
CH ₃ COOCH ₃	10.0	7.4	-16.7	9.7	129.2
C ₂ H ₅ OH	10.1	8.1	-13.7	45.1	182.4
(H ₃ C) ₂ NCHO	11.1	9.3	-17.0	18.6	158.8
pyrimidine	12.0	9.9	-17.4	24.4	163.0
C ₆ H ₅ NO ₂	12.3	10.4	-22.1	16.7	105.2
CH ₃ CONH ₂	14.7	12.5	-20.0	67.9	139.9
<i>p</i> -C ₆ H ₄ (NO ₂) ₂	16.5	17.9	-17.2	29.8	62.5
H ₃ CCN	17.1	15.5	-22.2	23.6	167.8
H ₂ NCHO	18.1	17.1	-20.0	85.5	233.6
CH ₃ NO ₂	19.9	19.4	-21.4	34.4	81.7
H ₂ O	21.6	19.8	-24.3	85.7	161.8

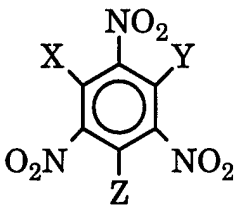
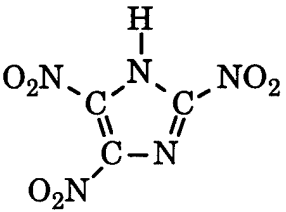
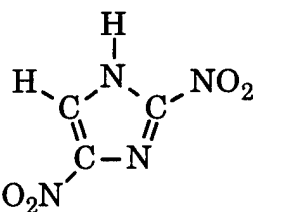
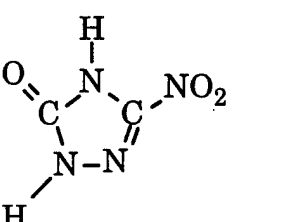
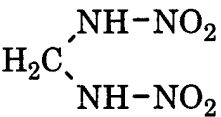
^aData are taken from references 65 and 68. Π , $\bar{V}_S^+$ and $\bar{V}_S^-$ are in kcal/mole; σ_+^2 and σ_-^2 are in (kcal/mole)².

[89]; thus, in going sequentially from benzene to tetranitrobenzene, the magnitudes of Π are 4.9, 12.3, 16.5, 19.5 and 21.4 kcal/mole. It is actually larger for H₂O, 21.6 kcal/mole, than for tetranitrobenzene!

Energetic molecules generally have several strong electron attractors, such as nitro groups and aza nitrogens, that are competing for the polarizable charge. Accordingly they tend to have $\bar{V}_S^+ > |\bar{V}_S^-|$ and $\sigma_+^2 > \sigma_-^2$, as can be seen for the examples in Table 2. This is in marked contrast to the more typical situation, illustrated in Table 1. For the former, Π levels off in the range 23 - 26 kcal/mole, and therefore cannot reflect the increasing sensitivity

Table 2.

Measured impact sensitivities and computed molecular surface quantities for some energetic molecules.^a

Molecule	h_{50}	Π	$\bar{V}_S^+$	$\bar{V}_S^-$	σ_+^2	σ_-^2
<u>nitroaromatics:</u>						
						
X, Y, Z						
CHO, H, H	36.	19.1	23.8	-13.9	152.3	49.0
OH, H, H	87.	20.9	24.9	-17.0	174.3	87.5
H, H, H	100.	19.5	23.9	-15.3	109.0	55.3
CH ₃ , H, H	160.	18.3	22.1	-15.2	95.5	51.7
NH ₂ , H, H	177.	18.6	22.0	-16.1	97.9	65.5
NH ₂ , NH ₂ , H	320.	17.1	19.4	-16.8	66.2	75.2
<u>nitroheterocycles:</u>						
	68.	20.7	27.4	-12.9	299.4	43.7
	105.	23.3	28.6	-17.9	312.1	70.6
	291.	20.1	23.4	-16.4	227.2	79.7
<u>nitramines:</u>						
	13.	23.4	29.6	-16.8	319.4	60.6

$ \begin{array}{c} \text{NO}_2 \\ \\ \text{H}_2\text{C}-\text{N}-\text{CH}_2 \\ \quad \\ \text{N} \quad \text{N} \\ \quad \\ \text{O}_2\text{N}-\text{C}-\text{NO}_2 \\ \\ \text{H}_2 \end{array} $	26.	23.2	27.8	-18.5	181.1	57.2
$ \begin{array}{c} \text{NO}_2 \\ \\ \text{O}=\text{C}-\text{N}-\text{CH}_3 \\ \\ \text{O}=\text{C}-\text{N}-\text{CH}_3 \\ \\ \text{NO}_2 \end{array} $	79.	16.4	18.3	-14.4	67.3	47.7
$ \begin{array}{c} \text{CH}_3 \\ \\ \text{O}_2\text{N}-\text{NH}-(\text{CH}_2)_2-\text{N}-\text{NO}_2 \end{array} $	114.	22.6	24.2	-21.4	164.0	85.6
$ \begin{array}{c} \text{NO}_2 \quad \text{O} \\ \quad \\ \text{H}_3\text{C}-\text{N}-\text{CH} \end{array} $	320.	17.4	18.8	-16.3	51.2	57.6

^aImpact sensitivities (in cm) are from reference 10; the computed data are from reference 89. Π , $\bar{V}_S^+$ and $\bar{V}_S^-$ are in kcal/mole; σ_+^2 and σ_-^2 are in (kcal/mole)².

that accompanies a continuing introduction of electron-withdrawing constituents.

Our analysis led eventually to the conclusion that impact sensitivity can be related to this characteristic imbalance between the larger $\bar{V}_S^+$ and the smaller $|\bar{V}_S^-|$ [89]. There are of course a variety of possible measures of such imbalance, including the quantity v , defined by eq. (6), which we have used

$$v = \frac{\sigma_+^2 \sigma_-^2}{(\sigma_{\text{tot}}^2)^2} \quad (6)$$

effectively for this purpose in the past [64-66]. By definition, v attains a maximum value of 0.250 when $\sigma_+^2 = \sigma_-^2$, but approaches zero when $\sigma_+^2 \gg \sigma_-^2$ or $\sigma_-^2 \gg \sigma_+^2$. Among other possibilities are ratios and differences of $\bar{V}_S^+$ and $|\bar{V}_S^-|$ or σ_+^2 and σ_-^2 . We investigated a number of options [89], and eventually settled upon eqs. (7) - (9) to represent the impact sensitivities of the original 13 nitroaromatics and 5 nitroheterocycles, as well as a group of 8 nitramines. The good correlation coefficients and relatively low standard deviations are gratifying, given the uncertainties in the data bases.

nitroaromatics:

$$h_{50} = \alpha \left(\frac{1}{V_{S,\max}} \right)^2 + \beta \left[\frac{1}{(\bar{V}_S^+)^4 - (\bar{V}_S^-)^4} \right] + \gamma \quad (7)$$

$\alpha, \beta > 0; \gamma < 0$. Correlation coefficient = 0.990; standard deviation = 14 cm.

nitroheterocycles:

$$h_{50} = \alpha \left(\frac{|\bar{V}_S^-|}{(\bar{V}_S^+)^3} \right) + \beta \left[\frac{(\sigma_+^2)^3}{\sigma_-^2} \right] + \gamma \quad (8)$$

$\alpha, \beta > 0; \gamma < 0$. Correlation coefficient = 0.998; standard deviation = 8 cm.

nitramines:

$$h_{50} = \alpha \left[\frac{\sigma_+^2 \sigma_-^2}{|\sigma_+^2 - \sigma_-^2|} \right] + \beta \left[\frac{\sigma_-^2}{\sigma_+^2} \right]^2 + \gamma \quad (9)$$

$\alpha > 0; \beta, \gamma < 0$. Correlation coefficient = 0.997; standard deviation = 9 cm.

There is a unifying element in these equations, in that they all focus upon the relative magnitudes of $\bar{V}_S^+$ and $|\bar{V}_S^-|$ or σ_+^2 and σ_-^2 . The additional dependence upon $V_{S,\max}$ in eq. (7) may be due to the symmetrical trinitrobenzene framework that is common to all 13 nitroaromatics. In eqs. (8) and (9), the contribution of the first variable term is larger than that of the second by an order of magnitude; the latter can be viewed as a correction term.

A general conclusion that seems to be indicated by these results is that the anomalous imbalance between the strengths of the positive and negative surface potentials is at least symptomatic of the degree of instability within these three classes of molecules. It should be noted that the very strong positive potentials produced by the electron-withdrawing components do not lead to as high levels of internal charge separation (and values of Π) as might be anticipated, because the negative potentials are uncharacteristically weak.

4. SUMMARY

We have presented an overview of various attempts to relate the impact and shock sensitivities of energetic materials to their molecular structures. The objectives of such efforts are to better understand the chemical and structural determinants of these sensitivities, and to develop a predictive capability to facilitate the evaluation of new and proposed energetic compounds.

Our particular emphasis in this discussion has been upon the relationship of impact sensitivities to the electrostatic potential patterns on the molecular surfaces. The current status of our analyses is represented by eqs. (7) - (9). While the success of these expressions is pleasing, we certainly do not claim that they are in final form. They reflect small data bases and measurements with a relatively high level of uncertainty. As more compounds are included, it may well be that the specific formulations given in eqs. (7) - (9) will be modified; i.e. other functions of $\bar{V}_S^-$ and $\bar{V}_S^+$ or σ_-^2 and σ_+^2 may turn out to be more effective. What is important at present, however, is the unifying concept that we have found to apply to all three of these classes of compounds, namely that their impact sensitivities can be related to the degree of imbalance between their typically stronger positive surface electrostatic potentials and weaker negative ones.

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REFERENCES

1. C. M. Tarver, J. Chem. Eng. Data **24** (1979) 136.
2. J. R. Holden, Z. Du and H. L. Ammon, J. Comp. Chem. **14** (1993) 422.
3. J. R. Stine, in *Structure and Properties of Energetic Materials*, D. H. Liebenberg, R. W. Armstrong and J. J. Gilman, eds., Materials Research Society, Pittsburgh, 1993, p. 3.
4. M. D. Allendorf and C. F. Melius, J. Phys. Chem. **97** (1993) 720.
5. D. Habibollahzadeh, M. E. Grice, M. C. Concha, J. S. Murray and P. Politzer, J. Comp. Chem. **16** (1995) 654.
6. P. Politzer, J. S. Murray, M. E. Grice, M. DeSalvo and E. Miller, Mol. Phys. in press.
7. M. J. Kamlet and S. J. Jacobs, J. Chem. Phys. **48** (1968) 23.
8. S. Iyer and N. Slagg, in *Structure and Reactivity (Molecular Structure and Energetics)*, J. F. Liebman and A. Greenberg, eds., VCH Publishers, New York, 1988, ch. 7.
9. P. Politzer, J. S. Murray, M. E. Grice and P. Sjoberg, in *Chemistry of Energetic Materials*, G. A. Olah and D. R. Squire, eds., Academic Press, New York, 1991, ch. 4.

10. C. B. Storm, J. R. Stine and J. F. Kramer, in *Chemistry and Physics of Energetic Materials*, S. N. Bulusu, ed., Kluwer, Dordrecht, The Netherlands, 1990, ch. 27.
11. J. E. Field, *Acc. Chem. Res.* **25** (1992) 489.
12. C. L. Mader, in *Organic Energetic Compounds*, P. L. Marinkas, ed., Nova, Commack, NY, 1996, ch. 3.
13. C. M. Tarver, S. K. Chidester and A. L. Nichols, III, *J. Phys. Chem.* **100** (1996) 5794.
14. M. J. Ehrlich, J. W. Wagner, J. Friedman and H. Egghart, in *Structure and Properties of Energetic Materials*, D. H. Liebenberg, R. W. Armstrong and J. J. Gilman, eds., Materials Research Society, Pittsburgh, 1993, 305.
15. M. J. Kamlet, *Proc. Sixth Symposium (International) on Detonation*, Office of Naval Research, Report ACR 221, 1976.
16. M. J. Kamlet and H. G. Adolph, *Propell. Expl.* **4** (1979) 30.
17. J. S. Murray and P. Politzer, in *Chemistry and Physics of Energetic Materials*, S. N. Bulusu, ed., Kluwer, Dordrecht, The Netherlands, 1990, ch. 8.
18. M. J. Kamlet and H. G. Adolph, *Proc. Seventh Symposium (International) on Detonations*, Naval Surface Warfare Center, Silver Springs, MD, Report NSWCMP-82-334, 1981, p. 84.
19. R. Sundararajan and S. R. Jain, *Ind. J. Tech.* **21** (1983) 474.
20. G. T. Afanas'ev, T. S. Pivina and D. V. Sukhachev, *Propell. Expl. Pyrotech.* **18** (1993) 309.
21. J. Sharma and F. J. Owens, *Chem. Phys. Lett.* **61** (1979) 280.
22. S. Bulusu and T. Axenrod, *Org. Mass Spectr.* **14** (1979) 585.
23. M. Farber and R. D. Srivastava, *Chem. Phys. Lett.* **64** (1979) 307.
24. F. I. Dubovitskii and B. L. Korsunskii, *Russ. Chem. Revs.* **50** (1981) 958.
25. S. Zeman, M. Dimun and S. Truchlik, *Thermochim. Acta* **78** (1984) 181.
26. A. C. Gonzalez, C. W. Larson, D. F. McMillen and D. M. Golden, *J. Phys. Chem.* **89** (1985) 4809.
27. F. J. Owens and J. Sharma, *J. Appl. Phys.* **51** (1985) 1494.
28. W. Tsang, D. Robaugh and W. G. Mallard, *J. Phys. Chem.* **90** (1986) 5968.
29. C. Capellos, P. Papagiannakopoulos and Y.-L. Liang, *Chem. Phys. Lett.* **164** (1989) 533.
30. T. D. Sewell and D. L. Thompson, *J. Phys. Chem.* **95** (1991) 6228.
31. C. A. Wight and T. R. Botcher, *J. Am. Chem. Soc.* **114** (1992) 8303.

32. G. F. Adams and R. W. Shaw Jr., in *Annual Reviews of Physical Chemistry*, Vol. 43, H. L. Strauss, ed., Annual Reviews Inc., Palo Alto, CA, 1992, p. 311.
33. T. B. Brill and K. J. James, *J. Phys. Chem.* **97** (1993) 8752, 8759.
34. M. D. Pace, *J. Phys. Chem.* **98** (1994) 6251.
35. J. C. Oxley, J. L. Smith, H. Ye, R. L. McKenney and P. R. Bolduc, *J. Phys. Chem.* **99** (1995) 9593.
36. L. E. Fried and A. J. Ruggiero, *J. Phys. Chem.* **98** (1994) 9786.
37. X. Hong, S. Chen and D. D. Dlott, *J. Phys. Chem.* **99** (1995) 9102.
38. F. J. Owens, *J. Mol. Struct. (Theochem)* **121** (1985) 213.
39. P. Politzer, J. S. Murray, P. Lane, P. Sjoberg and H. G. Adolph, *Chem. Phys. Lett.* **181** (1991) 78.
40. F. J. Owens, K. Jayasuriya, L. Abrahmsen and P. Politzer, *Chem. Phys. Lett.* **116** (1985) 434.
41. J. S. Murray, P. Lane, P. Politzer and P. R. Bolduc, *Chem. Phys. Lett.* **168** (1990) 135.
42. A. Delpuech and J. Cherville, *Propell. Expl.* **3** (1978) 169; **4**, (1979) 61, 121.
43. Y. Kohno, K. Maekawa, T. Tsuchioka, T. Hashizume and A. Imamura, *Combust. Flame* **96** (1994) 343.
44. Y. Kohno, K. Ueda and A. Imamura, *J. Phys. Chem.* **100** (1996) 4701.
45. K. Suryanarayanan and C. Capellos, *Int. J. Chem. Kinet.* **6** (1974) 89.
46. J. R. Cox and I. H. Hillier, *Chem. Phys.* **124** (1988) 39.
47. A. T. Nielsen, in *The Chemistry of the Nitro and Nitroso Groups, Part 1*, H. Feuer, ed., Wiley/Interscience, New York, 1969, ch. 7.
48. P. Politzer, J. M. Seminario and P. R. Bolduc, *Chem. Phys. Lett.* **158** (1989) 463.
49. R. Engelke, W. L. Earl and C. M. Rohlfing, *J. Chem. Phys.* **84** (1986) 142.
50. R. Engelke, D. Schiferl, C. B. Storm and W. L. Earl, *J. Phys. Chem.* **92** (1988) 6815.
51. P. Politzer, J. M. Seminario and A. G. Zacarías, *Mol. Phys.* in press.
52. J. Sharma, J. C. Hoffsomer, D. J. Glover, C. S. Coffey, F. Santiago, A. Stolovy and S. Yasuda, in *Shock Waves in Condensed Matter*, J. R. Assay, R. A. Graham and G. K. Straub, eds., Elsevier, Amsterdam, 1983, ch. 12.
53. J. Sharma, J. W. Forbes, C. S. Coffey and T. P. Liddiard, *J. Phys. Chem.* **91** (1987) 5139.
54. J. S. Murray, P. Lane, P. Politzer, P. R. Bolduc and R. L. McKenney, Jr., *J. Mol. Struct. (Theochem)* **209** (1990) 349.

55. C. B. Storm and J. R. Travis, in *Structure and Properties of Energetic Materials*, D. H. Liebenberg, R. W. Armstrong and J. J. Gilman, eds., Materials Research Society, Pittsburgh, 1993, 25.
56. R. N. Rogers, *Anal. Chem.* **39** (1967) 731.
57. J. C. Dacons, H. G. Adolph and M. J. Kamlet, *J. Phys. Chem.* **74** (1970) 3035.
58. F. R. Benson, *The High Nitrogen Compounds*, Wiley-Interscience, New York, 1984 .
59. C. B. Storm, R. R. Ryan, J. P. Ritchie, J. H. Hall and S. M. Bachrach, *J. Phys. Chem.* **93** (1989) 1000.
60. P. Politzer, M. E. Grice and J. M. Seminario, *Int. J. Quant. Chem.* **61** (1997) 389.
61. R. Pflieger, E. Garthe and K. Raner, *Chem. Ber.* **96** (1963) 1827.
62. R. A. Carboni, J. C. Kauer, J. E. Castle and H. E. Simmons, *J. Am. Chem. Soc.* **89** (1967) 2618.
63. M. E. Grice and P. Politzer, *J. Mol. Struct. (Theochem)* **358** (1995) 63.
64. J. S. Murray and P. Politzer, in *Quantitative Treatments of Solute/Solvent Interactions*, J. S. Murray and P. Politzer, eds., Elsevier, Amsterdam, 1994, ch. 8.
65. J. S. Murray, T. Brinck, P. Lane, K. Paulsen and P. Politzer, *J. Mol. Struct. (Theochem)* **307** (1994) 55.
66. P. Politzer, J. S. Murray, T. Brinck and P. Lane, in *Immunoanalysis of Agrochemicals; Emerging Technologies*, J. O. Nelson, A. E. Karu and R. B. Wong, eds., ACS, Washington, 1995, ch. 8.
67. R. F. W. Bader, M. T. Carroll, J. R. Cheeseman and C. Chang, *J. Am. Chem. Soc.* **109** (1987) 7968.
68. T. Brinck, J. S. Murray and P. Politzer, *Mol. Phys.* **76** (1992) 609.
69. J. S. Murray, P. Lane, T. Brinck, K. Paulsen, M. E. Grice and P. Politzer, *J. Phys. Chem.* **97** (1993) 9369.
70. P. Politzer, P. Lane, J. S. Murray and T. Brinck, *J. Phys. Chem.* **96** (1992) 7938.
71. J. S. Murray, S. G. Gagarin and P. Politzer, *J. Phys. Chem.* **99** (1995) 12081.
72. K. D. Sen and P. Politzer, *J. Chem. Phys.* **90** (1989) 4370.
73. P. Politzer and J. S. Murray, in *Theoretical Biochemistry and Molecular Biophysics: A Comprehensive Survey*, Vol. 2, D. L. Beveridge and R. Lavery, eds., Adenine Press, Schenectady, NY, 1991, ch. 13.

74. P. Politzer and J. S. Murray, in *Reviews in Computational Chemistry*, Vol. 2, K. B. Lipkowitz and D. B. Boyd, eds., VCH Publishers, New York, 1991, ch. 7.
75. P. Politzer, L. Abrahmsen and P. Sjoberg, *J. Am. Chem. Soc.* **106** (1984) 855.
76. P. Politzer and R. Bar-Adon, *J. Am. Chem. Soc.* **109** (1987) 3529.
77. J. S. Murray, P. Lane and P. Politzer, *Mol. Phys.* **85** (1995) 1.
78. P. Politzer, P. R. Laurence, L. Abrahmsen, B. A. Zilles and P. Sjoberg, *Chem. Phys. Lett.* **111** (1984) 75.
79. P. Politzer, P. Lane, K. Jayasuriya and L. N. Domelsmith, *J. Am. Chem. Soc.* **109** (1987) 1899.
80. P. Politzer and N. Sukumar, *J. Mol. Struct. (Theochem)* **179** (1988) 439.
81. J. S. Murray and P. Politzer, *J. Mol. Struct. (Theochem)* **163** (1988) 111; 180 (1988) 161.
82. J. S. Murray and P. Politzer, *J. Mol. Struct. (Theochem)* **180** (1988) 161.
83. J. S. Murray, J. M. Seminario and P. Politzer, *J. Mol. Struct. (Theochem)* **187** (1989) 95.
84. J. S. Murray, P. Lane and P. Politzer, *J. Mol. Struct. (Theochem)* **209** (1990) 163.
85. SAS, SAS Institute Inc., Cary, NC 27511.
86. P. Politzer and J. S. Murray, *Mol. Phys.* **86** (1995) 251.
87. P. Politzer and J. S. Murray, *J. Mol. Struct.* **376** (1996) 419.
88. P. Politzer, G. P. Kirschenheuter and J. Alster, *J. Am. Chem. Soc.* **109** (1987) 1033.
89. J. S. Murray, P. Lane and P. Politzer, *Mol. Phys.*, submitted.